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Inhibition of corrosion and hydrogen embrittlement of a HSLA steel in 0.5 M H_2SO_4 by nitrile compounds

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The inhibitive action of valeronitrile, benzonitrile and derivatives of benzonitrile on the corrosion and hydrogen embrittlement behaviour of HSLA steel in 0.5 M H_2SO_4 was investigated. All these inhibitors reduced the corrosion rate of the steel with naphthonitrile showing the highest inhibitive efficiency and valeronitrile the lowest. All the inhibitors adsorbed on the steel as per the Temkin adsorption isotherm. The steel become less active on the addition of benzonitrile, 3-chlorobenzonitrile, 4-chlorobenzonitrile, 4-methylbenzonitrile and naphthonitrile to the acid while valeronitrile and 2-chlorobenzonitrile made the steel more active. Naphthonitrile reduced the rate of the hydrogen evolution reaction most efficiently. Derivatives of benzonitrile inhibited hydrogen absorption most effectively.

Keywords: *corrosion, hydrogen embrittlement, inhibitors, HSLA steel, nitrite compounds*

1. Introduction

Pipeline transportation of natural gas containing significant amounts of H_2S has increased greatly in the past few decades [1, 2]. HSLA steels have found application in this industry due to their higher strength, toughness and weldability as compared to ordinary structural steels. However, HSLA pipe lines are susceptible to failures from hydrogen induced cracking (HIC) [3, 4] and sulfide stress corrosion cracking (SSCC) [5–7]. In addition, these steels have shown susceptibility to corrosion when used in acidic environments [8].

Prompted by these considerations, research has been directed towards the study of hydrogen embrittlement (HE) and corrosion characteristics of HSLA steels in recent years [9–11]. Inhibition by the addition of certain chemicals is a possible means of protection against corrosion in closed systems. The present study was carried out to determine the effectiveness of nitrile compounds in suppressing the corrosion rate, the cathodic hydrogen evolution reaction and the hydrogen embrittlement of HSLA steels in 0.5 M H_2SO_4. The experimental investigations comprised weight loss measurements, potentiodynamic polarization, scanning electron microscopy, hydrogen concentration measurements and optical metallography. The nitriles used in the present investigation were valeronitrile, naphthonitrile, benzonitrile and derivatives of benzonitrile.

2. Experimental method

The commercial grade HSLA steel (SAIL MA 350) used in the experimental study was supplied by Rourkela Steel Plant of the Steel Authority of India Ltd. The steel, received as 12 mm thick hot rolled strip, had the chemical composition shown in Table 1.

The sulphuric acid and the inhibitors used were of analar grade. Table 2 gives the details of the inhibitors used in the study. The nitriles were insoluble in aqueous solutions and so were dissolved in petroleum ether before adding them to 0.5 M H_2SO_4 solution.

2.1. *Weight loss study*

The steel was cut into rectangular pieces (5 cm × 3 cm) and cold rolled to 1 mm thickness with intermediate annealing at 650 °C for 90 min. Samples of 1 cm^2 area were cut from this cold rolled sheet and were annealed at 650 °C for 90 min. These samples were polished with emery papers upto 4/0 grade and cleaned with water and acetone and dried. Their weight losses were evaluated after exposure to 0.5 M H_2SO_4 containing various inhibitors.

2.2. *Polarization*

Cylindrical specimens (9 mm dia. × 12 mm long) from as-received material were prepared for polarization studies. An EG&G PARC model 331–3 corrosion measurement system was used for polarization measurements. The corrosion cell contained two graphite rods as counter electrodes and a saturated calomel reference electrode. The polarization curves of the steel were obtained in deaerated electrolytes. Deaeration of the electrolyte was carried out for 2 h prior to the start of polarization. All measurements were performed at a scanning rate 1 mV s^{-1} at room temperature (34 ± 2 °C).

