Influence of Anions on the Inhibition of Corrosion of Zinc in Acidic Solutions by Pyrrole and its Derivatives

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The influence of pyrrole and its derivatives on the corrosion of zinc in 1.0 M HCl and 0.5 M H_2SO_4 has been studied using weight loss and gasometric measurements, potentiodynamic studies and a.c. impedance measurements. All the compounds inhibit the corrosion of zinc effectively in 1.0 M HCl. Potentiodynamic polarisation studies clearly reveal that the inhibition of corrosion of zinc in both the acids by these compounds is under mixed control, but predominantly under cathodic control. Double layer capacitance (C_{dl}) and charge transfer resistance (R_{ct}) were determined from Nyquist plots of a.c. impedance data. The adsorption of these compounds on the surface of zinc obeys Temkin's adsorption isotherm. UV reflectance studies were also carried out to establish the actual mechanism of inhibition of corrosion.

Key words: Pyrroles, corrosion inhibition, adsorption isotherm, impedance spectroscopy, UV reflectance studies

Introduction

Nitrogen containing organic compounds have been found to serve as good inhibitors of corrosion [1-10] and their inhibiting action has been explained in terms of the number of mobile electron pairs [11], the *p*-orbital character of free electrons [12] and the electron density around the nitrogen atom [13]. Heterocyclic compounds containing nitrogen as the hetero-atom in the ring have been reported [14-25] to perform more effectively as corrosion inhibitors. This can be attributed to the fact that these compounds are p-excessive heterocyclic compounds and the electron cloud on the aromatic ring is expected to induce greater adsorption on the metal surface. Pyrroles are a group of N-heterocyclic compounds whose efficacy as corrosion inhibitors for metals in aqueous corrosive environments have been investigated by several authors [26-32].

Cumper et al. [26] have studied the influence of pyrrole and its dimethyl derivative on the dissolution of magnetite in hydrochloric acid solutions. It was observed earlier that the addition of halide ions to sulphuric acid solution containing pyrroles had a synergistic effect in enhancing the corrosion of iron in the acidic solution [27-28]. Stupnisek Lisac et al. have studied the influence of substitution of N-aryl pyrrole derivatives on the inhibition of corrosion of iron in strong acid pickling solution in the presence of different halide ions [29]. It was also found that the substitution increases the activity of 2,5 dimethyl pyrroles [30,31]. The inhibition of corrosion of iron during pickling by substitution of N-aryl pyrroles showed that the substitution improves the inhibitive property of the compound [32]. But, so far detailed studies on the inhibition of corrosion of zinc in acidic solution by pyrroles have not been reported. In the present study the inhibition of corrosion of zinc in 1.0 M HCl and 0.5 M H_2SO_4 by pyrrole and its derivatives has been studied using weight loss and gasometric studies, potentiodynamic studies, a.c. impedance measure-ments and UV reflectance studies.

Experimental

Rectangular zinc specimens (composition Pb 1.03%, Cd = 0.04%, Fe = 0.001% and Zn remainder) of size 5 x 2 x 0.13 cm were used for weight loss and gasometric studies. These specimens were given fine mechanical polishing and then degreased with trichloroethylene before use. For potentiodynamic polarisation studies and a.c. impedance measurements, a cylindrical rod zinc of the same composition as above and axially embedded in Teflon with an exposed area of 0.44 cm² and provided with an electrical contact was used. The electrode was polished using a sequence of emery papers of different grades and then degreased. AR grade acids and triple distilled water were used for preparing all solutions.

