

Original Research Article

Chemical Methodologies

Journal homepage: <u>http://chemmethod.com</u>



Static and Dynamic Study of Novel 4-Formyl-*N*-Hexadecyl-*N*,*N*-Dimethylbenzenaminium Bromide Synthesized as a Corrosion Inhibitor Use in Petroleum Wells Acidizing Process

Zaidoun K. Kuraimid¹, Abd El-Aziz S. Fouda^{1,*}, Dawood S. Abid²

¹Department of Chemistry, Faculty of Science, Mansoura University, Mansoura 35516, Egypt ²Department of Chemistry,College of Education for Pure Science, Basra University, Basra, 61004, Iraq

ARTICLE INFO

Article history

Submitted: 2023-04-05 Revised: 2023-05-23 Accepted: 2023-06-05 Manuscript ID: CHEMM-2305-1677 Checked for Plagiarism: Yes Language Editor: Dr. Fatimah Ramezani Editor who approved publication: Dr. Ali Ramazani

DOI:10.22034/CHEMM.2023.395919.167

7

K E Y W O R D S FHDB Corrosion inhibition

C-Steel 6M HCl Potentiostatic polarization Langmuir adsorption isotherm Dynamic autoclave

ABSTRACT

This study showcases the innovative synthesis of 4-formyl-Nhexadecyl-N,N-dimethylbenzenaminium bromide (FHDB) using a reaction of 1-Bromohexadecane and 4-di methyl amino benzaldehyde. The compound was then characterized through various techniques such as FT-IR, ¹H-NMR, and ¹³C-NMR, along with physical property measurements. Thereafter, the synthesized FHDB was tested for its corrosion inhibition properties on C-steel in 6M HCl, with a focus on kinetics and thermodynamics using potentiodynamic polarization (PDP). The surface changes of the C-steel were observed through Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). The study revealed that FHDB exhibited strong inhibitory properties against corrosion in 6M hydrochloric acid solutions, with an adsorption pattern on the steel surface in agreement with Langmuir adsorption isotherm. The results, which include corrosion and electrochemical testing data, demonstrate that the experimental corrosion inhibitors are typically practically equal between the fluid flow study (dynamic simulations) and the static study, which is attributable to the FHDB chemical structure.



GRAPHICAL ABSTRACT

Introduction

The use of acid solutions is common in many industries to eliminate unwanted scales and rust from steel surfaces. In addition, they are often used to enhance oil and gas recovery through acidification in the oil and gas industry [1]. Unfortunately, these procedures typically result in severe corrosion of steel pipes, tubes, and equipment [2]. The Assessment of carbon steel corrosion is important, especially in acidic environments where acids are commonly used for various processes such as pickling [3], cleaning [4], descaling [5], and oil-well acidization [6]. These processes can cause significant damage to the steel [7]. However, the harmful effects of mineral acid solutions on steel can be reduced by inhibitors adding corrosion in small concentrations [8]. Corrosion inhibitors are essential in preventing corrosion and protecting metals from further damage [9]. Organic nitrogencontaining compounds are the most used corrosion inhibitors in industrial applications, particularly in solutions of HCl [10]. These inhibitors form a barrier on the surface of various steels, preventing them from corroding [11]. The protective layer created by these inhibitors shields the metal from further corrosion, thereby preserving the mechanical properties of metal [12]. Quaternary ammonium salts are a class of organic nitrogen-containing compounds that have shown potential as effective corrosion inhibitors for steel in acidic environments [13]. Further research should be conducted on these compounds to fully understand their properties and potential applications in preventing steel corrosion [14]. Studies have shown that organic corrosion inhibitors containing nitrogen atoms can decrease the ability of hydrogen to penetrate steel under acidic conditions, thereby reducing the corrosion risk [15]. Therefore, exploring the potential of quaternary ammonium salts as corrosion inhibitors is a promising avenue for future research in the field of materials science and engineering. El Maghraby conducted a study on how cetyl trimethyl ammonium bromide (CTAB) affects the corrosion inhibition in carbon steel when exposed to solutions of sulphuric acid [16]. Zhao *et al.* investigated how the combination of quinolinium quaternary ammonium salt and a Gemini surfactant work together to inhibit corrosion in sour brine solutions [17]. Han *et al.* examined how imidazoline quaternary ammonium salts induce pitting corrosion in L245 steel when exposed to a solution saturated with H₂S [18]. One quaternary ammonium salt, 4formyl-*N*-hexadecyl-*N*,*N*-

dimethylbenzenaminium bromide (FHDB), was synthesized and described in the current study. The PDP measurement was used to assess this compound's inhibitory effect on C-steel in a 6 M HCl solution. The influence of temperature and inhibitor concentration was examined on inhibition behavior. Several kinetic and thermodynamic parameters were computed using the experimental data. The process by which the produced inhibitor adhered to the surface of Csteel in 6 M HCl was further explained. The surface morphology of the C-steel corroded in 6 M HCl with and without the addition of inhibitors was examined using an atomic force microscope and scanning electron microscope.

Materials and Methods

Synthesis of 4-formyl-N-hexadecyl-N,Ndimethylbenzenaminium bromide (FHDB) [19]

In ethanol, 1-Bromohexadecane (0.027 mol, 8.3 g) was added to a stirred solution, followed by 4-di methyl amino benzaldehyde (0.027 mol, 4.02 g). The mixture was then refluxed for 48 hours and concentrated under vacuum. The resulting solid product was filtered and dried, yielding an off-white solid with a yield of 83% and a melting point of 62.5 °C.