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Table 1. Chemical composition of HSLA steel studied (wt %)

Material	*C*	*Mn*	*P*	*S*	*Nb*	*Fe*
HSLA steel	0.25	1.50	0.055	0.055	0.3max (Nb/V/Ti)	balance

2.3. *HIC study*

Samples of dimension 5 cm × 1 cm × 1.2 cm were cut from the as-received HSLA steel along the rolling direction for the hydrogen induced cracking study. These samples were cathodically hydrogen charged in sulphuric acid in the presence/absence of inhibitors at a constant current density of 10 mA cm^{-2} for 96 h. Samples were washed and dried after the charging. The charged samples were sectioned longitudinally and the cut surfaces were polished metallographically and etched with 2% nital. A fixed area (10 mm × 5 mm) in the centre of the polished surface was observed by optical microscopy and crack dimensions were measured at a magnification of 200 using VIDS-III computer software.

2.4. *Hydrogen analysis*

Samples of dimension 15 mm × 5 mm × 5 mm were cut from the as received HSLA steel for hydrogen analysis. These were thoroughly cleaned and weighed. Subsequently, they were cathodically hydrogen charged at a current density of 10 mA cm^{-2} in sulphuric acid containing inhibitors for 96 h. Samples were immediately plated with a thin copper layer to prevent charged hydrogen from diffusing out of the sample. These samples were analysed in a LECO hydrogen analyser for their hydrogen contents. Samples were heated to 1000 °C and the amounts of hydrogen released were measured. The analyser gives the concentration of hydrogen in ppm.

To study the morphology of the corroded surfaces Jeol JSM-840 scanning electron microscope was used.

3. Experimental results

3.1. *Corrosion of HSLA steel in 0.5 M H_2SO_4 and its inhibition*

3.1.1. Weight loss measurements. Weight loss increased with increasing exposure time and decreased with increasing concentration of nitriles as shown in Table 3 for benzonitrile and naphthonitrile. These and similar results for the other inhibitors were used to calculate the corrosion rates and inhibition efficiencies which are tabulated in Table 4. The corrosion rate in uninhibited 0.5 M H_2SO_4 was found to increase from 929 mpy to 1002 mpy, for immersion times

Table 2. Nitrile inhibitors evaluated

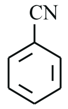
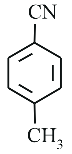
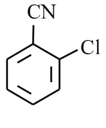
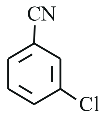
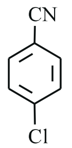
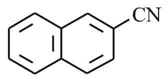
S	*Name*	*Structure*	*Molecular weight*	*Solubility in H_2SO_4*
1	Valeronitrile	$CH_3(CH_2)_3CN$	83.13	Insoluble (soluble in ether)
2	Benzonitrile		103.12	Insoluble (soluble in ether)
3	4-methylbenzonitrile		117.15	Insoluble (soluble in ether)
4	2-chlorobenzonitrile		137.57	Insoluble (soluble in ether)
5	3-chlorobenzonitrile		137.57	Insoluble (soluble in ether)
6	2-chlorobenzonitrile		137.57	Insoluble (soluble in ether)
7	Naphthonitrile		153.18	Insoluble (soluble in ether)

Table 3. Weight loss variation with time in the presence of benzonitrile and naphthonitrile

Surface area of samples 2.4 cm^2

S	*Time*/h	*Weight loss*/mg						
		Inhibitor concentration/mM						
		0.0	0.195		0.585		0.974	
			B	*N*	*B*	*N*	*B*	*N*
1	2	10.1	9.2	5.3	1.6	4.6	1.2	4.0
2	4	19.0	17.1	6.0	2.6	4.6	2.0	3.3
3	6	32.5	28.3	7.0	4.2	6.8	3.3	5.3
4	18	81.8	60.8	15.6	10.2	7.2	7.3	5.2
5	24	120.8	86.8	20.9	14.3	2.3	9.7	1.9
6	48	238.0	161.8	36.7	25.2	3.7	18.2	1.8
7	72	391.8	235.9	55.2	70.7	4.3	24.3	0.1

B: benzonitrile, *N*: naphthonitrile

ranging from 2 to 72 h upon calculation from weight loss data (Table 3). Corrosion rate decreased with increasing inhibitor concentration for all the inhibitors. It also decreased with increase of exposure time in all cases. Addition of benzonitrile reduced the corrosion rate by two orders of magnitude (Fig. 1). The corrosion rate decreased with exposure time and tended to stabilize at longer exposure times in most cases. The lowest corrosion rate for HSLA steel in 0.5 M H_2SO_4 was in the presence of naphthonitrile and highest in the presence of valeronitrile (Table 4).