All compounds under study were preliminarily screened by weight loss and gasometric measurements as described earlier [6]. Both anodic and cathodic polarisation curves were recorded potentiodynamically (1 mV sec⁻¹) using corrosion measurement system BAS Model 100A Electrochemical Analyser. A platinum foil

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of large surface area was used as the auxiliary electrode and Hg/Hg_2Cl_2 /1 N HCl and Hg/Hg_2SO_4/1 N H_2SO_4 as reference electrodes. Double layer capacitance (C_{dl}) and charge transfer resistance values (R_{ct}) were obtained from impedance measurements [7]. UV reflectance measurements were carried out on surfaces of polished, corroded and corrosion inhibited zinc specimens in the range of 200-700 nm using normal incident angle (90°) using UV visible NIR Spectrophotometer (Model U-3400, Hitachi, Japan).

Results and discussions

Table 1 gives values of inhibition efficiency for pyrrole and its derivatives in 1.0 M HCl and 0.5 M H_2SO_4. These compounds inhibit the corrosion of zinc in both the acids, in the following order:

Table 1. Inhibition efficiencies for the corrosion of mild steel in 1.0 M HCl in the presence of different concentrations of pyrrole and its derivatives from weight loss and gasometric measurements.

Inhibitor Concentration mM	Inhibition efficiency (%) 1.0 M HCl 0.5 M H_2SO_4			
	Weight loss	Gaso-metry	Weight loss	Gaso-metry
Pyrrole				
10	30.4	51.8	44.6	44.6
20	55.2	56.9	48.2	46.5
30	58.4	57.3	52.2	53.5
40	64.4	62.7	60.2	60.9
50	72.6	74.9	65.4	65.8
2-Methyl Pyrrole				
10	56.4	56.9	50.1	50.5
20	62.1	62.7	54.4	56.4
30	65.9	67.8	59.2	60.9
40	69.6	69.8	66.6	65.3
50	78.5	78.8	69.4	69.8
Benzopyrrole				
10	59.0	58.8	55.2	53.5
20	70.0	69.8	58.2	60.9
30	80.8	80.6	66.8	65.3
40	87.3	87.5	72.8	72.3
50	88.9	90.6	76.6	75.2

benzopyrrole > 2-methyl pyrrole > pyrrole

This can be explained way a follows. Pyrrole can be considered as a typical example of p-excessive N-heterocyclic compound. Due to the presence of an heteroatom (nitrogen) having an unshared pair of electrons in the pyrrole ring it disposes its 6p electrons in the ring, and therefore belongs to a group of aromatic compounds [33]. These compounds inhibit the corrosion by the following, (i) interaction between lone pairs of electrons of the nitrogen atom and the positively charged metal surface [34,35], (ii) interaction of p-electrons of the pyrrole ring with the positively charged metal surface [36,37] and the interaction of pyrrolinium cations (py H^+) formed in acidic solutions with negatively charged metal surface. The formation of pyrrolinium cations in acidic solution has been supported by nuclear magnetic resonance measurements [38].

The presence of nucleophilic methyl group leads to an enhancement of electron density at the nitrogen atom, which enhances its adsorption on the metal surface. This in turn leads to an increase in the value of inhibition efficiency in both the acids [39]. In the case of benzopyrrole the introduction of a six membered ring, leads to an increase in p-electron density which in turn leads to more adsorption of the compound on the metal surface. This is responsible for very high values of inhibition efficiency shown by this compound in both the acids. It is found that there is a very good agreement between the values of inhibition efficiency obtained by both the methods.

It is found from the table that pyrrole and its derivatives perform as inhibitors better in 1.0 M HCl than in 0.5M H_2SO_4. Anions in the solution play a significant role in influencing the inhibitive property of organic compounds used as corrosion inhibitors [5,40]. The better performance of pyrroles in 1.0 N HCl can be explained as follows.