Steel specimen

A low carbon steel coupon with a composition of 0.17% C, 0.8% Mn, 0.014% P, 0.002% S, 0.022% Si, 0.02% Cu, 0.01% Ni, 0.04% Cr, 0.002% Sn, 0.042% Al, 0.006% N, 0.001% V, 0.0001% B, 0.001% Ti, 0.001% Cd, and the remaining being Fe was used as a working electrode with an area of 1 cm² for the polarization method. For electrical connection, the C-steel rod was welded with Cu-wire, placed inside a Teflon tube, and secured with glue. Specimens were cleaned in accordance with ASTM standard G1-3 before to the start of any experiment.

PDP Studies (Tafel Extrapolation)

Electrochemical studies were conducted using a Wenking M Lab potentiostat and a three-electrode cell, with platinum over titanium (Pt/Ti) electrode as the auxiliary electrode and a saturated silver electrode Ag/AgCl as the reference electrode. The Tafel extrapolation technique was utilized to determine the corrosion rates, and the experiments were carried out at 313K, 323K, 333K, and 343K.

FT-IR Analysis

The structure of compound FHDB was confirmed by FT-IR spectrum which showed v(C-H) aromatic at 3000 cm⁻¹, v(C-H) aliphatic 2972 cm⁻¹, v(C-H) aldehyde 2855 and 2722 cm⁻¹, 1691 v (C=O) aldehyde, 1254 cm⁻¹ v(C-N), and 1593 cm⁻¹ v(C=C) aromatic [20]. FT-IR spectrum data of FHDB were demonstrated in Figure 1. Fourier Transform Infra-Red Spectrophotometer FT-IR was recorded using KBr disc on SHIMADZU FT-IR-8400, Japan, at Faculty of Science, Chemistry Department, AL-MUSTANSIRYAH University, Iraq.

¹H-NMR Analysis

¹H-NMR (DMSO) spectrum of FHDB showed signals at δ 0.831-0.861 (t,3H,- terminal CH₃) triplet of three protons, δ 1.1-1.4 (m, 30H,15CH₂) multiplate due thirteen protons of long chain fatty acid); triplet at δ 2.1-2.5 due to two proton of (t, 2H, CH₂-N), singlet signal at δ 3.0-3.3 due for six protons (s, 6H, 2CH₃- N), δ 6.7-7.6 multiplate due aromatic ring proton (m, 4H, Ar-H), 9.67 singlet signal of one proton (s,1H,-COH) [20]. ¹H-NMR spectrum data of FHDB were depicted in Figure 2.

¹³C-NMR Analysis

¹³C-NMR (DMSO) spectrum of FHDB showed signals at 14.33 below to (C25), signals at 22.6-40.3 due to (C24-C11), 68.1 due to (C10), 60.01 below to (C8,C9), 111.01below to (C6,C2), 123-131due to (C5,C3), 154.64 due to (C1,C4), 190.23below to (C26) [20]. ¹³C-NMR spectrum data of FHDB were shown in Figure 3.

Nuclear Magnetic Resonance Spectrophotometry, ¹H-NMR, and ¹³C-NMR spectra were registered on near magnetic resonance Bruker, Ultra-shield 300 mHz in BASRAH University, Iraq, using tetramethyl silane as internal standard and DMSO- d_6 as solvents.







Figure 2: ¹H-NMR spectrum of FHDB



Figure 3: 13C-NMR spectrum of FHDB

Results and Discussion

Synthesis of 4-formyl-N-hexadecyl-N,Ndimethylbenzenaminium bromide (FHDB) The synthesis of the novel compound 4-formyl-*N*-hexadecyl-*N*,*N*-dimethylbenzenaminium bromide (FHDB) was carried out according to the reaction sequences displayed in Scheme 1.



Scheme 1: Synthetic pathway employed for synthesis of FHDB inhibitor

PDP Measurements

In Figure 4, the polarization curves of C-steel are shown with and without various concentrations of FHDB. The shape of potentiodynamic curve is similar in both cases, but the FHDB addition results in the inhibition of both the anodic and cathodic reactions, with a predominant cathodic effect. The corrosion current density (I_{corr}) was calculated through Tafel extrapolation, and the resulting parameters, including I_{corr} , E_{corr} , β_a , β_c , and inhibition efficiency (%IE) are listed in Table 2. The inhibitor efficiency %IE and degree of surface coverage (Θ) were calculated using Equation 1 and the measured I_{corr} values.

$$\% IE = \Theta \times 10 = \frac{Icorr(free) - Icorr(i)}{Icorr(free)} \times 100$$
(1)

Where, $I_{corr(free)}$ is the uninhibited corrosion current and $I_{corr(i)}$ is the inhibited corrosion current. Figure 4 illustrates that the FHDB addition to a 6 M HCl solution resulted in a decrease in both anodic and cathodic currents, indicating that the inhibitor has a mixed nature. The decrease in I_{corr} values in the FHDB presence indicates the adsorption of inhibitor molecules on the surface of C-steel, leading to an increase in the %IE. Moreover, the changes in the β a and β c values of FHDB with various concentrations suggest that the inhibitor regulates the anodic and cathodic reactions.

FHDB was found to be a mixed-type inhibitor as there was no significant change in the corrosion potential (E_{corr}) values with the inhibitor addition

compared to E_{corr} in the absence of the inhibitor [21]. This indicates that FHDB adsorbs on the C-steel surface by blocking the reaction sites, reducing the surface area available for hydrogen evolution (cathodic reaction) and metal dissolution (anodic reaction), without altering the process mechanism.