As seen from Table 4, the inhibition efficiencies of benzonitrile and its derivatives are seen to increase with concentration approaching values of 99% for

Table 4. Corrosion parameters obtained from weight loss studies

Surface area of samples 2.4 cm^2; exposure time 72 h

S	*Inhibitor*	*Inhibitor concentration in 0.5 M H_2SO_4*	*Weight loss* /mg	*Corrosion rate* /mpy	*Corrosion inhibition efficiency* %
1	Uninhibited	0	391.8	1002	–
2	Valeronitrile	0.195	278.2	711	29.0
		0.584	179.1	458	54.3
		0.974	184.9	472	52.8
		4.870	132.0	337	66.3
		9.740	75.6	193	80.7
3	Benzonitrile	0.195	235.9	603	39.8
		0.584	40.7	104	89.6
		0.974	24.3	62	93.8
		4.870	9.0	23	97.7
		9.740	5.6	14	98.6
4	4-Methylbenzonitrile	0.05	83.7	214	78.6
		0.19	72.3	185	81.5
		0.58	35.2	90	91.0
		0.97	22.3	57	94.3
		4.87	2.3	6	99.4
5	2-Chlorobenzonitrile	0.050	248.86	636	36.5
		0.195	208.0	532	46.9
		0.584	172.5	441	56.0
		0.974	106.0	271	72.9
		4.870	16.1	41	95.9
6	3-Chlorobenzonitrile	0.05	283.7	725	27.6
		0.195	147.3	376	62.4
		0.584	105.3	269	73.1
		0.974	78.6	201	79.9
		4.870	6.2	16	98.4
7	4-Chlorobenzonitrile	0.05	308.7	789	21.2
		0.19	264.7	676	32.4
		0.58	216.3	533	44.8
		0.97	201.2	514	48.6
		4.87	72.5	185	81.5
8	Naphthonitrile	0.195	55.2	141	85.9
		0.584	4.3	11	98.9
		0.974	0.1	0.3	99.97