Pyrroles can exist either as neutral molecules or in the form of cations in aqueous acidic solutions. As neutral molecules they can adsorb through sharing of electrons between the nitrogen atom and the metal surface. Through the electrostatic interaction between the positively charged pyrrolinium cations (py H^+) and the negatively charged metal surface. The extent of adsorption is also influenced by the anions present in acidic solution [5,40]. The specific adsorption of anions is expected to be more pronounced with anions having a smaller degree of hydration, such as chloride ions. Being specifically adsorbed they create an excess negative charge towards the solution phase and favours the adsorption of pyrrolinium cations leading to enhanced adsorption and thereby more corrosion inhibition [41]. It is also possible that the stronger adsorption of organic molecules is always a direct combination of organic molecules with the metal surface. In some cases the adsorption occurs through already adsorbed chloride or sulphate ions, which interfere with the adsorption of adsorbed organic molecules. The lesser interference by sulphate ions results in lower adsorption and lesser inhibition of corrosion.

Potentiodynamic polarisation studies

Tables 2 and 3 give the values of kinetic parameters for corrosion of zinc in both the acids in the presence of

different concentrations of pyrrole and its derivatives obtained from potentiodynamic polarisation studies. E_{corr} shifts to less negative values in both the acids, in the presence of these compounds, indicating the formation of an adsorbed film on the metal surface.

Table 2. Potentiodynamic polarisation parameters for the corrosion zinc in 1.0 M HCl in the presence of different concentrations of pyrrole and its derivatives

Inhibitor Concentration	Ecorr (mV)	Tafel slopes (mV.dec^{-1})		Icorr (mA.cm^{-2})	I.E. (%)
		b_a	b_c		
Blank	-1075	45	120	3.40	
Pyrrole					
10	-1065	50	120	1.72	49.4
30	-1055	53	133	1.34	60.5
50	-1052	56	140	0.93	72.6
2-Methyl pyrrole					
10	-1060	52	128	1.48	56.5
30	-1055	55	135	1.10	67.6
50	-1050	60	142	0.78	77.1
Benzo Pyrrole					
10	-1055	55	130	1.34	60.5
30	-1050	60	140	0.65	80.9
50	-1045	65	150	0.42	87.6

Table 3. Potentiodynamic polarisation parameters for the corrosion zinc in 0.5 M H_2SO_4 in the presence of different concentrations of pyrrole and its derivatives

Inhibitor Concerntration	Ecorr (mV)	Tafel slopes (mV.dec^{-1})		Icorr (mA.cm^{-2})	I.E. (%)
		b_a	b_c		
Blank	-1034	60	125	2.80	...
Pyrrole					
10	-1026	65	130	1.50	46.4
30	-1015	68	138	1.38	50.7
50	-1005	72	143	0.95	66.1
2-Methyl pyrrole					
10	-1023	68	135	1.30	58.7
30	-1015	72	145	1.05	62.5
50	-1002	75	150	0.80	71.4
Benzo Pyrrole					
10	-1018	70	138	1.20	57.1
30	-1006	75	150	0.95	66.1
50	-993	78	155	0.62	77.8

Increasing concentrations of pyrrole and its derivatives in both the acids enhance both anodic (b_a) and cathodic (b_c) Tafel slopes, but anodic Tafel slope (b_a) to a lesser extent. Thus the inhibition of corrosion of zinc in both the acids by pyrrole and its derivatives is under mixed control, but predominantly under cathodic control.

Pyrrole and its derivatives bring down the values of I_{corr} in both the acids, but to a greater extent in HCl. So they are more effective as corrosion inhibitors in this medium. Among these compounds the decrease in I_{corr} values follows the order.

benzo pyrrole > 2-methyl pyrrole > pyrrole
The values of inhibition efficiency obtained by these compounds in both the acids follow a similar order. The values of inhibition efficiency obtained by this method and those by weight loss and gasometric studies agree very well for both the acids.