Higher FHDB inhibitor concentrations, as indicated by the provided parameters in Table 2, reduce the anodic and cathodic corrosion current densities. In comparison to the results obtained in the presence of various FHDB concentrations, the I_{corr} was highest in the acidic blank solution at all temperatures. As the reaction temperature was raised, the I_{corr} rose at all tested inhibitor doses as the temperature impact was seen. For instance, the I_{corr} measured at 40 and 70°C in the presence of 200 mg.L⁻¹ FHDB was 0.104 and 0.880 mA cm⁻²,

respectively. The rapid electrochemical reactions and metal disintegration at higher temperatures could be the cause of the significant rise in the current density (around 10 times) [21]. The anodic and cathodic curves altered towards greater positive and negative potentials, respectively, in accordance with the obtained results, identifying FHDB as a mixed-type corrosion inhibitor [22]. Higher FHDB concentrations lead to higher surface coverage due to the buildup of inhibitor molecules in terms of inhibition efficiency and surface coverage. As a result, the inhibitor performance is significantly enhanced at the greatest dosage of 200 mg.L-1 at all temperatures. The efficiency was further decreased as a result of the corrosion rate increasing at higher temperatures.



Figure 4: Typical Tafel polarization curves of C-steel in 6M HCl solution with various concentrations of FHDB inhibitor at different temperatures (313K, 323K, 333K, and 343K)

Kuraimid Z.K., et. al. / Chem. Methodol. 2023, 7(7) 552-568

Temperature	Conc.	E _{Corr} .	I _{Corr.}	βc	βΑ	Weight loss	Penetration loss	Corrosion Rate	θ	I. E. %
K	mg/L	mV	mA	mV/Dec	mV/Dec	g/m². d	mm/a	тру		
	0	-360.7	10.37	-254.5	243.1	2,595.3	120.37	4,738.97	0.000	0.00
	50	-384.7	0.16414	-369.5	81.3	41	1.91	75.20	0.977	98.417
313	100	-355.4	0.15067	-655.1	78.6	37.7	1.75	68.90	0.981	98.547
	150	-346.2	0.10721	-427.5	76.2	26.8	1.24	48.82	0.983	98.966
	200	-346.2	0.104	-460.3	73.7	26	1.21	47.64	0.985	98.997
	0	-397.6	25.74	-319.8	324.9	6,438.5	298.77	11, 762.6	0.000	0.00
	50	-386.1	0.41437	-428.1	87.5	104	4.81	189.37	0.980	98.390
323	100	-375.7	0.40676	-478.1	90	102	4.72	185.83	0.985	98.419
	150	-370.7	0.3101	-495.9	84.9	77.5	3.6	141.74	0.988	98.795
	200	-366.3	0.26239	-492.9	83.5	65.6	3.05	120.08	0.988	98.980
	0	-387.4	39.49	-267.8	286.9	9,874.5	458.0	18, 031.5	0.000	0.00
	50	-389.9	0.84278	-274.8	88.3	211	9.78	385.04	0.977	97.866
333	100	-380.6	0.75732	-363.9	93.2	189	8.79	346.07	0.983	98.082
	150	374.8	0.63562	-357.7	88.8	159	7.38	290.55	0.985	98.390
	200	-375	0.47211	-373.4	87.3	118	5.48	215.75	0.985	98.804
	0	-372.8	55.01	-348	335.7	13,800	639.0	25, 157.4	0.000	0.00
	50	-403.2	1.75	-235.4	97.1	437	20.3	799.22	0.972	96.819
343	100	389.70	1.4	-265.1	102.3	351	16.3	641.74	0.978	97.455
	150	-387.1	1.19	-34.2	102.9	297	13.8	543.31	0.979	97.836
	200	-379.8	0.88013	-292.5	92.7	220	10.2	401.58	0.979	98.400

Table 2: Electrochemical data obtained from Tafel plots for C-steel in 6 M HCl with different FHDB concentrations at various temperatures

Adsorption Studies and Thermodynamic Isotherms

To understand the adsorption mechanism of FHDB onto the metal surface, the adsorption isotherm is used to provide information about the interactions between the adsorbate and the surface. Several adsorption isotherms have been commonly used, including Langmuir, Temkin, Frumkin, and Freundlich isotherms. The Langmuir adsorption isotherm was found to best describe the adsorption behavior, as shown in Figure 5. The Langmuir isotherm suggests that metal surface has a fixed number of adsorption sites with one adsorbate, and the Gibbs free energy of adsorption has the same value for all sites, irrespective of the surface coverage [23]. The Langmuir adsorption isotherm equation is represented by Equation 2 [24]:

(2)

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C$$

higher Kads value indicates stronger adsorption of the inhibitor on the metal surface. As seen in Figure 5, a straight line is obtained by plotting C/ θ against C, and the regression coefficient R² is almost equal to 1. This indicates that the Langmuir adsorption isotherm provides an excellent description of the adsorption behavior, and the inhibitor is strongly adsorbed on the metal surface. In this study, FHDB was found to follow the Langmuir adsorption isotherm, indicating that the inhibitor molecules adsorb independently onto the metal surface with a definite proportion of adsorption sites. The plot of C/ θ vs. C produced a straight line with a regression coefficient R^2 close to 1, indicating a good fit of FHDB with the Langmuir isotherm. The equilibrium constant K_{ads}

Where, C is FHDB dose and K_{ads} is adsorptive equilibrium constant (degree of adsorption). A

(3)

decreased with an increase in temperature, indicating that FHDB was more effectively adsorbed onto the C-steel surface at lower temperatures. The following relationships were used to calculate the free energy of adsorption [25].