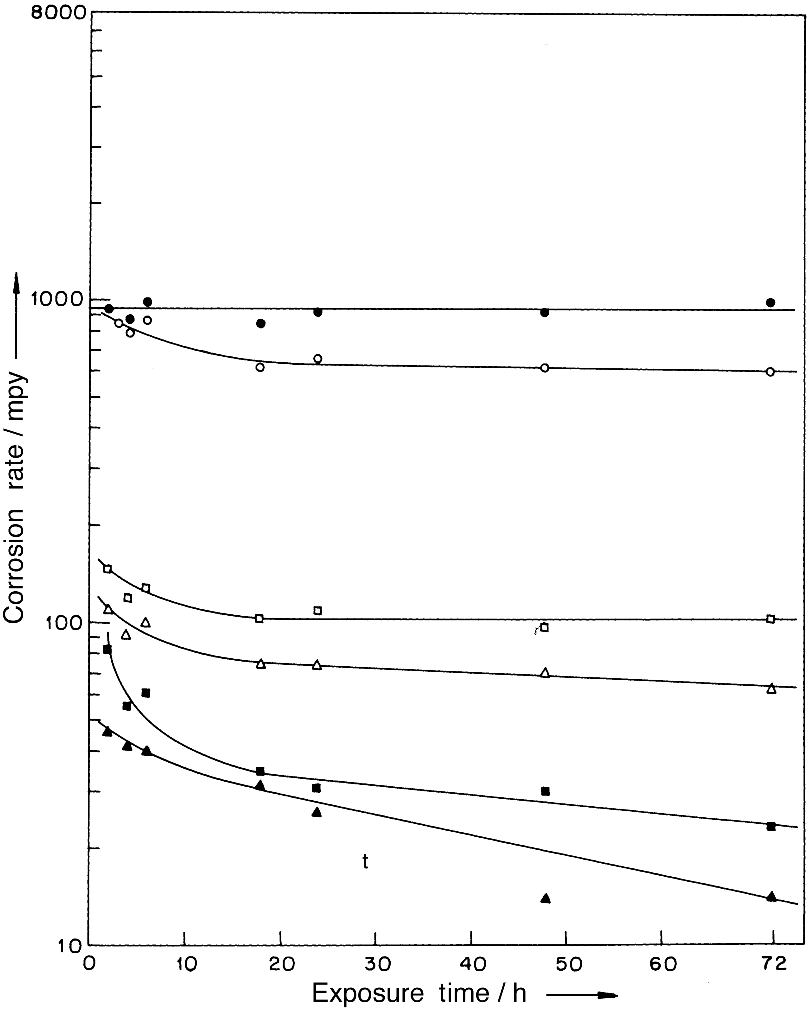


Fig. 1. Variation of corrosion rate of HSLA steel in 0.5 M H_2SO_4+ benzonitrile with exposure time at 34 °C ± 2 °C. Benzonitrile concentration: (●) 0.0, (○) 0.195, (□) 0.584, (△) 0.974, (■) 4.87 and (▲) 9.74 mM.

naphthonitrile. The increase in inhibition efficiency was large at low concentrations (upto 1.0 mM) for all the inhibitors. Inhibition efficiency tended to stabilize or increase more slowly beyond a concentration of 1 mM.

3.1.2. Polarization studies. Potentiodynamic polarization curves were obtained for the HSLA steel in 0.5 M H_2SO_4 containing various inhibitors at various concentrations ranging from 0.05 to 9.74 mM. A typical set of curves for the various concentrations of benzonitrile is shown in Fig. 2. Similar behaviour was also exhibited by the other inhibitors. Figure 2 shows that the curves shift towards lower current densities with increasing inhibitor concentration.

Various corrosion parameters calculated from polarization curves such as those in Fig. 2. are tabulated in Table 5. The corrosion potential shifted to active values in the case of valeronitrile and 2-chlorobenzonitrile while other nitriles ennobled the steel. The cathodic Tafel slopes were found to vary over the range of 102–135 mV decade^{-1} with the average Tafel slope being 120 ± 15 mV decade^{-1}. The corrosion current density is seen to decrease with increasing inhibitor concentration. Table 5 also shows the corrosion rates calculated from the polarization data. The results indicate a continuous reduction in corrosion rate with increasing inhibitor concentration. Corrosion inhibition efficiency was calculated on the basis of corrosion current densities (Table 5), which increased with inhibitor concentration in all cases.

3.1.3. Scanning electron microscopy. To determine the nature of the corrosive attack of HSLA steel, SEM observation were carried out on samples exposed to the corroding media for 72 h. Figure 3(a) depicts the excessive corrosion caused by uninhibited H_2SO_4. Deep pits have been created on the steel surface besides the severe edge attack.

Figure 3(b) to (d) indicate the effect of benzonitrile and two of its derivatives, 3-chlorobenzonitrile and 4-methylbenzonitrile, on the corrosion behaviour. In general, the corrosive attack is low. 0.5 M H_2SO_4 with 4.87 mM 3-chlorobenzonitrile causes the least amount of corrosive damage among these three compounds.

Figure 4(a) shows the effect of naphthonitrile on the corrosion behaviour. This compound, which gave an inhibition efficiency of 99%, gives minimal corrosion of the HSLA steel surface. Figure 4(b) shows