Impedance measurements

Impedance diagrams obtained for the frequency range 100 mHz to 100 KHz at the open circuit potential for zinc in 1.0 M HCl and 0.5 M H_2SO_4 in the absence and presence of different concentrations of pyrrole and its derivatives are shown in Figs. 1 and 2. The pattern is very similar for other compounds also in above two acids. It can be seen that impedance diagrams are not perfect semicircles in most of the cases due to frequency dispersion [42]. Impedance parameters such as R_{ct}, C_{dl}, and I_{corr} are derived from Nyquist plots for zinc in 1.0 M HCl and 0.5 M H_2SO_4 in the presence of 50 mM pyrroles and are given in Tables 4 and 5. R_{ct} value increases with increase in the concentration of these compounds and this in turn leads to a decrease in I_{corr} values for zinc in both the acids. Values of R_{ct} are enhanced to a maximum in both the acids in the presence of benzopyrrole followed by 2-methyl pyrrole and pyrrole in the decreasing order. Inhibition efficiency values obtained from I_{corr} values for different compounds agree very well with those obtained from potentiodynamic polarisation studies and weight loss measurement. Values of C_{dl} also decrease to a maximum extent in the presence of benzopyrrole followed by 2-methyl pyrrole and pyrrole in the decreasing order. The decrease in C_{dl} values can be attributed to the adsorption of these compounds from acidic solutions on the metal surface.
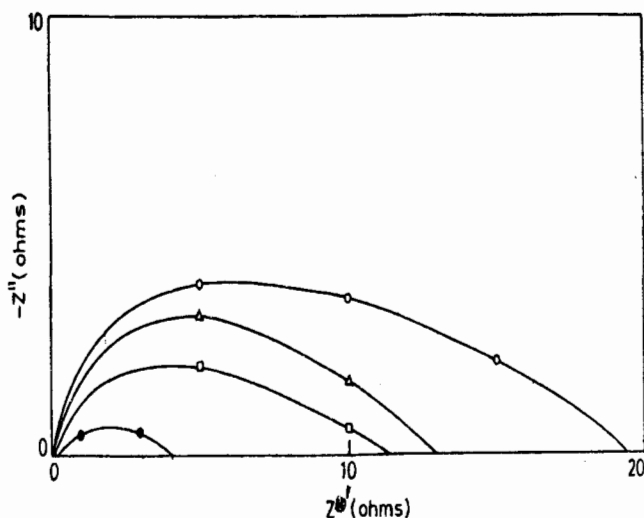

Fig. 1. Nyquist plot for zinc in 1.0 M HCl containing different concentrations of pyrrole ●—● blank □—□ 10 mM pyrrole, Δ—Δ 30 mM Pyrrole, O—O 50 mM pyrrole.
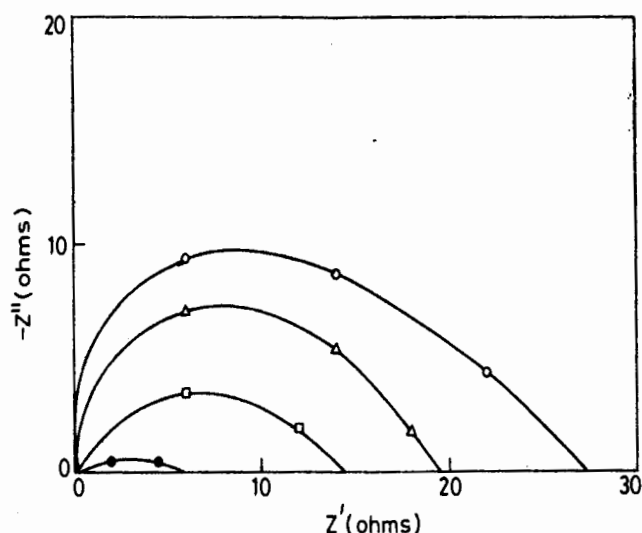
Fig.2. Nyquist plot for zinc in 0.5 M H_2SO_4 containing different concentrations of benzopyrrole ●__● blank ▢—▢ 10 mM benzopyrrole, △—△ 30 mM benzopyrrole, O—O 50 mM benzopyrrole

Table 4. Impedance parameters for the corrosion of zinc in 1.0 M HCl in the presence of 50 mM concentrations of pyrrole and its derivatives

