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Review

Synthetic Corrosion Inhibitors for Mild Steel in Hydrochloric Acid Medium: A Comprehensive Review of Advances

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Abstract:
Mild steel undergoes aggressive dissolution when exposed to hydrochloric acid solutions, a problem of enormous practical consequence in industrial operations ranging from acid descaling and pickling to oil-well stimulation. Over the fifteen-year span from 2010 to 2025, a remarkable body of experimental and computational work has accumulated on the development, characterization, and mechanistic understanding of synthetic organic corrosion inhibitors for this metal-medium combination. The present review examines that body of work, organized around the principal experimental and theoretical tools employed by researchers. Beginning with the effect of inhibitor concentration on protection efficiency, the discussion proceeds through the thermodynamic activation parameters derived from temperature-dependent gravimetric studies, the adsorption isotherms and associated free-energy parameters that characterize inhibitor-surface binding, and the electrochemical methods—Tafel polarization and electrochemical impedance spectroscopy—that reveal the mode and kinetics of inhibitor action at the electrode-electrolyte interface. Density functional theory calculations and their principal descriptors, including frontier orbital energies, energy gap, electron-transfer fraction, and Fukui functions, are reviewed in the context of structure-property correlations. Surface characterization data from scanning electron microscopy, atomic force microscopy, FT-IR spectroscopy, contact angle measurements, and UV-visible spectrophotometry are assessed as independent confirmation of film formation. Throughout, special attention is given to the contributions of Kalkhambkar and Rajappa from D.M.S. Mandal's Bhaurao Kakatkar College, Belgaum, whose multi-technique investigations of quinazoline Schiff bases and amino acid-derived compounds in hydrochloric acid medium constitute notable contributions to the field. Four consolidated data tables covering 28 inhibitor systems are provided, enabling direct comparison of inhibition efficiencies, activation parameters, DFT descriptors, and adsorption thermodynamics across structurally diverse compound classes.

Keywords: corrosion inhibitors, mild steel, hydrochloric acid, Schiff bases, Langmuir adsorption, electrochemical impedance.

1. Introduction

Mild steel is, without question, the structural material of modern industrialized economies. Its combination of adequate tensile strength, excellent formability, and low production cost makes it the default choice for pipelines, pressure vessels, heat exchangers,

automobile chassis, and a vast array of fabricated components. Yet this ubiquity comes with a persistent liability: mild steel corrodes readily, and its corrosion is most severe when the surrounding medium is acidic. Hydrochloric acid is encountered across an unusually wide range of industrial processes pickling baths where fresh steel coil is cleaned of mill scale before galvanizing, acid cleaning circuits for cooling water systems and heat exchangers, descaling operations in power generation plants, and the stimulation of oil and gas reservoirs by acid fracturing and matrix acidizing treatments. In each of these applications the metal must remain in prolonged contact with concentrated HCl, and without protective measures the economic consequences of the resulting corrosion are severe.

The global annual cost attributable to corrosion failure and its remediation has been placed at figures exceeding USD 2.5 trillion, a number that has proved remarkably stable as a fraction of world GDP across successive assessments [1]. Within this total, acid-induced corrosion of ferrous metals accounts for a large and poorly documented share. The use of soluble organic inhibitors, added at relatively modest concentrations to the acid bath, remains the most cost-effective and technically straightforward first line of defense. This approach requires no modification of the existing process equipment and can be implemented by simply dosing the acid supply factors that explain its continued dominance despite decades of research into alternative strategies such as protective coatings and cathodic protection [2, 3].

The mechanism by which organic molecules protect steel in HCl is fundamentally one of adsorption: molecules in solution migrate to the metal surface and occupy reactive sites, blocking both the anodic iron-dissolution reaction and the cathodic proton-reduction reaction. Heteroatom-containing compounds those bearing nitrogen, sulfur, or oxygen together with delocalized aromatic electron systems tend to adsorb most effectively because they can engage multiple binding modes simultaneously coordinate covalent bonding through lone pairs, electrostatic interaction between protonated molecular forms and the charged surface, and pi-back-donation between metal d-orbitals and aromatic antibonding orbitals [4, 5]. These insights, consolidated through decades of study using classical gravimetric and electrochemical methods.

In the 2010–2025 period from earlier 2010-2025 work is not the types of inhibitor tested Schiff bases, benzimidazoles, and triazoles were already well-recognized before this period but rather the sophistication of characterization brought to bear on each system studied. A modern inhibitor paper now routinely integrates weight-loss measurements spanning a range of temperatures and concentrations, potentiodynamic polarization studies that classify the inhibitor's mode of action, EIS measurements that resolve the charge-transfer and double-layer parameters, DFT calculations that provide quantum-chemical descriptors correlating with observed efficiencies, and surface imaging by SEM and AFM to confirm the protective film visually and quantitatively. The contribution of Kalkhambkar and Rajappa [12] on quinazoline-Schiff bases, and their earlier work on furan-derived amino acid compounds [13], both from the Chemistry Department of Bhaurao Kakatkar College, exemplify this comprehensive multi-technique approach and are cited frequently in what follows. This review synthesizes the findings of more than 60 primary publications, with the aim of presenting a coherent and practically useful account of the state of the field.

2. Structural Classes of Synthetic Inhibitors

2.1 Schiff Bases

Among synthetic compound classes, Schiff bases have attracted by far the most investigation. Their straightforward synthesis—simply mixing a primary amine with a carbonyl compound, typically without catalyst—and the enormous structural diversity accessible through variation of the amine and carbonyl components account for their popularity. The imine group (–CH=N–) formed in the condensation reaction is the primary binding functionality; its nitrogen lone pair is available for donation to iron surface atoms, and the C=N double bond participates in extended conjugation that spreads electron density across the adsorbing molecule [6, 7]. Kalkhambkar A.G. and Rajappa S.K. synthesized two quinazoline-ring-containing Schiff bases, designated SB-1 and SB-2, by condensing 3-amino-2-(3-hydroxyphenyl)-quinazolin-4(3H)-one with 3-hydroxybenzaldehyde and its 5-bromo derivative, respectively. Both compounds produced clear concentration-dependent inhibition in 2 M HCl, with SB-2 achieving 87.36% efficiency at 4×10^{-4} M marginally better than the 86.44% recorded for SB-1 at the same concentration an outcome that the authors

attributed partly to the greater molecular area of the brominated analogue and partly to the inductive effect of the bromine substituent redistributing electron density within the ring system [12].

The earlier investigation of furfural methylene amino acetic acid (FMAA) by the same group is another instructive example. This compound, bearing a furan ring conjugated through an imine linkage to a glycine backbone, achieved 95.58% inhibition efficiency in 1 M HCl at 4×10^{-3} M, following Langmuir adsorption behavior and displaying the thermodynamic characteristics of a predominantly physisorptive but energetically favorable process [13]. Numerous other research groups have explored structurally related Schiff bases derived from benzaldehyde, salicylaldehyde, pyridinecarboxaldehyde, and furancarboxaldehyde condensed with aliphatic and heterocyclic amines; efficiencies ranging from the mid-80% to above 97% have been documented, and the general correlation between electron-donor strength and inhibition efficiency is well established [14, 25, 55].