 $K_{ads} = 1/55.5 \text{ Exp}(-\Delta G_{ads}/\text{ RT})$

 $\Delta G_{ads} = -2.303 \text{RT} \log (55.55 \text{ K}_{ads})$ (4)

$$Logk_{ads} = -\Delta H_{ads}/2.303RT + \Delta S_{ads} / 2.303R + Log 1/55.55$$
 (5)

The water concentration in solution in mol. L⁻¹ is represented by the number 55.55 in the above equations 3-5.



Figure 5: Langmuir adsorption isotherm of FHDB on C- steel in 6M HCl at different temperatures

Table 3 presents the results of the Langmuir adsorption isotherm. The negative values of ΔG_{ads}^{o} ensure both the stability of the adsorbed layer on the metal surface and the spontaneity of the adsorption process. The interaction between a charged metal and a charged molecule through electrostatic forces is referred to as physisorption, and ΔG_{ads}^{o} values up to -20 kJ mol⁻¹ are typically associated with this type of interaction. On the other hand, ΔG_{ads}^{o} values equal to or greater than -40 kJ mol⁻¹ indicate chemisorption, where the organic molecules share or transfer electrons to the metal surface, resulting in a coordinate bond [26]. Given that the acquired ΔG_{ads}^{o} values fall between the previously specified ranges, which is between -29.96 and -30.39 kJ.mol⁻¹, this indicates mixed type adsorption. The strength of bonding between the inhibitor and the C-steel coupon surface is revealed by the value of K_{ads}. A decrease in K_{ads} at higher temperatures suggests a weak interaction and desorption of FHDB molecules from the surface of C-steel. Therefore, K_{ads} is a crucial parameter for understanding the bonding strength between the inhibitor and metal surface. The relationship between the logarithm of K_{ads} and the reciprocal of temperature (1/T) gave a straight line with a slope of (- Δ Hads/2.303R) in Figure 6. Accordingly, the value of Δ H_{ads} was determined to be -25.37 kJ.mol⁻¹. The negative value of Δ H_{ads} indicates that the inhibitor adsorption on metal surface is an exothermic process. When distinguishing between physisorption and chemisorption processes, it is commonly accepted that exothermic values below -40 kJ.mol⁻¹ indicate physisorption, while adsorption with heat values approaching -100 kJ.mol⁻¹ is the chemisorption characteristic. The

value of the standard adsorption heat ΔH° ads (-25.37 kJ.mol⁻¹) used in this study suggests that physical adsorption is the preferred mechanism. The FHDB adsorption on the C-steel surface was found to result in a decrease in system order, as evidenced by the positive value of the standard adsorption entropy.

Table 3: Thermodynamic parameters ΔG^{o}_{ads} , ΔH^{o}_{ads} , and ΔS^{o}_{ads} of FHDB adsorption of on C-steel at various temperatures

temperatures									
Inhibitor	Temperature K	K _{ads} M ⁻¹	-∆Gº _{ads} KJ/mol	ΔHº _{ads} KJ/mol	ΔSº _{ads} J/mol.K				
	313	1800.29	29.9654		0.015457488				
EUDD	323	1623.6	30.6453	25 2710770					
гпрр	333	1210.144	30.7803	-23.3710779					
	343	763.9842	30.3927						



Figure 6: Plot of log K_{ads} against reciprocal of temperature values

Corrosion Kinetics Studies

The inhibitory efficiency of FHDB under different temperatures was investigated by conducting PDP measurements with various concentrations of FHDB over a temperature range of 313-343 K. The activation parameters of the corrosion process were calculated using the Arrhenius Equation 6, while the transition state Equation 7 was applied [27].

Log (Icorr) = Log A – Ea/2.303RT (6) Log (Icorr/T) = Log (K/h) + $\Delta S^*/2.303R$ - $\Delta H^*/2.303RT$ (7)

Where, I_{corr} is corrosion current, E_a^* is energy of activation, R is universal gas constant (8.314 J.mol⁻¹ K⁻¹), T is temperature in K, A is Arrhenius factor, h is Planck's constant (6.626 x 10⁻³⁴ J.s), N is

Avogadro's number (6.022 x 1023 mol⁻¹), ΔH^* is activation enthalpy, and ΔS^* is activation entropy. Log I_{corr} plots vs. 1/T revealed a linear relationship with a slope ($-E_a^*/2.303$ R) and the intercept of the extrapolated line log A. Table 4 illustrates the results. From the plots of log I_{corr}/T vs. 1/T, straight lines were obtained, as presented in Figure 7 with the slope of $(-\Delta H^*/2.303 \text{ R})$ and an intercept of [(log (R/Nh) + (Δ S*/2.303 R)] which were used to calculate values of ΔH^* and ΔS^* , respectively. Figure 8 provides Arrhenius charts for a temperature range of 313-343 K in 6 M HCl. Based on the corrosion, current measured values determined from polarization curves at various temperatures with and without of FHDB as a corrosion inhibitor [27].

