

INHIBITION CHARACTERISTICS OF SOME ORGANIC HETEROCYCLES DURING ACID CORROSION OF NICKEL AS STUDIED IN THE LIGHT OF THEIR STRUCTURAL PARAMETERS AND INTERFACIAL REACTIONS*

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The corrosion inhibition characteristics of organic heterocycles like pyridine, pyrrole, furan and thiophene during acid corrosion of nickel have been investigated and it has been found that the results cannot be explained only on the basis of their structural parameters like aromaticities, charge densities on the heteroatoms, ionisation potentials of the molecules, basicities etc. and the simple chemisorption mechanism through $p_{\pi}-d_{\pi}$ interaction cannot explain all of their electrochemical behaviours at the nickel-acid interface. Rather protonation of the heterocycle ring and subsequent chemical transformation into some other species determine the route of inhibition mechanism in some cases. Pyridine, pyrrole and furan were found to inhibit the nickel corrosion in acid solution whereas thiophene catalysed the dissolution process. The catalytic activity of thiophene in acid corrosion of nickel has been explained from the fact that the compound in acid solution is adsorbed on the metal surface and is subsequently decomposed into metal sulphide which leads to higher dissolution of the metal. On the contrary the relatively higher inhibition characteristics of pyrrole were explained to be due to formation of dimeric and trimeric species in acid solutions which effectively blanket the metal surface from the corrosive media.

Keywords : Pyridine, Pyrrole, Furan; and Thiophene

INTRODUCTION

THE correlation between the inhibition characteristics and the structural parameters of the various organic inhibitors have been the field of interest for many years^{1,2}. Most of the studies are based on the assumption that metal-inhibitor interactions are mainly chemisorption in nature and the reactive centre of inhibitor molecules establish the adsorption bond with the metal surface by Lewis acid-Lewis base interaction generally with the inhibitor as electron donor and metal surface as electron acceptor. Although these attempts led to successful correlation between structural parameters and inhibition characteristics of many organic compounds, deviations are not unusual in some corrosive media particularly in which the

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organic additives undergo chemical changes by the influence of the medium as well as by the surface active metal atoms.

As a logical extension of the above observation we have taken a group of organic heterocycles with extensively delocalised π -electron systems and which may undergo chemical transformations in acid solutions particularly catalyzed by the metal substrates. This paper describes the corrosion inhibition characteristics of some structurally related organic heterocycles like pyridine, pyrrole, furan and thiophene during acid corrosion of nickel and an attempt to correlate this property with their structural parameters as well as chemical transformations in solutions at the metal/solution interface. Nickel has been chosen as corroding metal because of its well-known catalytic influence on many organic reactions.

EXPERIMENTAL

Nickel beads (99.99 per cent purity, Johnson Matthey) were used without further analysis. The detailed procedures for surface preparation of the electrode and the electro-chemical cell assembly have been described elsewhere¹⁰. Pyridine, pyrrole, furan and thiophene were procured from BDH (AR grade) and they were purified by distillation.

Corrosion currents, anodic and cathodic tafel slopes were calculated from polarisation resistance data. A small increment of 2mV potential was applied from the potentiostat through the counter electrode and the corresponding current was found out from the potential difference across a standard resistance in series in the circuit. Experiments were carried out in deaerated solutions and the temperature of the system was maintained thermostatically constant at $25 \pm 1^\circ\text{C}$. The metal electrodes were kept in solution for 2–3 hours to allow to come in equilibrium and the experiments were started when the open-circuit potential came practically to constant values. Cathodic and anodic polarisation data were taken maximum up to 20mV overpotential.

Corrosion currents were calculated from the measured polarisation data closed to open circuit potential by the method as described by Mansfeld¹¹. The calculation is based on the Stern-Geary equation¹²

$$I_{\text{corr}} = \frac{b_a \cdot b_c}{2.3 (b_a + b_c)} \cdot \frac{1}{R_p}$$

$$\text{where } R_p = \frac{b_a \cdot b_c}{2.3 I (b_a + b_c)} \exp\left(\frac{2.3 \Delta E}{b_a}\right) - \exp\left(\frac{2.3 \Delta E}{b_c}\right)$$

in which I and ΔE are the polarization current and corresponding overvoltage in the neighbourhood of corrosion potential ($\Delta E \rightarrow 0$).