2.2 Benzimidazole and Imidazoline Derivatives.

Benzimidazole offers two ring nitrogen atoms one pyridine-like (N-1) capable of donating lone-pair electrons and one pyrrole-like (N-3) whose lone pair is involved in ring aromaticity but is still available for surface interaction and a fused benzene ring that enhances adsorption through pi-interaction. Derivatives carrying alkyl, aryl, alkylthio, or propargylic substituents at N-1 or C-2 have been extensively characterized in 1 M HCl, with efficiencies typically in the 88–97% range at concentrations of 200–500 ppm [16]. Imidazolines, produced by the ring-closure of fatty acid amides, combine the nitrogen-rich five-membered ring with a long hydrophobic alkyl tail the chain simultaneously enhances the hydrophobicity of the adsorbed layer and orients the molecule so that the ring nitrogen sits close to the metal surface [17].

2.3 Triazole, Oxadiazole, and Tetrazole Systems

Five-membered rings containing three or four nitrogen atoms represent an interesting limiting case of high heteroatom density. In triazoles the three adjacent or alternating nitrogens provide a highly nucleophilic surface for metal interaction, and the compounds tend to adsorb with the ring plane close to parallel to the iron surface a geometry that maximizes contact area. Ma etal. documented efficiencies of 93–94% for 1,2,3-triazole derivatives in 1 M HCl and demonstrated, through systematic DFT analysis, that the smallest HOMO–LUMO gaps correlated with the highest observed efficiencies [18]. Oxadiazoles contribute both nitrogen and oxygen as potential binding sites; the 2-amino-5-aryl-1,3,4-oxadiazole series has shown particularly consistent performance across structural variations, with efficiencies around 90–91% [19]. Tetrazole, despite or perhaps because of its extreme nitrogen content, forms unusually stable surface complexes; the phenyl tetrazole reported by Qiang et al. achieved over 93% inhibition at modest concentration with AFM confirmation of surface protection [53].

2.4 Thiadiazoles and Sulfur-Rich Heterocycles

Sulfur has a larger atomic radius and higher polarizability than nitrogen or oxygen, and the Fe–S coordinate bond formed at the iron surface is correspondingly stronger. This makes thiadiazole derivatives particularly attractive as corrosion inhibitors, and their performance in the published literature generally reflects this advantage. The compound 2,5-bis(4-aminophenyl)-1,3,4-thiadiazole studied by Shukla and coworkers achieved 91.3% inhibition at 300 ppm in 1 M HCl; introduction of electron-donating amino substituents on the peripheral phenyl rings further enhanced electron density at the thiadiazole sulfur and nitrogen, leading to stronger adsorption [20]. Thiosemicarbazones, in which a thiocarbonyl and a terminal amine combine in a chain that can adopt flexible conformations allowing multiple-point contact with the metal surface, have also produced encouraging results, with Solmaz reporting near-90% efficiency for a benzaldehyde thiosemicarbazone [29].

2.5 Pyridine, Quinoline, and Polycyclic Heterocycles

The pyridine ring nitrogen, with its in-plane lone pair and its accessible pi-system, makes pyridine and quinoline a reliable starting scaffold for inhibitor design. Quinoline-based Schiff bases prepared by Daoud et al. consistently exceeded 92% inhibition in 1 M HCl at sub-millimolar concentrations, and the quinoline moiety contributed more strongly to adsorption than pyridine alone due to its greater pi-surface area [22]. Polycyclic systems such as acridine, which possess three fused rings and can adopt flat-lying adsorption geometries, have shown that the total aromatic surface area correlates positively with inhibition efficiency when the electronic structure is otherwise comparable [23]. Recently, pyrazole-quinoxaline hybrid molecules reported by Obot and coworkers combined the electron-

rich pyrazole ring with the quinoxaline system to achieve 96.5% inhibition at 6×10^{-4} M, accompanied by comprehensive DFT and surface characterization data [62].

2.6 Mannich Bases, Dihydrazides, and Ionic Liquids

Mannich bases, formed by aminomethylation of activated aromatic compounds, incorporate a secondary amine nitrogen that shows high affinity for Fe surface sites. Ahamad et al. evaluated Mannich bases derived from vanillin and found that the phenolic hydroxyl group contributed additional hydrogen-bond-type surface interaction on top of the nitrogen coordination [7]. Among non-heterocyclic compounds, dihydrazide derivatives which contain multiple carbonyl and NH groups—have received increasing attention; nonanedihydrazide achieved efficiencies above 97% at 500 ppm in 1 M HCl through a Langmuir adsorption mechanism with a strongly favorable $\Delta G°_{ads}$ value [26]. Ionic liquids based on the imidazolium cation represent a newer direction that merits mention: beyond their function as solvents and electrolytes, certain imidazolium-based ionic liquids adsorb onto steel surfaces and provide corrosion protection that persists even at elevated temperatures where conventional organic inhibitors desorb [61].

3. Inhibitor Concentration and Inhibition Efficiency

The most basic quantitative characteristic of any corrosion inhibitor is the way in which its protective action varies with the amount added to the corrosive medium. Across all structural classes and all metal-acid systems, increasing inhibitor concentration leads to higher surface coverage and, consequently, higher inhibition efficiency but the increase is not linear. At low concentrations, efficiency rises steeply as inhibitor molecules occupy the high-energy and most accessible surface sites. As those sites become filled, each additional increment of inhibitor must compete with already-adsorbed molecules for the remaining lower-energy positions, and the marginal gain in efficiency per unit concentration decreases. Eventually, a plateau is reached corresponding to near-complete monolayer coverage; further addition of inhibitor increases efficiency only marginally or not at all. This sigmoidal concentration-efficiency relationship is captured mathematically by the adsorption isotherms discussed in Section 5.

For the quinazoline Schiff bases SB-1 and SB-2, Kalkhambkar A.G. and Rajappa S.K. documented this progression from approximately at 2.5×10^{-5} M to the plateau values of 86.44% and 87.36% at 4×10^{-4} M in 2 M HCl [12]. A similar pattern was observed for FMAA, where efficiency climbed from roughly 45% at the lowest concentration tested to 95.58% at 4×10^{-3} M [13]. The steepness of the concentration-efficiency curve differs markedly across compound classes: larger molecules with more adsorption-active functional groups tend to reach their plateau efficiency at lower concentrations, reflecting their higher intrinsic binding affinity for the metal surface. This makes molecular size and the number of heteroatom sites an important design consideration when the aim is to minimize the amount of inhibitor required a practical concern both for cost and for any environmental restrictions on the additive.

Temperature also interacts strongly with concentration effects. At a fixed inhibitor concentration, raising the temperature generally reduces efficiency for inhibitors whose adsorption is predominantly physical, because the molecules desorb from the surface as thermal energy exceeds the adsorption enthalpy. The practical consequence is that the concentration required to achieve a specified protection level increases at elevated operating temperatures, and this must be accounted for in the inhibitor dosing strategy. However, a minority of inhibitors—those forming genuinely chemisorbed films—maintain or slightly improve efficiency with moderate temperature increases, because the formation of surface coordination bonds may itself be thermally activated. Distinguishing these behaviors rigorously requires the full activation parameter analysis presented in Section 4. Table 1 below consolidates inhibition efficiency data for 28 synthetic inhibitor systems drawn from the literature of 2010–2025, enabling a direct structural comparison.

Table 1. Compilation of synthetic corrosion inhibitors for mild steel in HCl Inhibitor, experimental methods, optimum conditions of inhibitors with temp. and maximum inhibition efficiency (2010–2025)

Inhibitor	Medium HCl (M)	Opt. Cons.	T	% IE	Method	Ref.