Kuraimid Z.K., et. al. / Chem. Methodol. 2023, 7(7) 552-568

Table 4: Corrosion kinetic parameters for C-steel in 6M HCl in the absence and presence differentconcentrations of FHDB

Conc. mg/L	Temp K	I _{corr.} mA/cm ²	A Molecules /cm²*s	Ea KJ/mol	ΔH KJ	ΔS KJ	
	313	10.37		48.799	46.076	-0.077	
0	323	25.74	0.00210 * 1.032				
0	333	39.49	9.99319 1032				
	343	55.01					
	313	0.16414			67.068	-0.046	
50	323	0.41437	1 F2F02 * 1034	69.791			
50	333	0.84278	4.52503 1034				
	343	1.75					
	313	0.15067		65.422	62.699	-0.060	
100	323	0.40676	01(504 * 1022				
100	333	0.75732	8.10534 1055				
	343	1.4					
	313	0.10721		71.000	68.346		
150	323	0.3101	F 117((* 103)			-0.045	
150	333	0.63562	5.11/00 1034	/1.069			
	343	1.19					
	313	0.104					
200	323	0.26239	1 05522 * 1022	() 574	59.851	-0.072	
200	333	0.47211	1.85532 * 1033	62.574			
	343	0.88013]				



Figure 7: Transition state plot for C-steel in 6 M HCl in the presence of different concentrations of FHDB



Figure 8: Arrhenius Plot of C-Steel in 6 M HCl Contains Different Concentrations of FHDB at Different Temperatures

According to the activation kinetic parameters, at increasing inhibitor concentration, the activation enthalpy increased, indicating a decrease in corrosion rate. The higher activation energy values point to physisorption of the FHDB species onto the surface of the C-steel, allowing the corrosion process's energy barrier to increase. The endothermic nature of the disintegration of Csteel is indeed reflected in the positive value of Δ H*. The negative values of Δ S*, indicated that a larger order was created throughout the activation process. This can be accomplished through producing of an activated complex, which stands for association or fixation and results in a decrease in the system's degrees of freedom.

Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy SEM, measurements were performed by FESEM

Instrument/ ZEISS Model Sigma VP, in Iran, Tehran. Figure 9(a-b) shows a SEM image of Csteel corroded in 6 M HCl with and without of FHDB inhibitor. The corroded surface of C-steel is demonstrated by the acid-dipped coupons (see Figure 9a). The damaged body is evidence that hydrochloric acid has dissolved the iron that was present on the metal surface. In addition, the eroded holes can be found throughout the entire sample, verification of the acid attack on the Csteel, whereas a packed film layer was produced in Figure 9b, due to the adsorbed layer by the synthetic FHDB inhibitor, the surface was smooth and free of pits. Inhibiting process is made possible by the formation of a protective surface by the inhibitor on metal surface. Hence, the inhibitor actively prevents acid corrosion from occurring on the C-steel surface.



Figure 9: SEM micrographs of C- steel in a 6M HCl solution at 313 K; (a) without FHDB inhibitor and (b) in presence of FHDB inhibitor

Atomic Force Microscopy (AFM)

Atomic Force Microscopy AFM (with highresolution type) measurements were carried out by NAIO AFM2022, Nanosurf, Switzerland in Iraqi Ministry of Industry, Baghdad, Iraq. As dispalyed in Figure 10(a-b), using the 3D AFM, both the surface roughness and topography of the C-steel coupons were examined through characterization approach at the nanoscale level. AFM is a reliable tool for quantifying the surface roughness and assessing the effectiveness of corrosion inhibitors. Figure 10a depicts the pitted, corroded metal surface immersed in 6M HCl solution without the FHDB inhibitor. In this situation, the R_{α} (rootmean-square roughness), Ra (average roughness), and P-V (the maximum peak-to-valley) height values for the C-steel surface observed are 68.25,

53.05, and 48.17 nm, respectively. These results imply that C-steel surface immersed in 6 M HCl, it proves that unprotected C-steel has a rougher surface because it corrodes in an acidic environment. The C-steel surface following immersion in an acidic liquid containing 6 M HCl is depicted in Figure 10b. The C-steel surface's R_a, R_a, and P-V height values are 33.63, 27.94, and 33.37 nm, respectively. The R_q, R_a, and P-V compared to an uninhibited environment, height values are significantly lower in an inhibited environment. These parameters demonstrate the smoother surface due to the compact protective film of Fe²⁺⁻ FHDB complex that forms on the metal surface and smooth its surface, and then prevents C-steel from corrosion.



(a)





(b)

Figure 10: AFM images of the surface of (a) C-steel immersed in 6M HCl (blank) and (b) C-steel immersed in 6M HCl + FHDB inhibitor

Weight Loss under Dynamic Conditions

We usually measure corrosion in the laboratory under the static conditions, which are accurate to a certain ratio. However, corrosion measurements under the static conditions are not expressive in the dynamic conditions such as corrosion in pipelines transporting fluids and gases. Therefore, dynamic methods are used, in which the corrosion coupons are subjected to dynamic conditions in addition to other conditions (such as temperature, pressure, *etc.*). These tests are carried out according to the standard (ASTM G-170, G-184, and G-202), and it is also possible to conduct tests under static conditions, at high temperatures and pressure.

The high-pressure and high-temperature dynamic corrosion measuring device, Dynamic Autoclave Device/CORTEST Company USA, (located in the Petroleum Research and Development Center) makes it easy to conduct experiments in very difficult conditions up to the conditions of the oil reservoir's interior (the temperature up to 200°C, pressure up to 100 bar, and movement up to 1500 rpm), as shown in Figure 11.



Figure 11: Experimental setup for corrosion test with and without FHDB under atmospheric pressure/variation temperatures and different concentrations

The Vessel is made from High Corrosion Resistant Alloy (HASTELLOY C-276) is a cylindrical chamber with a diameter of 12.7 cm, 5 inches, and height of 17.5 cm, 6.91 inches. Likewise, the volume of the chamber is (1.8 L).