Inhibitor	Rct $(\Omega.cm^2)$	Cdl $(\mu F.cm^{-2})$	Icorr $(mA.cm^{-2})$	I.E. (%)
Blank	4.04	262	3.52	...
Pyrrole	19.25	183	0.90	74.43
Methyl pyrrole	25.54	172	0.82	79.55
Benzo pyrrole	46.5	141	0.42	88.07

Table 5. Impedance parameters for the corrosion of zinc in 0.5 M H_2SO_4 in the presence of 50 mM concentrations of pyrrole and its derivatives

Inhibitor	Rct $(\Omega.cm^2)$	Cdl $(\mu F.cm^{-2})$	Icorr $(mA.cm^{-2})$	I.E. (%)
Blank	5.91	198	2.98	...
Pyrrole	19.21	148	1.08	63.76
Methyl pyrrole	24.2	139	0.90	69.8
Benzo pyrrole	27.3	117	0.83	72.15

UV reflectance studies

The film formation at the metal surface is also supported by the reflectance studies for different specimens under similar conditions. A comparison of specular reflectance curves drawn on a uniform scale for a polished zinc specimen, polished specimens dipped

in HCl alone and those containing 50 mM pyrroles are shown in Fig. 3. It can be seen that percentage of reflectance is maximum for the polished specimen and it decreases considerably in the case of the specimen dipped in the plain acid. This fact clearly reveals that the change in surface characteristics is due to the corrosion of zinc in the plain acid. However in the case of specimens dipped in HCl containing pyrrole and its derivatives reflectance decreases only to a very little extent. This shows that surface characteristics are not very much changed in the presence of pyrrole and its derivatives in HCl due to the formation of a film on the metal surface.
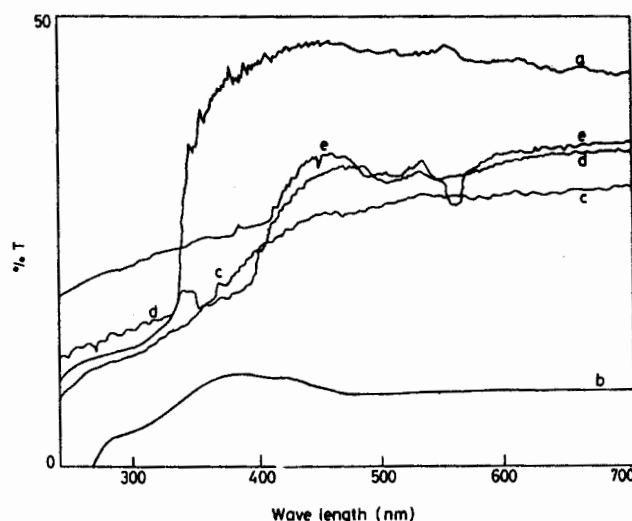

Fig.3. UV reflectance curves for zinc specimens with different concentrationsPolished, dipped in 1.0 M HCl, 50 mM pyrrole, 50 mM 2-methyl pyrrole, 50 mM benzopyrrole.

Adsorption isotherms

The values of surface coverage (q) obtained from values of metal losses in the absence and presence of different concentrations of pyrrole and its derivatives have been used for testing the best fit of isotherms, the systems obey. A plot of θ vs log C for the adsorption of these compounds from both the acids on the zinc surface is found to have a linear relationship. This observation clearly shows that the adsorption of pyrrole and derivatives on the zinc surface from both acidic solutions obeys Temkin's adsorption isotherm.

Conclusion

The main conclusions drawn from this study are, Pyrrole and its derivatives inhibit the corrosion of zinc in both the acids, but more effectively in HCl and the corrosion inhibition follows the order: benzopyrrole > 2-methyl pyrrole > pyrrole. All these compounds function as mixed inhibitors but predominantly as cathodic inhibitors in both the acidic solutions. The inhibition of

corrosion of zinc by these compounds is due to their adsorption on the metal surface and the adsorption is found to obey Temkin's adsorption isotherm.

Acknowledgement

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