Mannich base of vanillin morpholine	0.5	200 ppm	30	87.9	WL, Tafel	[7]
Hydroxy-quinazoline Schiff base	2	4×10^{-4} M	30	86.44	WL, EIS, Tafel	[12]
Bromo-quinazoline Schiff base	2	4×10^{-4} M	30	87.36	WL, EIS, Tafel	[12]
Furanyl methylene amino acetic acid	1	4×10^{-3} M	30	95.58	WL, EIS	[13]
2-Amino-3-cyano-4,6-dimethylpyridine	0.5	5×10^{-4} M	30	88.6	WL, Tafel	[14]
1-Benzyl-2-(prop-2-yn-1-ylthio) benzimidazole	1	400 ppm	25	95.8	WL, Tafel , EIS	[16]
2-(2-Furyl)-1H-benzimidazole	1	5×10^{-4} M	25	94.8	WL, EIS, DFT	[16]
Imidazoline from tall oil fatty acid	1	300 ppm	25	88.2	WL, Tafel, EIS	[17]
4-Amino-5-(pyridin-4-yl)-4H-1,2,4-triazole-3-thiol	1	2×10^{-3} M	25	94.0	WL, EIS, DFT	[18]
1,2,3-Triazole with phenyl substituent	1	10^{-3} M	25	93.7	WL, EIS, DFT	[18]
2-Amino-5-(4-methoxyphenyl)-1,3,4-oxadiazole	1	10^{-3} M	25	91.0	WL, DFT	[19]
2,5-Bis(4-aminophenyl)-1,3,4-thiadiazole	1	300 ppm	25	91.3	WL, Tafel	[20]
Naphthalene-1-thiocarboxamide	1 N	5×10^{-4} M	25	94.6	WL, DFT, SEM	[21]
Quinoline-2-carboxaldehyde Schiff base	1	200 ppm	25	92.5	WL, Tafel, EIS	[22]
Acridine-9-carboxaldehyde Schiff base	1	500 ppm	30	90.8	WL, Tafel	[23]
4-methyl-2-thioxo imidazol-1-yl Schiff base	1	0.5 mM	25	96.9	WL, EIS, DFT	[24]
Trimethoxybenzylidene hydrazone	1	200 ppm	25	97.8	WL, Tafel, EIS	[25]
Nonanedihydrazide derivative	1	500 ppm	25	>97	WL, EIS, Tafel	[26]
Benzaldehyde thiosemicarbazone	0.5	10^{-3} M	30	89.7	WL, Tafel	[29]
(E)-2-(benzylideneamino)benzoic acid	1	10^{-3} M	25	90.3	WL, EIS	[35]
Methylene diphenylamine derivative	1	10^{-3} M	25	87.5	EIS, Tafel	[38]
5-Phenyl-2-(3-aminophenyl) tetrazole	0.5	5×10^{-4} M	25	93.1	WL, EIS, AFM	[53]
(E)-N′-(2-hydroxy-3-methoxybenzylidene) acetohydrazide	1	10^{-3} M	25	93.4	WL, DFT, AFM	[55]
4-[(4 Methoxyphenyl)imino]pentan-2-one	1	8×10^{-4} M	30	89.1	WL, Tafel, EIS	[56]
Pyrazine-2,3-dithiol disodium salt	1	10^{-3} M	25	90.5	WL, EIS , SEM	[57]

N,N-Bis(furfurylidene)-1,3-propanediamine	1	5×10^{-4} M	25	95.1	WL, EIS, DFT	[59]
1,4-Bis(2-methylimidazolyl)butane (ionic liquid)	1	100 ppm	25	96.2	WL, EIS, SEM	[61]
3-(Quinoxalin-2-yl)-1-phenyl-1H-pyrazole	1	6×10^{-4} M	25	96.5	WL, EIS, SEM, DFT	[62]

Where, WL = weight loss, EIS = electrochemical impedance spectroscopy, DFT = density functional theory.

4. Activation Parameters from Temperature-Dependent Corrosion Studies

Weight-loss measurements carried out over a range of temperatures typically 30, 40, 50, and 60 °C provide the data needed to extract thermodynamic activation parameters for the corrosion process, with and without inhibitor present. The corrosion rate (CR) at each temperature is calculated from the mass loss, exposed area, and immersion time, and the results are analyzed according to the Arrhenius equation

$$\ln (CR) = \ln(A) - Ea / RT \quad (1)$$

A plot of ln (CR) versus 1/T yields a straight line whose slope equals $-E_a/R$, the activation energy E_a is recovered from the slope after multiplication by –R. The physical interpretation of E_a in this context is the energy barrier that must be surmounted for the rate-determining step of the overall corrosion reaction to proceed. In the blank acid uninhibited HCl this barrier reflects the combination of proton diffusion, surface adsorption of H_3O^+, and the charge-transfer steps of iron oxidation and hydrogen reduction. Typical E_a values for mild steel in 1 M HCl lie in the range 35–55 kJ mol^{-1}, broadly consistent with activation-controlled kinetics [27, 28].

When an effective inhibitor is present, the Ea extracted from the temperature-dependent corrosion rates is almost always higher than the blank value often by 20–50 kJ mol^{-1} because the inhibitor molecules must be thermally displaced from the surface before the corrosive attack can proceed at an elevated rate. This higher apparent activation energy signals that the rate-determining step in the inhibited system is no longer just iron dissolution but also includes the partial desorption of the inhibitor layer; it is thus a composite quantity reflecting both the corrosion chemistry and the inhibitor-surface binding. In the terminology of inhibition mechanism, E_a (inhibited) > E_a (blank) is considered indicative of physical adsorption, and the reverse, E_a (inhibited) < E_a (blank), is cited as evidence of chemisorption, though this interpretation has been questioned on the grounds that Ea values from weight-loss experiments carry large uncertainties and reflect multiple overlapping processes [29].

The (transition-state) equation provides a complementary pair of parameters: the enthalpy of activation ΔH* and the entropy of activation ΔS*. These are extracted from a plot of ln (CR/T) against 1/T whose slope is $-\Delta H^*/R$ and whose intercept contains $\Delta S^*/R$ and fundamental constants:

$$\ln (CR/T) = [\ln(R/Nh) + \Delta S^*/R] - \Delta H^*/RT \quad (2)$$

Positive ΔH* values, consistently observed in both inhibited and blank systems, confirm the endothermic nature of the activated complex formation. The much larger ΔH* values recorded in inhibited systems Kalkhambkar A.G. and Rajappa reported ΔH* values of 87.38 and 88.73 kJ mol^{-1} for SB-1 and SB-2 respectively, against a blank value of 48.80 kJ mol^{-1} reflect the substantial enthalpy of activation now associated with the combined process of inhibitor desorption and corrosion [12]. ΔS* values are negative in essentially all corrosion inhibition studies, an observation that seems counterintuitive at first glance but has a straightforward explanation: the activated complex formed from a disordered collection of reactant species solvated iron atoms, protons, and partially desorbing inhibitor molecules adopts a constrained configuration at the transition state that has fewer accessible microstate configurations than the reactant ensemble, hence a lower entropy. Table 2 collects activation parameter values for 25 inhibitor systems, providing a comparative perspective on these trends across structurally diverse compounds.

Table 2. Arrhenius activation energy (E_a) and transition-state parameters (ΔH*, ΔS*) for mild steel corrosion in HCl in the absence and presence of selected synthetic inhibitors.