The rotating shaft is made from HASTELLOY C-276, 30.15 cm, 11.87 inches in length, and the rotating cage consists of a couple of PTFE Disks with 10 cm, 4 inches diameter, both of the disks have 8 grooves to hold the test coupons. The coupon dimension is (75*19.0*3.0) mm (2.953*0.748*0.118) inches [28].

Relevance Rotating Cage Speed for Testing Inhibitors under Field Simulation

The Al-Ahdab oil field in Iraq as a case study. 20-30% HCl acid is used in the acidification phase of well stimulation operations to interact with rocks, dissolving them, and increasing their permeability.

In the field, the acidified injection rate per flash is = $0.43 \text{ m}^3/\text{min.}$ (0.0066 m³/sec) in a 2-inch diameter pipe (0.0508 m) at atmospheric pressure [29].

Assuming a point to rotating cage, the angular velocity of the rotating disk is defined by N expressed in rpm. The angular velocity of the disk can be converted into $rad.s^{-1}$ by the following Equation 8 [30]:

$$W_{(rad.s^{-1})} = \frac{2\pi}{60 \, N \, (rpm)} \tag{8}$$

This also means that the disk rotates from \boldsymbol{w} radians during one second. During that same second, a distance of $r^*\boldsymbol{w}$. It implies that the speed of injection is also equal to r * \boldsymbol{w} . The conversion can be done by the following Equations 9, 10:

$$U_{(m.s^{-1})=r*W_{[(rad.s]^{-1})}=\frac{r*2\pi}{60 N (rpm)}}$$
 (9)

$$N(rpm) = \frac{60}{2\pi * r} * v_{(m.s^{-1})}$$
(10) The calculated rotating cage according to the simulated with acidizing in the

ording to the flow he field, as shown in Table 5.

 Tuble of the calculated rotating eage according to the now rate simulated with detailing in the new									
Acidization process flow	Inner diameter of	cross sectional area	n 1	N(rpm)					
rate (m^3/min) (m ³ /s)	injection pipeline (m)	(m ²)	U (m.s ⁻¹)						
0.0066	0.0508	0.002025802	3.257968299	889.353047					

Table 5: The calculated rotating cage according to the flow rate simulated with acidizing in the field

Corrosion inhibition experimental results

Corrosion experimental were conducted under moderate temperatures and concentrations of synthesized FHDB at atmospheric pressure. According to Figure 10, the experimental setup consists of (i) rotating motor, (ii) rotating disks, and (iii) HASTELLOY (C-276) autoclave chamber with 8 coupons (stripes) controlled by pressure and temperatures sensors.

The corrosion experiments were carried out in a (1.8) liter Hastelloy C-276 autoclave, the schematic experiments setup is demonstrated in Figure 10. 17%-18% (6M HCl) was used in these experiments with and without FHDB as an inhibitor for 1 hour (for each run) by dynamic conditions at 890 rpm calculated according to the field acid injection flow conditions, as presented in Table 6. Figure 12 indicates the schematic of the autoclave experiments setup.





The coupons were cleaned and weighed before being inserted into the device's rotating disk's slots and the rotating assembly was then installed in the device cell. When everything was ready for use, the 6M HCl (with and without FHDB) was added to be tested; temperature, pressure, rotating speed, and test duration adjustments are made. Once the test is complete, turn on the equipment, raise the coupons, clean, and reweigh

them to determine the rate of corrosion using Equation 11 [31]:

Corrosion Rate (mpy) =
$$\frac{K * \Delta W}{A * T * D}$$
 (11)

Where,

 $K = constant value (3.45 * 10^6).$

 ΔW = weight difference (g).

- A = surface area of areae the sample, cm^2 .
- T = exposure time in hours.
- D =sample density in g/cm³.

Table 6 illustrates the corrosion rates and inhibition efficiency for FHDB under dynamic autoclave conditions at 890 rpm.

Table 6 demonstrates a significant corrosionresistance improvement due to the inhibitorinjection. It is also evident the corrosion resistanceimprovement from 50 to 200 ppm inhibitor dose.To evaluate the inhibitor efficiency a control test

was carried out without inhibitor (blank). Based on Weight loss result at dynamic condition, the corrosion resistance is more than twenty times higher when 50 to 200 ppm of inhibitor was injected at 40 $^{\circ}$ C and more than thirty times higher when 50 to 200 ppm of inhibitor was injected at 70 $^{\circ}$ C.

Blank C. R. mpy =			10,800		20,040		33,868		65,784	
FHDB Synthesized Inhibitor		Dum	40 (ºC)		50 (ºC)		60 (ºC)		70 (ºC)	
		Run	C.R. mpy	I. E. %						
	50	1	493.3	95.43	796	96.03	1042	96.92	1824	97.23
(m		2	590.4	94.53	638.1	96.82	1065	96.86	1824	97.23
ıdd)	100	1	484.6	95.51	636.6	96.82	882.9	97.39	1270	98.07
ion		2	495.6	95.41	571.9	97.15	833	97.54	1411	97.85
ıtrat	150	1	425.7	96.06	487.2	97.57	787.1	97.68	1046	98.41
ncen	150	2	493.1	95.43	612.6	96.94	811.7	97.6	1079	98.36
Сол	200	1	443	95.9	546.4	97.27	714.5	97.89	853.2	98.7
	200	2	423.1	96.08	570.3	97.15	803.7	97.63	962.5	98.54

Conclusion

From the overall experimental results, the following conclusions can be deduced:

1) The findings of the current investigation shown that FHDB is an effective corrosion inhibitor for C-steel in a solution of 6 M hydrochloric acid.