Corrosion currents were calculated as follows :

(i) Current density-potential relationship for the anodic and cathodic polarisation studies were plotted between $\pm \Delta E = 20\text{mV}$. A tangent was then drawn along $\Delta E = 0$ and the slope of the tangent was then determined from $(dE/dI)_{\text{corr}} = R_p$.

(ii) At a certain value of ΔE , the corresponding current density was multiplied by $2.3 R_p$ and a plot of $2.3 R_p$ against ΔE was made.

(iii) From the above curves, tafel slopes b_a and b_c were determined by curve fitting method using theoretical curves calculated for various values of b_a and b_c 's.

(iv) I_{corr} was then finally calculated using the above Stern-Geary equation substituting the calculated values of R_p , b_a and b_c .

RESULTS

Corrosion currents and other dissolution parameters of nickel in sulphuric acid in absence and in presence of organic additives are shown in Table I. Solutions containing pyridine, pyrrole and furan exhibit higher polarisation resistance than that in pure sulphuric acid and the calculated corrosion current values are all lower in presence of these additives than that in pure sulphuric acid. Very little changes in the cathodic tafel slope values depict that these organic compounds have little influence on the mechanism of cathodic hydrogen evolution reaction. Furan, however, at high concentration changed the cathodic tafel slope considerably. Anodic tafel slopes are increased in solutions containing pyridine whereas those in solutions containing pyrrole are decreased slightly. Pyridine and furan did not inhibit at low concentrations but significant lowering of corrosion currents occurred in presence of these additives at higher concentrations. Pyrrole, of course, exhibited as an effective inhibitor for nickel in sulphuric acid at all concentrations.

TABLE I

Polarisation data of acid corrosion of nickel in presence of various amounts of organic heterocycles

Solution	R_p (Ohm)	$2.3 R_p I$ at	b_c mv/dec. (calculated)	b_a mv/dec.	I_{corr} $\mu A/cm^2$ (calculated)	I_{corr} $\mu A/cm^2$ (Galvet)	Inhibition efficiency (I%) calculated
$^1N H_2SO_4$	1.84	23.06	115	120	13.23	13.0	—
+ $10^{-5}M$ pyridine	1.94	22.94	119	130	13.92	10.8	—
+ $10^{-3}M$ „	4.0	22.84	113.5	130	6.59	7.4	48.67
+ $10^{-1}M$ „	6.0	22.63	105	132	4.32	4.5	67.34
+ $10^{-5}M$ pyrrole	2.5	23.96	120	90	8.944	8.0	33.93
+ $10^{-3}M$ „	3.16	23.31	115	108	7.66	7.8	42.10
+ $10^{-1}M$ „	5.4	23.16	110	110	4.42	4.4	66.51
+ $10^{-5}M$ Furan	1.84	23.06	115	120	13.23	9.0	—
+ $10^{-3}M$ „	2.68	23.11	116	118	9.5	8.7	28.19
+ $10^{-1}M$ „	4.0	22.08	79	120	5.18	6.0	60.84
+ $10^{-5}M$ Thiophene	1.31	20.93	120	130	13.9	13.5	—
$10^{-3}M$ „	1.15	20.53	54	135	14.53	15.0	—
$10^{-1}M$ „	1.32	22.05	85	135	17.18	22.5	—

Thiophene does not behave in the same way as the other three heterocycles. On the contrary this compound catalysed the dissolution of nickel in sulphuric acid.

DISCUSSION

In order to understand the various inhibition characteristics of these organic heterocycles during acid corrosion of nickel it is necessary to discuss their chemical behaviour in sulphuric acid solution particularly at the nickel/acid interface. All the four compounds-pyridine, pyrrole, furan and thiophene are conjugated molecules with various ring heteroatoms and the aromaticity of the molecules and the charge density at the various ring atoms depend on the electronegativity of the heteroatom and the tendency of the π -electrons of the heteroatom to participate in the extensively delocalized π -electron system. If the inhibition by these compounds is supposed to be due to adsorption of these molecules on the metal surface through their d_{π} - p_{π} interaction, then the π electron charge densities on the heteroatoms, their electronegativities and electron affinities should play important roles during acid corrosion of nickel in presence of these organic additives. The values, as shown in the following Table II show that a strong adsorber is rather a weak inhibitor in this case.