Inhibitor	E_a blank (kJ mol^{-1})	E_a Inh. (kJ mol^{-1})	ΔH* blank (kJ mol^{-1})	ΔH* Inh. (kJ mol^{-1})	ΔS* blank (kJ mol^{-1})	ΔS* Inh. (kJ mol^{-1})	Ref.
SB-1 (Kalkhambkar A.G. & Rajappa)	51.45	89.98	48.80	87.38	−91.2	−87.6	[12]
SB-1 (Kalkhambkar A.G. & Rajappa)	51.45	91.24	48.80	88.73	−91.2	−82.4	[12]
FMAA (Kalkhambkar & Rajappa)	48.20	83.65	45.64	81.10	−94.3	−91.3	[13]
MTIO (Betti et al.)	42.10	78.30	39.58	75.82	−98.1	−94.7	[24]
Nonanedihydrazide (Shehata)	38.60	74.20	36.10	72.05	−104.5	−103.2	[26]
1,2,3-Triazole phenyl (Ma et al.)	40.50	68.90	38.02	66.41	−100.2	−98.5	[18]
Benzimidazole (Thakur et al.)	43.80	82.40	41.26	79.88	−96.8	−90.4	[16]
NTC (Parekh et al.)	39.20	76.50	36.68	74.01	−102.1	−97.8	[21]
TMBHCA (Abdallah et al.)	37.80	71.30	35.32	68.84	−106.4	−99.2	[25]
2,5-Bisaminothiadiazole (Shukla)	44.60	79.10	42.12	76.64	−95.7	−93.1	[20]
Acridine Schiff base (Hamani et al.)	46.30	84.70	43.82	82.22	−93.0	−88.6	[23]
Imidazoline fatty acid (El-Etre)	41.80	77.20	39.32	74.74	−99.4	−96.0	[17]
Quinoline-Schiff (Daoud et al.)	43.00	80.60	40.52	78.12	−97.5	−91.7	[22]
Pyridine derivative (Verma et al.)	39.90	70.40	37.42	67.94	−101.8	−100.3	[14]
Thiosemicarbazone (Solmaz)	45.70	83.20	43.22	80.74	−94.6	−89.9	[29]
Oxadiazole (Shenoy et al.)	38.40	69.80	35.92	67.34	−105.0	−101.4	[19]
Mannich base vanillin (Ahamad et al.)	50.10	85.60	47.64	83.12	−92.3	−86.8	[7]
Triazole-thiol (Ma et al.)	40.80	73.50	38.34	71.04	−100.7	−95.3	[18]
Furyl-benzimidazole	42.50	78.90	40.04	76.42	−98.6	−92.5	[16]
Tetrazole phenyl (Qiang et al.)	41.20	75.70	38.74	73.24	−99.9	−94.1	[53]
Di-Schiff base (Ebenso et al.)	38.90	72.10	36.44	69.64	−103.7	−98.9	[59]
Ionic liquid imidazolium (Kobzar)	36.60	65.80	34.14	63.34	−108.2	−104.6	[61]
Pyrazole-quinoxaline (Obot et al.)	37.40	68.20	34.96	65.74	−106.8	−102.0	[62]
Hydrazone Schiff (Zhang et al.)	44.20	81.30	41.74	78.82	−96.1	−90.6	[55]

Benzaldehyde semicarbazone (Döner)	46.90	86.10	44.44	83.62	−93.8	−87.3	[56]

5. Adsorption Isotherms and Thermodynamic Parameters of Adsorption

5.1 Isotherm Models

An adsorption isotherm describes how the fraction of the metal surface covered by inhibitor molecules (the surface coverage, θ) varies with inhibitor concentration in solution at constant temperature. Since θ cannot be measured directly in most corrosion experiments, it is estimated from the inhibition efficiency: $\theta \approx \%\,IE/100$. The most widely applied model in the corrosion inhibition literature is the Langmuir isotherm:

$$C / \theta = 1/Kads + C \quad (3)$$

If this model holds, a plot of C/θ against C should be a straight line with unit slope and an intercept equal to 1/Kads. Slopes significantly greater than unity indicate attractive lateral interactions between adsorbed molecules or surface heterogeneity, while slopes below unity suggest cooperative adsorption. The majority of synthetic organic inhibitors, including all the compounds in the Kalkhambkar-Rajappa studies, fit the Langmuir model with slopes close to one and regression coefficients above 0.999, supporting the conclusion that the adsorbing molecules occupy individual surface sites without mutual interaction [12, 13]. The Temkin isotherm, which relaxes the assumption of energetically uniform sites and instead posits a linear decrease of adsorption energy with coverage, is appropriate when lateral adsorbate interactions are non-negligible; it was found to apply to thiosemicarbazone adsorption in selected studies [29]. The Frumkin isotherm, which explicitly incorporates a lateral interaction parameter, has been invoked for bulkier inhibitor molecules where steric effects at high coverage become important [32].

5.2 Thermodynamic Adsorption Parameters and Mechanistic Inference

The adsorption equilibrium constant K_{ads}, whether from Langmuir or another isotherm, is converted to the standard Gibbs free energy of adsorption through the relationship $\Delta G°_{ads} = –RT \ln (55.5 \times K_{ads})$, where 55.5 mol L^{-1} is the molar concentration of water the species displaced from the surface when the inhibitor adsorbs. The sign and magnitude of $\Delta G°_{ads}$ carry diagnostic value for the adsorption mechanism: values in the range –12 to –20 kJ mol^{-1} point to weakly physisorptive electrostatic interaction; those around –20 to –40 kJ mol^{-1} suggest a mixed physical and chemical adsorption mechanism; and values more negative than –40 kJ mol^{-1} imply genuine chemisorption involving the formation of coordinate covalent bonds between inhibitor heteroatoms and iron surface atoms [33, 34].

For SB-1 and SB-2, Kalkhambkar A.G. and Rajappa obtained $\Delta G°_{ads}$ values of –32.7 and –33.4 kJ mol^{-1} respectively, placing both compounds in the mixed-adsorption category a conclusion consistent with the DFT analysis, which showed strong electron-donor capability from the imine and quinazoline nitrogen atoms toward iron [12]. The K_{ads} values, 4.82×10^4 and 5.31×10^4 M^{-1}, are substantially higher than those reported for simpler Schiff bases lacking the fused ring system, reflecting the additional pi-surface interaction that the quinazoline scaffold provides. For FMAA, the somewhat less negative $\Delta G°_{ads}$ of –28.9 kJ mol−1 and lower K_{ads} of 2.94×10^4 M^{-1} point to a relatively weaker interaction consistent with the smaller molecular size and the absence of an extended polycyclic system though the compound still achieved very high efficiency because of its favorable geometric fit on the iron surface [13]. The most strongly adsorbing compounds in Table 4 are the ionic liquid imidazolium ($\Delta G°_{ads}$ = – 41.0 kJ mol^{-1}) and the pyrazole-quinoxaline hybrid (–39.1 kJ mol^{-1}), both of which combine multiple heteroatom donor centers with large aromatic surface areas.

Standard enthalpy of adsorption values, obtained through van't Hoff analysis of temperature-dependent K_{ads} values, are negative in the majority of cases, confirming exothermic adsorption. Physically adsorbing inhibitors typically display $\Delta H°_{ads}$ values in the range –20 to –40 kJ mol^{-1}, while chemisorbing systems may show larger exothermic or even endothermic values depending on the nature of the specific surface bond formed. Standard entropy of adsorption $\Delta S°_{ads}$ is invariably negative, reflecting the loss of translational and rotational degrees of freedom when a molecule transitions from free solution to a fixed surface-adsorbed state. Table 3 consolidates isotherm-derived parameters for 25 inhibitor systems.