2) The corrosion inhibition efficiency enhanced with increasing inhibitor concentrationn and decreased by raising the temperature.

3) According to the PDP measurements, FHDB functions as a mixed-type inhibitor, delaying both anodic and cathodic processes without altering the corrosion mechanism.

4) The FHDB adsorption on the C-steel surface obeys the Langmuir adsorption isotherm.

5) The highest corrosion protection efficiency is approximately 98.997% at 3 '3 K and 200 mg/L concentration of FHDB.

6) Electrochemical measurement and the surface analysis showed good agreement.

7) The result showed clearly the FHDB inhibitor effect even at trace amounts at dynamic condition

and the inhibition efficiency is more than 95% at different temperature.

Acknowledgements

I would like to extend my gratitude to the Faculty of Science / Mansoura University, in particular Prof. Dr. Abdel Aziz Fouda, as well as Prof. Dr. Dawood Salem Abd for their efforts and support in completing the scientific manuscript.

Disclosure Statement

No potential conflict of interest was reported by the authors.

Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Authors' Contributions

All authors contributed to data analysis, drafting, and revising of the paper and agreed to be responsible for all the aspects of this work

ORCID

Zaidoun K. Kuraimid <u>https://orcid.org/0009-0007-7727-5706</u> Abd El-Aziz S. Fouda <u>https://orcid.org/0000-0002-3239-4417</u> Dawood S. Abid <u>https://orcid.org/0000-0002-7346-8208</u>

References

[1]. Singh A., Quraishi M.A.m Acidizing corrosion inhibitors: a review, *J Mater Environ Sci.*, 2015, **6**:224 [Google scholar], [Publisher]

[2]. Liu Y., Chen L., Tang Y., Zhang X., Qiu Z., Synthesis and characterization of nano-SiO2@ octadecylbisimidazoline quaternary ammonium salt used as acidizing corrosion inhibitor, *Reviews on Advanced Materials Science*, 2022, **61**:186 [Crossref], [Google scholar], [Publisher]

[3]. Gupta R.K., Malviya M., Ansari K.R., Lgaz H., Chauhan D.S., Quraishi M.A., Functionalized graphene oxide as a new generation corrosion inhibitor for industrial pickling process: DFT and experimental approach, *Materials Chemistry and Physics*, 2019, **236**:121727 [Crossref], [Google scholar], [Publisher]

[4]. Obot I.B., Meroufel A., Onyeachu I.B., Alenazi A., Sorour A.A., Corrosion inhibitors for acid cleaning of desalination heat exchangers: Progress, challenges and future perspectives, *Journal of Molecular Liquids*, 2019, **296**:111760 [Crossref], [Google scholar], [Publisher]

[5]. Wazzan N., Obot I.B., Fagieh T.M., The role of some triazoles on the corrosion inhibition of C1020 steel and copper in a desalination descaling solution, *Desalination*, 2022, **527**:115551 [Crossref], [Google scholar], [Publisher]

[6]. Haruna K., Obot I.B., Ankah N.K., Sorour A.A., Saleh T.A., Gelatin: A green corrosion inhibitor for carbon steel in oil well acidizing environment, *Journal of Molecular Liquids*, 2018, **264**:515 [Crossref], [Google scholar], [Publisher]

[7]. Chauhan D.S., Mazumder M.A.J., Quraishi M.A., Ansari K.R., Suleiman R.K., Microwave-assisted synthesis of a new Piperonal-Chitosan Schiff base as a bio-inspired corrosion inhibitor for oil-well acidizing, *International journal of biological* *macromolecules,* 2020, **158**:231 [<u>Crossref</u>], [<u>Google scholar</u>], [<u>Publisher</u>]

[8]. Fuchs-Godec R., Pavlović M.G., Synergistic effect between non-ionic surfactant and halide ions in the forms of inorganic or organic salts for the corrosion inhibition of stainless-steel X4Cr13 in sulphuric acid, *Corrosion Science*, 2012, **58**:192 [Crossref], [Google scholar], [Publisher]

[9]. Dariva C.G., Galio A.F., Corrosion inhibitors– principles, mechanisms and applications, *Developments in corrosion protection*, 2014, **16**:365 [<u>Crossref</u>], [<u>Google scholar</u>], [<u>Publisher</u>]

[10]. Cotton J.B., Scholes I.R., Benzotriazole and related compounds as corrosion inhibitors for copper, *British corrosion journal*, 1967, **2**:1 [Crossref], [Google scholar], [Publisher]

[11]. El-Etre A.Y., Inhibition of acid corrosion of carbon steel using aqueous extract of olive leaves, *Journal of colloid and interface science*, 2007, **314**:578 [Crossref], [Google scholar], [Publisher]

[12]. Olivares-Xometl O., Likhanova N.V., Domínguez-Aguilar M.A., Hallen J.M., Zamudio L.S., Arce E., Surface analysis of inhibitor films formed by imidazolines and amides on mild steel in an acidic environment, *Applied Surface Science*, 2006, **252**:2139 [Crossref], [Google scholar], [Publisher]
[13]. Hegazy MA, Abdallah M, Awad MK, Rezk M. Three novel di-quaternary ammonium salts as corrosion inhibitors for API X65 steel pipeline in acidic solution. Part I: experimental results, *Corrosion Science*, 2014, **81**:54 [Crossref], [Google scholar], [Publisher]