From Table II it is apparent that simple d_{π} - p_{π} interaction is not the only phenomenon which is responsible for corrosion inhibition action by these organic heterocycles.

The π -electron charge densities at the various positions of the pyridine ring have been calculated by self consistent field method¹³ which shows that there is a considerable drift of electrons from the ring towards the nitrogen atom. Pyridine is thus a weak monoacid base and forms stable pyridinium cation in acid solution. On the other hand the two of the six π -electrons required for aromaticity for other five membered heterocycles-pyrrole, furan and thiophene must come from the heteroatoms. Hoffman and Cronowitz¹⁴ have found from NMR measurements that chemical shifts of α - and β -hydrogen atoms in pyrrole, furan and thiophene

TABLE II

Some quantum chemical parameters of the organic heterocycles and corrosion current data of nickel in sulphuric acid and presence of these heterocycles

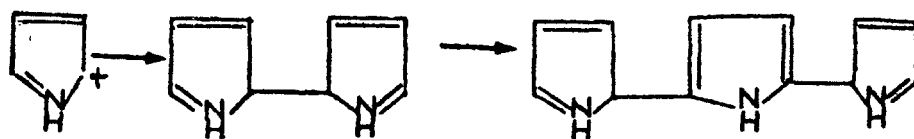
	Pyridine	Pyrrole	Furan	Thiophene
π -electron charge density on heteroatom	1.194 ^(a)	1.692 ^(a)	1.705 ^(a)	1.810 ^(a)
Ionization Potential (eV.)		8.40 ^(b)	8.99 ^(b)	9.12 ^(b)
Corrosion Current of Ni in presence of 10^{-3} M organic additive (μ A/cm ²)	4.50 ^(c)	4.40 ^(c)	6.00 ^(c)	22.50 ^(c)

(a) Same as ref. 17.
 (b) P Linda, G Marino and S Pignataro, *Ris. Sci.* **39**, 666 (1969).
 (c) Data taken from Table I.

are 0.6ppm, 1.05ppm and 0.125ppm respectively with respect to that of benzene as zero. This shows that the aromatic character of the thiophene ring is much closer to benzene. The increasing aromatic character of the series furan, pyrrole and thiophene can, therefore, be related to both the polarizability and electronegativity of the heteroatoms as the electronegativity decreases and the polarizability increases in this order O-N-S.

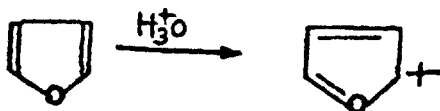
Pyridine has produced a shift in open-circuit potentials slightly towards negative direction. The direction of the shift of potential is an indication that the compound has either little influence on the cathodic partial process or influence on both cathodic and anodic processes simultaneously. It is quite obvious that, owing to the acidity of the medium, pyridine interacts with the metal surface through ion-pair formation between positively charged pyridinium ions and negatively charged metal surface. Pyridine does not reduce the corrosion current appreciably at low concentrations although at high concentrations considerable inhibition of the dissolution of nickel takes place. Felloni and Cozi¹⁵ have studied the effect of pyridine on the acid corrosion of iron and have observed that the compound is adsorbed on the metal surface as free base which is formed by the electrochemical reduction of proton at the electrode surface. Pyridine was found to have no influence on the dissolution parameters during anodic dissolution of nickel in sulphuric acid¹⁶. This shows that the compound acts mainly as a cathodic inhibitor and is adsorbed on the nickel surface through electrostatic interaction between pyridinium cation and negatively charged metal surface. The charge on nickel surface in sulphuric acid at open-circuit potential is very near to zero (relative to pzc of nickel)¹⁷. So the electrostatic interaction between pyridine and metal surface, at open circuit potential, cannot be strong. Relatively low inhibition characteristics of pyridine on nickel corrosion, particularly at low pyridine concentration, show that the inhibition is mainly cathodic in nature and unlike in iron-acid system, the adsorption through π -electron system is not so predominant.