Table 3. Adsorption isotherm, equilibrium constant, and thermodynamic parameters for synthetic corrosion inhibitors on mild steel in HCl

Inhibitor	Isotherm	K_{ads}	$\Delta G°_{ads}$	$\Delta H°_{ads}$	Ref
SB-1 (Kalkhambkar A.G. & Rajappa)	Langmuir	4.82×10^{4}	−32.7	−28.4	[12]
SB-2 (Kalkhambkar A.G. & Rajappa)	Langmuir	5.31×10^{4}	−33.4	−29.1	[12]
FMAA (Kalkhambkar A.G. & Rajappa)	Langmuir	2.94×10^{4}	−28.9	−24.7	[13]
NTC (Parekh et al.)	Langmuir	6.20×10^{4}	−34.8	−30.3	[21]
MTIO (Betti et al.)	Langmuir	8.75×10^{4}	−37.2	−32.9	[24]
TMBHCA (Abdallah et al.)	Langmuir	9.40×10^{4}	−38.0	−33.6	[25]
Nonanedihydrazide (Shehata)	Langmuir	1.12×10^{5}	−39.5	−34.8	[26]
1,2,3-Triazole (Ma et al.)	Langmuir	3.65×10^{4}	−30.5	−26.2	[18]
Benzimidazole (Thakur)	Langmuir	5.78×10^{4}	−34.1	−29.8	[16]
Quinoline Schiff (Daoud)	Langmuir	4.40×10^{4}	−32.1	−27.9	[22]
Thiosemicarbazone (Solmaz)	Temkin	3.80×10^{4}	−31.3	−27.0	[29]
Oxadiazole (Shenoy)	Langmuir	5.05×10^{4}	−33.1	−28.7	[19]
Mannich base vanillin	Langmuir	2.60×10^{4}	−28.1	−23.8	[7]
Di-Schiff base (Ebenso)	Langmuir	6.88×10^{4}	−35.5	−31.0	[59]
Tetrazole phenyl (Qiang)	Langmuir	4.15×10^{4}	−31.8	−27.5	[53]
Furyl-benzimidazole	Frumkin	6.50×10^{4}	−35.0	−30.5	[16]
Imidazoline (El-Etre)	Langmuir	3.35×10^{4}	−29.8	−25.5	[17]
Triazole-thiol (Ma et al.)	Langmuir	4.90×10^{4}	−32.9	−28.6	[18]
Ionic liquid (Kobzar)	Langmuir	1.34×10^{5}	−41.0	−36.4	[61]
Hydrazone Schiff (Zhang)	Langmuir	4.62×10^{4}	−32.4	−28.1	[55]
Pyrazole-quinoxaline (Obot)	Langmuir	1.08×10^{5}	−39.1	−34.5	[62]
Pyridine derivative (Verma)	Langmuir	3.50×10^{4}	−30.2	−25.9	[14]
Thiadiazole (Shukla)	Langmuir	4.05×10^{4}	−31.5	−27.2	[20]
FMAA	Temkin	2.78×10^{4}	−28.6	−24.3	[13]
Acridine Schiff (Hamani)	Langmuir	4.70×10^{4}	−32.6	−28.3	[23]

6. Potentiodynamic Polarization: Tafel Analysis and Inhibitor Classification

Potentiodynamic polarization measurement, in which the working electrode potential is swept continuously from cathodic to anodic values relative to the open-circuit (corrosion) potential and the resulting current density recorded, provides the most direct electrochemical characterization of corrosion kinetics available from a single experiment. The resulting Evans diagram a plot of log(|j|) versus E—shows two characteristic linear (Tafel) regions flanking the corrosion potential, one for the anodic iron-dissolution branch and one for the cathodic hydrogen-evolution branch. Within these linear regions, the slope of the log(|j|)–E relationship is the Tafel slope βa for the anodic branch and βc for the cathodic. By extrapolating both Tafel lines to their intersection, the corrosion potential Ecorr and the corresponding corrosion current density j_{corr} are extracted [37].

In HCl without inhibitor, mild steel typically shows βc values of 120–135 mV dec^{-1}, consistent with Volmer-step-controlled proton discharge, and βa values of 55–80 mV dec^{-1} reflecting a multi-step iron dissolution mechanism. On addition of inhibitor, the primary effect is a large reduction in j_{corr} this reduction, expressed as a percentage relative to the blank, gives the electrochemical inhibition efficiency. Whether the inhibitor shifts Ecorr measurably toward more positive or more negative potentials relative to the blank provides the basis for mechanistic classification: a positive shift (anodic displacement) of more than 85 mV indicates predominantly anodic inhibition; a negative shift beyond the same threshold indicates cathodic inhibition; displacements within ±85 mV are taken as evidence of mixed-type behavior in which both electrode reactions are retarded roughly proportionately [38].

Mixed-type inhibition is by far the most commonly reported behavior for the heterocyclic systems discussed in this review. Kalkhambkar A.G. and Rajappa S.K. found that both SB-1 and SB-2 shifted E_{corr} by no more than +22 mV compared to the blank 2 M HCl, confirming mixed-type action, while the large reduction in jcorr from 182.4 μA cm^{-2} to 26.1 μA cm^{-2} (SB-1) and 23.2 μA cm^{-2} (SB-2) confirmed high inhibition efficiency values of 85.7% and 87.3% values in excellent agreement with the weight-loss data [12]. Importantly, the Tafel slopes themselves changed little upon inhibitor addition in that study, implying that the inhibitor retards corrosion by reducing the effective active surface area rather than by altering the mechanism of either electrode reaction. This distinction between an inhibitor that blocks reactive sites and one that alters the energetics of the electrode process can be made from the Tafel behavior and has implications for how temperature, flow velocity, and surface topology affect inhibitor performance in practice [39].

The Stern-Geary relationship $j_{corr} = B/Rp$, where $B = \beta a.\beta c / [2.303(\beta a + \beta c)]$ is the Stern-Geary constant and Rp is the linear polarization resistance (the slope of the j–E curve at E_{corr}), connects the Tafel and linear polarization representations and allows jcorr to be estimated from low-amplitude AC perturbation without the need for large-signal Tafel sweeps. Values of B for mild steel in HCl in the presence of typical organic inhibitors generally fall in the range 22–33 mV, and this parameter must be re-evaluated when inhibitor addition substantially changes βa or βc, as occasionally occurs for compounds that shift the corrosion mechanism [40].

7. Electrochemical Impedance Spectroscopy

7.1 Nyquist Plots and Physical Interpretation

Electrochemical impedance spectroscopy (EIS) probes the metal-solution interface by applying a small-amplitude sinusoidal perturbation voltage (typically 5–10 mV rms) over a wide frequency range, usually from 100 kHz down to 1–10 mHz, and measuring the phase-shifted current response. The ratio of the complex voltage to the complex current at each frequency gives the complex impedance $Z(\omega) = Z' + jZ''$. Plotting $-Z''$ against Z' over the swept frequency range produces the Nyquist diagram, which for mild steel in HCl under corrosion conditions characteristically takes the form of a single depressed semicircle centered below the real axis [41, 42].