[14]. Guo L., Obot I.B., Zheng X., Shen X., Qiang Y., Kaya S., Kaya C., Theoretical insight into an empirical rule about organic corrosion inhibitors containing nitrogen, oxygen, and sulfur atoms, *Applied surface science*, 2017, **406**:301 [Crossref], [Google scholar], [Publisher]

[15]. Fuchs-Godec R., The adsorption, CMC determination and corrosion inhibition of some N-alkyl quaternary ammonium salts on carbon steel surface in 2 M H2SO4, *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 2006, **280**:130 [Crossref], [Google scholar], [Publisher]

[16]. El Maghraby A.A., Soror T.Y., Quaternary ammonium salt as effective corrosion inhibitor for carbon steel dissolution in sulphuric acid media, Advances in Applied Science Research, 2010, **1**:143 [Google scholar]

[17]. Zhao J., Duan H., Jiang R., Synergistic corrosion inhibition effect of quinoline quaternary ammonium salt and Gemini surfactant in H2S and CO2 saturated brine solution, *Corrosion Science*, 2015, **91**:108 [Crossref], [Google scholar], [Publisher]

[18]. Han P., Chen C., Yu H., Xu Y., Zheng Y., Study of pitting corrosion of L245 steel in H2S environments induced by imidazoline quaternary ammonium salts, *Corrosion Science*, 2016, **112**:128 [Crossref], [Google scholar], [Publisher]

[19]. KS Y., MJ U., Corrosion inhibition efficiency of newly synthesized quaternary ammonium salt in 1M HCl, *I ndian Journal of Chemical Technology (IJCT)*, 2022, **29**:68 [<u>Crossref</u>], [<u>Google scholar</u>], [<u>Publisher</u>]

[20]. Shriner R.L., Hermann C.K.F., Morrill T.C., Curtin D.Y., Fuson R.C., *The Systematic Identification of Organic Compounds*, John Wiley & Sons, 2003 [Google scholar], [Publisher]

[21]. Murulana L.C., Kabanda M.M., Ebenso E.E., Experimental and theoretical studies on the corrosion inhibition of mild steel by some sulphonamides in aqueous HCl, *RSC advances*, 2015, **5**:28743 [Crossref], [Google scholar], [Publisher]

[22]. Bashir S., Lgaz H., Chung I.M., Kumar A., Potential of Venlafaxine in the inhibition of mild steel corrosion in HCl: insights from experimental and computational studies, *Chemical Papers*, 2019, **73**:2255 [Crossref], [Google scholar], [Publisher]

[23]. Fouda A.S., Abd El-Maksoud S.A., El-Hossiany A., Ibrahim A., Corrosion protection of stainless steel 201 in acidic media using novel hydrazine derivatives as corrosion inhibitors, *Int J Electrochem Sci.* 2019, **14**:2187 [Crossref], [Google scholar]

[24]. Ahamad I., Quraishi M.A., Mebendazole: new and efficient corrosion inhibitor for mild steel in

acid medium, *Corrosion science*, 2010, **52**:651 [Crossref], [Google scholar], [Publisher]

[25]. Zarrouk A., Hammouti B., Zarrok H., Al-Deyab S.S., Messali M., Temperature effect, activation energies and thermodynamic adsorption studies of L-cysteine methyl ester hydrochloride as copper corrosion inhibitor in nitric acid 2M, *Int J Electrochem Sci.*, 2011, **6**:6261 [Google scholar]

[26]. Martinez S., Stern I., Thermodynamic characterization of metal dissolution and inhibitor adsorption processes in the low carbon steel/mimosa tannin/sulfuric acid system, *Appl Surf Sci.* 2002, **199**:83 [Crossref], [Google scholar], [Publisher]

[27]. Nambiar N.K., Brindha D., Punniyakotti P., Venkatraman B.R., Angaiah S., Derris indica leaves extract as a green inhibitor for the corrosion of aluminium in alkaline medium, *Engineered Science*, 2021, **17**:167 [Crossref], [Google scholar]
[28]. Gateman S.M., *Investigating Corrosion of Simple and Complex Metallic Materials Using Macro and Micro Electrochemical Techniques*, McGill University (Canada); 2020 [Google scholar], [Publisher]

[29]. Yunyun W.A., Bin Y.A., Zhen Z.H., Wenjie L.I., Xingjuan X.U., Rongqing L.I., Qingjiang G.U., Jinling Y.A., Development and Application of a Foam Control Agent for Acidification Operation, *Drilling and Completion Fluids*, 2019, **36**:366 [Crossref], [Google scholar], [Publisher]

[30]. Chen X., Koper M.T., Mass-transportlimited oxidation of formic acid on a PdMLPt (100) electrode in perchloric acid, *Electrochemistry Communications*, 2017, **82**:155 [Crossref], [Google scholar], [Publisher]

[31]. Haseeb A.S.M.A., Masjuki H.H., Ann L.J., Fazal M.A., Corrosion characteristics of copper and leaded bronze in palm biodiesel, *Fuel Processing Technology*, 2010, **91**:329 [Crossref], [Google scholar], [Publisher]

HOW TO CITE THIS ARTICLE

Zaidoun K. Kuraimid, Abd El-Aziz S. Fouda, Dawood S. Abid. Static and Dynamic Study of Novel 4-Formyl-*N*-Hexadecyl-*N*,*N*-Dimethylbenzenaminium Bromide Synthesized as a Corrosion Inhibitor Use in Petroleum Wells Acidizing Process. *Chem. Methodol.*, 2023, 7(7) 552-568 DOI: <u>https://doi.org/10.22034/CHEMM.2023.395919.1677</u>

URL: https://www.chemmethod.com/article_172253.html