Pyrrole behaves mainly as a very reactive aromatic compound towards electrophilic reagents and hence this compound is expected to be adsorbed on the cathodically charged metal surface and thereby behaves as a cathodic inhibitor. The high inhibition characteristics of the compound cannot be explained simply on the basis of its adsorption on the metal surface because pyrrole ring possesses neither very high aromatic character nor strong basicity like pyridine. Nuclear magnetic resonance studies show that in aqueous acid solutions pyrrole accepts protons at the α -position to give stable cations¹⁸. These cations have no aromatic stability due to lack of π -electron sextet but they are very reactive and can readily polymerize by radical and/or ionic mechanism as follows¹⁹.



In presence of pyrrole sudden increase of passive current density during potentiostatic anodic polarisation of nickel in sulphuric acid between the potential range + 550mV and + 800mV was observed¹⁶ and was explained to be due to rupture of the polymeric coatings and subsequent formation of the stable passive layer. Pyrrole solution in sulphuric acid turns turbid during the experiment because of polymerization. The above physico-chemical characteristics of pyrrole show that the corrosion inhibition property of the compound is, perhaps, due to interaction between the positively charged organic species and the metal surface as well as π -electron system of the polymeric molecule and the vacant d-orbitals of the metal atoms. The lowering of the anodic tafel slopes as calculated from the polarisation resistance data is supposed to be due to formation of (Metal-inhibitor)_{ads} or (Metal oxide-inhibitor)_{ads} species on the anodic metal surface. The slight shift of the open circuit potentials to the negative direction indicate that although pyrrole acts as a mixed inhibitor, the cathodic inhibition is more predominant than anodic inhibition. The preferential adsorption of the compound on the cathodically charged metal surface has been observed from the fact that inhibition by pyrrole is considerably reduced in presence of chloride ions. Hudson *et al.*²⁰ have studied the effects of pyrrole-halide mixture on the acid corrosion of iron and concluded that in presence of chloride ions, the pzc of the metal is shifted more towards anodic direction and thereby reduces the adsorbability of the protonated pyrrole species. At very high concentrations, of course, the polymeric species blanket the metal surface and influence both on the cathodic and anodic reactions.

Furan, like pyrrole, is an aromatic heterocyclic five membered ring. The physico-chemical data suggest that furan behaves chemically as diene ether which possesses unusually great resonance stabilization. Although enol ethers are, in general, very easily hydrolysed by dilute acids to the corresponding carbonyl compounds furan is not so easily hydrolysed because of the initial attack of the proton involves the electrons of the oxygen atom which contribute to the six π -electron system required for aromaticity. Their withdrawal reduces the resonance energy of the ring and converts aromatic furan into very much less stabilized cation. Hockerman

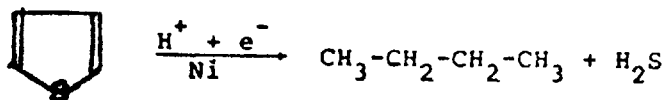


and after^{21,22} have shown that the extent of adsorption of furan derivatives on the metal surface depends on the charge density of the oxygen atom of furan. Because of the electrophilic nature of the heterocyclic oxygen atom, the compound is less effective as inhibitor than pyridine in pyrrole. Shifting of the open circuit potentials towards negative direction may be an indication of the interaction of the positively charged oxygen atom of the ring and metal surface. Calculations of anodic tafel slopes from the polarisation data show that the compound has no influence on the anodic metal dissolution reactions. Furan, as shown in the table, is not an effective

inhibitor for acid corrosion nickel particularly at lower concentrations. At high concentration, it may be concluded that furan inhibits the acid corrosion of nickel by suppressing mainly the hydrogen evolution reaction and therefore, the inhibition action is perhaps, due to adsorption, primarily through coulombic interaction between nickel surface and positively charged furan species. Anodic dissolution of nickel in presence of furan in sulphuric acid showed that the compound has no influence on the dissolution parameter of nickel and so the anodic interaction between the π -electron system of the compound and the positively charged metal surface is thought to be very weak¹⁸.