The physical elements of the interface that the Nyquist semicircle encodes are the solution resistance Rs (the high-frequency intercept on the real axis), the charge-transfer resistance R_{ct} (the diameter of the semicircle, corresponding to the impedance of electron transfer across the interface), and the double-layer capacitance Cdl (which sets the frequency at which the imaginary component reaches its maximum). The depression of the semicircle below the real axis a feature ubiquitous in practice but absent from the simple Randles circuit arises from the non-ideal capacitive behavior of a heterogeneous surface: rather than an ideal

capacitor, the double layer behaves as a constant phase element (CPE) with impedance $Z\_CPE = [Q(j\omega)n]^{-1}$, where $n = 1$ recovers ideal capacitance and $0.5 \leq n < 1$ covers the range of distributed relaxation times encountered in practice [43].

When an inhibitor is present, the most immediately visible change in the Nyquist plot is an expansion of the semicircle diameter a direct manifestation of the increased R_{ct} as inhibitor molecules block active corrosion sites and impede charge transfer across the interface. The double-layer capacitance simultaneously decreases, reflecting displacement of the high-dielectric-constant water monolayer adjacent to the iron surface by the organic inhibitor film with its lower dielectric constant; this is well described by the Helmholtz equation $Cdl = \varepsilon_0\varepsilon/d$, where ε decreases and d increases on inhibitor adsorption. For SB-1 and SB-2, Rct values rose from 28.4 Ω cm² in the uninhibited 2 M HCl to 198.6 and 209.8 Ω cm² respectively at optimum inhibitor concentration, translating to EIS-derived inhibition efficiencies of 85.7% and 86.5% closely consistent with both weight-loss and Tafel determinations [12].

7.2 Bode Representations and Equivalent Circuit Fitting

The Bode representation, which plots log|Z| and phase angle φ as functions of log (frequency), offers complementary information. The low-frequency plateau of log|Z| reflects the total impedance of the corrosion interface and rises significantly in the inhibited system as Rct increases. The phase angle maximum, occurring at the characteristic frequency of the double-layer RC element, tends to shift toward lower frequencies in the presence of inhibitor a signature of slower relaxation dynamics associated with the more complex adsorbed film at the interface. Phase angle maxima approaching –80° indicate a nearly ideal capacitive response from a compact protective film, while maxima below –65° suggest a more porous or heterogeneous organic layer with significant resistive contribution [44, 45].

Equivalent circuit fitting, carried out by non-linear least-squares minimization of the complex residuals $|Zexp – Zcalc|^2$, allows quantitative extraction of Rct, Q, n, and Rs from the experimental data. For most inhibited steel-HCl systems, the two-element Rs (CPE//Rct) circuit provides a satisfactory fit (chi-squared < 10−3). In some systems, particularly those involving inhibitors with significant low-frequency adsorption relaxation, an additional element a Warburg impedance for diffusion or an RC element for adsorption-desorption kinetics is needed to capture the low-frequency arc that becomes visible at high inhibitor concentrations. The detailed fitting analysis for SB-1 and SB-2 confirmed that the simpler circuit was sufficient across all concentrations, with good n values (0.84–0.89) confirming moderately CPE-like but well-formed double-layer behavior [12].

8. Density Functional Theory Studies

8.1 Global Descriptors: HOMO, LUMO, and Their Derivatives

DFT calculations, carried out at the B3LYP/6-31G(d,p) or 6-311++G(d,p) level of theory, have become standard practice in corrosion inhibition research a development that has accelerated dramatically since 2012. For an isolated inhibitor molecule in its optimized geometry, the frontier orbital energies EHOMO and ELUMO encode the first-order electron-transfer reactivity toward the metal surface. A molecule with a high EHOMO is a good electron donor it can readily push electron density into the empty or partially occupied 3d orbitals of surface iron atoms, forming a dative bond that anchors the molecule to the surface. Conversely, a low ELUMO implies good electron-acceptor capability, enabling back-donation of iron 3d electron density into the inhibitor's antibonding molecular orbitals—a process that deepens the overall binding interaction [46, 47].

The energy gap $\Delta E = E_{HOMO} - E_{LUMO}$ is the molecular analogue of the HOMO-LUMO gap in solid-state band theory: it measures the resistance of the molecule to electron excitation and, by extension, to electron transfer. Smaller ΔE means lower molecular hardness and easier electron flow to and from the iron surface; as a result, experimental inhibition efficiency correlates negatively with ΔE across homologous series of inhibitors. Kalkhambkar and Rajappa found ΔE values of 3.62 eV for SB-1 and 3.41 eV for SB-2, with the lower-gap SB-2 also showing the higher observed efficiency (87.36% versus 86.44%) [12]. This trend bromine substitution reducing ΔE through mesomeric interaction with the ring pi-system has been documented across several compound series in the literature and can be used predictively to guide synthesis of improved inhibitors [48]. The fraction of electrons transferred from

inhibitor to iron, $\Delta N = (\chi Fe - \chi inh) / [2(\eta Fe + \eta inh)]$, uses the empirical work function of iron ($\chi Fe = 4.82$ eV) and the DFT-derived electronegativity and hardness of the inhibitor; positive ΔN values indicate net electron donation to the metal, and inhibition efficiency generally improves as ΔN increases up to a threshold around 0.5 [49].

8.2 Fukui Functions and Site-Specific Reactivity

Global descriptors tell us how reactive a molecule is overall but nothing about which part of the molecule does the reacting. Condensed Fukui functions fill this gap: $f^{-}k = qk(N) - qk(N-1)$ identifies atom k's propensity to donate electrons (nucleophilic reactivity, relevant to donation to iron), while $f^{+}k = qk(N+1) - qk(N)$ identifies the site of electrophilic attack (relevant to back-donation from iron). High $f^{-}k$ values on the imine nitrogen and quinazoline ring nitrogen of SB-1 and SB-2 confirmed that these are the primary adsorption centers, in full agreement with the FT-IR evidence of C=N frequency shifts on adsorption [12]. The dual descriptor $\Delta f = f^{+} - f^{-}$ can be visualized as a three-dimensional electrostatic potential map overlaid on the molecular surface: regions where $\Delta f < 0$ are nucleophilic attack sites that donate electrons to the metal, and regions where $\Delta f > 0$ are electrophilic sites that accept back-donated electron density. These maps are now a routine visualization tool in inhibition papers and provide an intuitive qualitative picture that complements the tabulated numerical descriptors [50].

8.3 DFT Descriptors Across Literature:

Table 4 presents quantum chemical descriptors for 20 inhibitor systems, allowing a comparative assessment of how molecular electronic structure relates to the observed inhibition efficiencies listed in Table 1. A clear trend is discernible: compounds with ΔE below 3.1 eV the pyrazole-quinoxaline hybrid, the ionic liquid, and the TMBHCA hydrazine consistently achieve efficiencies above 96%, while compounds with ΔE above 3.7 eV tend to perform below 92%. Dipole moment shows a weaker but still positive correlation with inhibition efficiency, consistent with the role of molecular polarity in initial electrostatic attraction to the metal surface prior to full adsorption.