Thiophene resembles benzene rather than furan and pyrrole in many of its physico-chemical characteristics. Since sulphur atom is less electronegative than oxygen or nitrogen atom, it releases more readily the π -electrons to the ring system to form sextet required for aromaticity. Similarity between benzene and thiophene, thus, allows us to assume that thiophene may be adsorbed on the metal surface through its π -electron system also.

The influence of thiophene on the acid corrosion of nickel in sulphuric acid shows that the compound behaves in a completely different way from that of other three compounds. Thiophene accelerates the rate of metal dissolution at all concentrations. The electrochemical behaviour of the iron group of metals in acid solutions containing organic sulphur compounds have been investigated by many investigators⁹. In most of the cases it was observed that organic sulphur compounds inhibit the acid dissolution of iron through adsorption of the compounds on the metal surface by their extensively delocalised π -electron system whereas they activate the dissolution of nickel in acid solutions by being decomposed into S^{2-} or HS^- ions at the metal/solution interface. Rosey and Shreir and others²³ have interpreted the results of inhibition or activation of nickel in acid solutions in presence of organic sulphur compounds in terms of the actual relative concentration of sulphur compound and its decomposition products (S^{2-} or HS^-). Desulphurization of thiophene and its derivatives by hydrogenolysis in presence of nickel catalyst is a well known reaction²⁴.



Nickel catalysts are shown to be rapidly poisoned by thiophene indicating formation of nickel sulphide on the metal surface. The strong catalytic activity of thiophene on the acid corrosion of nickel should, thus, be explained on the basis of its adsorption and subsequent decomposition equilibrium at the metal/solution interface. The compound shifts the open circuit potentials in the negative direction indicating thus that the interaction of the compound with the metal surface takes place through ion-pair formation between the positively charged protonated thiophene species and negatively charged surface metal atoms.

Low cathodic Tafel slope values indicate that thiophene influences on the mechanism of the hydrogen evolution reaction. Moreover, from the galvanostatic studies²⁵ in the higher overpotential ranges, thiophene is shown to increase the rate of hydrogen evolution reaction during cathodic polarisation, thus indicating that the compound, after adsorption on the metal surface, is decomposed into some degraded product which are rapidly desorbed from the metal surface. In the cathodic potential range, because of the presence of hydrogen ions in the vicinity of the interface, the decomposed sulphide ions come into the bulk phase leaving the metal surface exposed into the corrosive media. In the anodic potential region, due to lack of aqueous hydrogen ions near the interface, the decomposed sulphide ions unite with nickel ions forming insoluble nickel sulphide coatings and thereby exhibiting irregular corrosion current densities as are usually shown from the potentiostatic polarisation curves of nickel in presence of organic sulphur compounds.

CONCLUSION

From the overall investigations of the acid corrosion of nickel presence of pyridine, pyrrole, furan and thiophene, it may be concluded that all the compounds are adsorbed on the metal surface primarily through the interaction between the positively charged protonated organic species and surface metal atoms. This interaction is very weak because of very small negative charge on the nickel surface in sulphuric acid at the open circuit potential. Pyridine and furan exhibit relatively poor inhibition action particularly at low concentration because of this weak electrostatic interaction. Pyridine, however, acts as a better inhibitor than furan due to stronger basicity of nitrogen atom and thereby forms stable protonated species. Pyrrole, in acid solution, is protonated and polymerizes at the metal/solution interface which blankets the metal surface and thereby protects it effectively from further dissolution. The compound behaves as a mixed inhibitor and shows that in addition to electrostatic metal-cation interaction, the compound, in the form of polymeric species, is adsorbed on the metal surface through $d_{\pi} - p_{\pi}$ interaction which might lead to the formation of (Metal-inhibitor)_{ads} or (Metal-OH-inhibitor)_{ads} complexes and thereby changes the mechanism of anodic reactions. Thiophene catalyzes the dissolution of nickel in sulphuric acid. In the acid solution the compound reacts with proton and the adsorbed species is desulphurized at the metal/solution interface in contact with nickel as catalyst. The rapid desorption of sulphide ions thus increases the rate of hydrogen evolution reaction at the cathodic surface and consequently increases metal dissolution.

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