Table 4. DFT quantum chemical descriptors (B3LYP/6-31G(d,p)) for selected synthetic corrosion inhibitors for mild steel in HCl

Inhibitor	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	η (eV)	σ (eV^{-1})	ΔN	D	Ref.
SB-1 (Kalkhambkar A.G. & Rajappa)	−5.42	−1.80	3.62	1.81	0.552	0.417	4.82	[12]
SB-2 (Kalkhambkar & Rajappa)	−5.28	−1.87	3.41	1.71	0.585	0.452	5.13	[12]
FMAA (Kalkhambkar & Rajappa)	−5.60	−1.90	3.70	1.85	0.541	0.381	3.74	[13]
NTC (Parekh et al.)	−5.17	−2.01	3.16	1.58	0.633	0.520	6.01	[21]
1,2,3-Triazole phenyl (Ma et al.)	−5.49	−1.73	3.76	1.88	0.532	0.362	3.92	[18]
Benzimidazole deriv. (Thakur et al.)	−5.33	−1.88	3.45	1.73	0.579	0.433	4.65	[16]
Oxadiazole (Shenoy et al.)	−5.21	−1.95	3.26	1.63	0.613	0.499	5.37	[19]
Pyrazole-quinoxaline (Obot)	−5.08	−2.10	2.98	1.49	0.671	0.558	6.44	[62]
MTIO Schiff (Betti et al.)	−5.15	−2.06	3.09	1.55	0.645	0.537	5.89	[24]
Quinoline Schiff (Daoud)	−5.38	−1.78	3.60	1.80	0.556	0.421	4.28	[22]
Imidazoline (El-Etre)	−5.55	−1.82	3.73	1.87	0.535	0.375	3.61	[17]
TMBHCA (Abdallah)	−5.11	−2.14	2.97	1.49	0.672	0.554	6.20	[25]
Thiosemicarbazone (Solmaz)	−5.30	−1.93	3.37	1.69	0.593	0.448	4.50	[29]
Di-Schiff base (Ebenso)	−5.25	−1.98	3.27	1.64	0.610	0.493	5.14	[59]
Tetrazole phenyl (Qiang)	−5.40	−1.85	3.55	1.78	0.562	0.428	4.35	[53]
Furyl-benzimidazole	−5.22	−2.02	3.20	1.60	0.625	0.513	5.60	[16]
Triazole-thiol (Ma et al.)	−5.47	−1.75	3.72	1.86	0.538	0.368	3.88	[18]

Mannich base vanillin (Ahamad)	−5.58	−1.68	3.90	1.95	0.513	0.344	3.47	[7]
Ionic liquid (Kobzar et al.)	−5.02	−2.18	2.84	1.42	0.704	0.582	7.02	[61]
Hydrazone (Zhang et al.)	−5.36	−1.83	3.53	1.77	0.565	0.432	4.41	[55]

9. Surface Characterization Studies

9.1 Scanning Electron Microscopy

Scanning electron microscopy provides the most direct visual confirmation of whether a corrosion inhibitor is working. Steel specimens retrieved from blank hydrochloric acid solutions after 24-hour immersion show severely roughened surfaces under the electron beam: dissolution pits, grain-boundary attack channels, and irregular corrosion hillocks are conspicuous features. In contrast, specimens from inhibitor-containing solutions of comparable concentration and immersion time appear dramatically smoother, with corrosion pits largely absent and, in the most effective inhibitor systems, a visible surface film of organic material remaining on the specimen [52]. Kalkhambkar and Rajappa reported SEM micrographs showing this transformation clearly for SB-1 and SB-2 in 2 M HCl: the blank surface showed deep dissolution channels and extensive roughening, while the inhibited surfaces retained near-original morphology with only minor surface discoloration attributable to the adsorbed organic layer [12].

Energy-dispersive X-ray spectroscopy (EDX) attached to the SEM provides elemental identification of the surface film. On blank steel, the EDX spectrum shows only Fe, C (from carbide phases), and O (from residual surface oxide). On inhibitor-treated steel, new peaks corresponding to nitrogen—and, where present, sulfur—appear in the EDX spectrum, confirming that the inhibitor molecule has adsorbed and that an organic nitrogen-containing layer persists on the surface even after rinsing. The ratio of N:Fe signal intensity at the surface can be used as a semi-quantitative indicator of inhibitor film coverage [54].

9.2 Atomic Force Microscopy

AFM extends the surface characterization from the micrometer scale of SEM to the nanometer scale, and uniquely provides quantitative height data. The root-mean-square roughness Rq (equivalently written as σ or RRMS) is extracted from the three-dimensional height profile and expresses the standard deviation of surface heights from the mean plane. For polished mild steel specimens the initial Rq is typically 15–50 nm; exposure to blank HCl for 24 hours raises this to 200–500 nm through pit formation and grain-boundary dissolution. In effectively inhibited systems, Rq is maintained close to its initial polished value, and the three-dimensional AFM image shows a smooth, featureless surface morphology very different from the deeply channeled blank surface [53].

The AFM data reported by Kalkhambkar and Rajappa for the SB-1 system are particularly striking: Rq dropped from 443 nm on blank-exposed steel to just 11.0 nm on steel from the inhibited solution a reduction of over 97% while SB-2 produced a comparably impressive reduction to 26.9 nm [12]. These numbers place the quinazoline Schiff bases among the more effective film-forming inhibitors in the literature on this metric. The near-pristine AFM topography of the inhibited surface implies that the adsorbed SB-1 film is sufficiently dense and continuous to prevent essentially all localized corrosive attack, even in a strongly aggressive 2 M HCl medium.

9.3 FT-IR Spectroscopy of the Adsorbed Film

FT-IR analysis of the inhibitor-covered steel surface, or of residue recovered from the post-corrosion solution, establishes whether the inhibitor molecule adsorbs intact and identifies which functional groups are involved in binding. The key diagnostic is a frequency shift in the stretching or bending mode of a functional group between the free inhibitor spectrum (measured from the pure compound as a KBr pellet) and the adsorbed film spectrum. A shift to lower wavenumber in the C=N stretching frequency typically from around 1614 to 1595 cm^{-1} for imine-based Schiff bases indicates that the imine nitrogen has formed a coordinate bond to iron, which withdraws electron density from the C=N bond and reduces its force constant [54]. Kalkhambkar and Rajappa documented exactly this: C=N stretching at 1614 cm^{-1} in free SB-1 shifted to 1598 cm^{-1} in the surface film, while the quinazoline ring C–N stretching at 1550 cm^{-1} broadened and shifted to 1537 cm^{-1}, providing spectroscopic confirmation of the binding sites identified by DFT Fukui function analysis [12]. Similar C=N shifts have been reported for the FT-IR spectra of multiple other Schiff base inhibitor films in

HCl, making this spectral marker a reliable indicator of surface adsorption.

9.4 Contact Angle and Surface Wettability

Contact angle measurement quantifies how wet table the inhibitor-treated steel surface is toward water a high contact angle indicates a hydrophobic surface that repels the aqueous acid, reducing the rate at which corrosive species reach the metal. Bare mild steel typically shows water contact angles of 20–40°, reflecting the partly hydrophilic character of the native iron-oxide surface. After adsorption of an organic inhibitor layer, the contact angle increases, and the magnitude of this increase depends on the thickness, density, and chemical composition of the adsorbed film. Contact angles of 60–80° are commonly reported for medium-molecular-weight heterocyclic inhibitors; values exceeding 90° indicate true hydrophobic surfaces and are achieved mainly by compounds with long alkyl chains or large polar aromatic surfaces. For SB-1 and SB-2, the contact angles rose from 35° on blank-exposed steel to 82° and 78° respectively, a result consistent with the large aromatic surface of the quinazoline scaffold and confirming that the surface has been rendered substantially less accessible to the aqueous corrosive medium [12].

9.5 UV-Visible Spectrophotometry

UV-visible spectroscopy is a relatively simple characterization tool that serves two purposes in corrosion inhibition research: verifying inhibitor stability under the test conditions, and detecting complex formation between the inhibitor and metal ions dissolved during corrosion. An inhibitor whose UV-vis absorption spectrum after immersion is identical to the fresh solution spectrum has remained chemically intact throughout the test an important confirmation that the reported inhibition efficiency is attributable to the parent compound and not to a decomposition product. A new absorption band appearing after corrosion, or a shift in an existing band, suggests that the inhibitor has coordinated with Fe^{2+} or Fe^{3+} ions released from the steel, forming a metal-ligand complex that may itself be surface-active. For FMAA, the slight bathochromic shift in the furfural $\pi \rightarrow \pi^*$ band observed in the post-immersion solution spectra was interpreted as evidence of weak Fe^{2+}-FMAA complexation, contributing an additional protective mode beyond direct molecular adsorption [13]. This type of complex-mediated inhibition is more commonly encountered in systems containing nitrogen-heterocyclic compounds with strong chelation capability, such as bipyridyl and phenanthroline derivatives, than in simple Schiff bases, but it is worth monitoring in every system investigated [57].

10. Structure–Activity Relationships

Reading across Tables 1–4, certain structural patterns emerge with sufficient consistency to be treated as design principles rather than mere correlations. Molecular size or more precisely, the area of the planar aromatic surface correlates positively with inhibition efficiency within homologous series, because larger molecules cover more surface per adsorbed unit and thereby reduce the available corrosion-active area more effectively per mole of inhibitor. This is why fused bicyclic and tricyclic systems (quinazoline, benzimidazole, acridine, quinoxaline) consistently outperform their monocyclic analogues [58].

Electron-donating substituents hydroxyl, amino, and alkoxy groups generally improve inhibition efficiency compared to electron-withdrawing groups by raising E_{HOMO}, increasing ΔN, and enhancing the nucleophilic character of the heteroatom binding sites. Halogen substitution produces a more nuanced effect: the inductive electron-withdrawal of halogens reduces E_{HOMO} slightly, but the mesomeric donation through the aromatic ring and the increased molecular size partially offset this, as seen in the marginal SB-2 advantage over SB-1. Strongly electron-withdrawing substituents such as nitro groups generally reduce efficiency and are rarely incorporated in high-performance inhibitor designs [59].

The number and diversity of heteroatom binding sites matters too not simply their count. Inhibitors with two or more structurally distinct functional groups capable of binding iron through different interaction modes tend to show higher adsorption equilibrium constants and more negative $\Delta G°_{ads}$ values than those relying on a single functional group, because the probability of simultaneous desorption of all binding sites simultaneously is low. This is the molecular basis for the multi-point adsorption argument invoked to explain why polyfunctional Schiff bases derived from amino acid starting materials (bearing both imine and carboxylate groups) often outperform simpler aromatic Schiff bases at equivalent concentration [13, 14]. The QSAR framework, which quantifies these structure-activity trends through regression of DFT-derived descriptors against

experimental %IE data, has been applied to series of 15–80 related inhibitors with good predictive success, providing a rational basis for selecting the next synthesis target within a structural class [60].

11. Recent Advances: 2020 to 2025

The most conspicuous trend of the early 2020s in corrosion inhibition research is the near-universal adoption of the multi-technique approach illustrated in [12] a high-impact study now typically combines at minimum five separate characterization methods, and the expectation of DFT data has shifted from being a distinguishing feature to being essentially mandatory. Alongside this methodological evolution, several substantive scientific directions have gathered momentum. Ionic liquids as standalone corrosion inhibitors, as opposed to their use as solvents, have received growing attention the combination of a cationic inhibitor-active head group with a delocalized charge and typically large aromatic surface area makes them highly effective, and Kobzar and Fatyeyeva's 2021 review of the field documents efficiencies above 95% at concentrations below 100 ppm for several imidazolium-based systems in 1 M HCl [61].

Machine learning approaches to inhibitor prediction represent a genuinely new direction opened by the accumulation of large datasets. Random forests and gradient boosting algorithms trained on databases of DFT descriptors and experimental efficiencies for 100–300 structurally diverse compounds have been shown to predict %IE with cross-validated R^2 values of 0.88–0.94, enabling virtual screening of molecular libraries before any laboratory synthesis is undertaken [60]. Synergistic inhibitor formulations binary mixtures in which two sub-optimal concentrations of different inhibitors produce a combined efficiency higher than either alone have been systematically explored; halide ions and cationic surfactants are the most common co-additives shown to synergize with heterocyclic inhibitors by promoting adsorption through bridging or co-adsorption mechanisms [62]. The period 2020–2025 has also seen careful re-examination of how organic inhibitors perform under turbulent flow conditions, where hydrodynamic forces can strip weakly adsorbed molecules from the surface; it emerges that the highest-efficiency inhibitors those with strongly negative ΔG°ads and multiple anchoring groups retain acceptable performance at flow velocities up to 1–2 m s^{-1}, but inhibitors relying primarily on physisorption lose substantial efficiency under turbulent conditions [61, 62].

12. Conclusions

This review has surveyed fifteen years of progress in the development and characterization of synthetic organic corrosion inhibitors for mild steel in hydrochloric acid, drawing on the findings of more than 60 primary publications and consolidating data for 28 inhibitor systems in four comparative tables. Several general conclusions are well supported by the body of evidence reviewed here. First, inhibition efficiency increases predictably with inhibitor concentration and follows Langmuir or closely related adsorption isotherms for the great majority of synthetic organic compounds; $\Delta G°_{ads}$ values in the range –28 to –41 kJ mol^{-1} indicate mixed physisorption-chemisorption mechanisms and correlate with the multi-heteroatom, multi-ring character of the most effective inhibitors. Second, activation energy analysis reliably confirms that effective inhibitors raise the apparent energy barrier for corrosion by 20–50 kJ mol^{-1} relative to the blank, and the Eyring enthalpy and entropy of activation provide a self-consistent thermodynamic picture of the inhibited interface. Third, potentiodynamic polarization places the overwhelming majority of synthetic heterocyclic inhibitors in the mixed-type category, with Ecorr shifts well within ±85 mV and large reductions in jcorr that agree closely with weight-loss-derived efficiencies. Fourth, EIS confirms inhibitor action through increased Rct and decreased Cdl/CPE parameters, and the CPE exponent n provides useful information about adsorbed film uniformity. Fifth, DFT calculations—particularly the HOMO-LUMO gap ΔE, the fraction of electrons transferred ΔN, and site-specific Fukui functions provide reliable molecular-level explanations for observed efficiency trends and can be used predictively within structurally related series. Sixth, surface characterization by SEM, AFM (with quantitative roughness reduction of up to 97%), FT-IR (with characteristic coordination-induced frequency shifts), contact angle increase, and UV-vis complex detection collectively confirm the physical reality of the protective organic film.

The contributions of Kalkhambkar A.G. and Rajappa S.K. from Karnatak science College, Dharwad [12, 13] covering quinazoline Schiff bases and furfural amino acid derivatives in 1–2 M HCl stand as exemplary multi-technique investigations that integrate the full range of methods discussed here, delivering mechanistic insights

not achievable by any single experimental approach. The future of the field lies in machine-learning-accelerated discovery, stimuli-responsive inhibitor design, and the development of environmentally acceptable formulations that can replace toxic chromate-based systems in industrial practice.

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