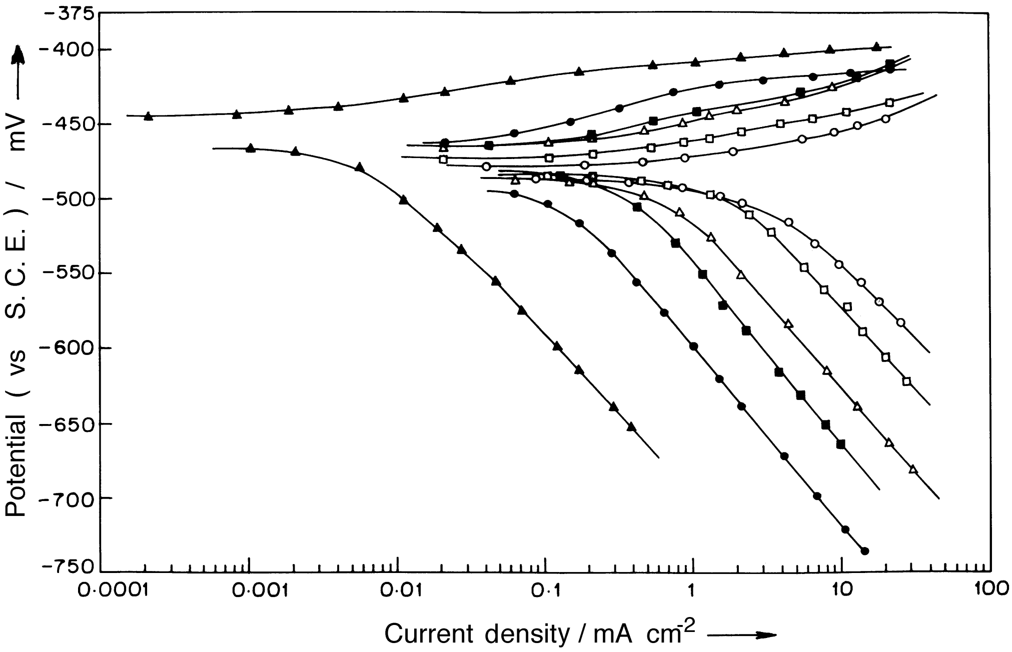


Fig. 2. Potentiodynamic polarization curve in 0.5 M H_2SO_4 + benzonitrile for HSLA steel at 34 °C ± 2 °C. Benzonitrile concentration: (○) 0.0, (□) 0.195, (△) 0.584, (■) 0.974, (●) 4.87 and (▲) 9.74.

Table 5. Corrosion parameters obtained from the potentiodynamic polarization curves of nitriles

S	*Inhibitor*	*Inhibitor concentration in 0.5 M H_2SO_4* /mV	*Corrosion potential* mV vs SCE	*Cathodic Tafel slope* /mV dec.$^{-1}$	*Corrosion current density* /mA cm^{-2}	*Corrosion rate* /mpy	*Corrosion inhibition efficiency* /%	*Cathodic* −*(600 mV) inhibition efficiency* /%
1	Uninhibited		−485	102.5	3.0	1323		
2	Valeronitrile	0.195	−497	102.5	2.7	1190	10.0	22.2
		0.584	−498	107.5	2.0	882	33.3	47.2
		0.974	−500	115.0	1.4	617	53.3	71.1
		4.870	−498	105.0	1.2	529	60.0	68.1
		9.740	−493	102.5	0.9	397	70.0	70.8
3	Benzonitrile	0.195	−483	110.0	1.600	705	46.7	50.0
		0.584	−484	112.5	0.580	256	80.7	83.1
		0.974	−478	120.0	0.310	137	89.7	91.7
		4.870	−484	120.0	0.115	51	96.2	97.1
		9.740	−465	110.0	0.007	3	99.8	99.7
4	4-methylbenzonitrile	0.050	−497	130.0	0.950	419	68.3	84.2
		0.190	−493	130.0	0.460	203	84.7	91.7
		0.580	−491	135.0	0.340	150	88.7	93.9
		0.970	−492	130.0	0.290	128	90.3	94.7
		4.870	−494	115.0	0.027	12	99.1	99.4
5	2-chlorobenzonitrile	0.050	−497	115.0	1.20	529	60.0	77.1
		0.195	−498	115.0	0.60	265	80.0	86.9
		0.584	-501	115.0	0.52	229	82.7	89.4
		0.974	-505	110.0	0.44	194	85.3	90.8
		4.870	-510	114.0	0.38	168	87.3	93.6
6	3-chlorobenzonitrile	0.050	-510	107.5	1.50	661	50.0	71.7
		0.195	-509	115.0	0.78	344	74.0	86.0
		0.584	-506	107.5	0.46	203	84.7	90.6
		0.974	-507	110.0	0.30	132	90.0	94.3
		4.870	−488	115.0	0.01	4	99.7	99.7
7	4-chlorobenzonitrile	0.050	−493	117.5	0.54	238	82.0	86.9
		0.190	−487	122.5	0.42	185	86.0	90.3
		0.580	−486	132.5	0.26	115	91.3	95.0
		0.970	−488	137.0	0.25	110	91.7	95.2
		4.870	−492	130.0	0.16	71	94.7	96.9
8	Naphthonitrile	0.195	-514	104.0	0.078	34	97.4	98.4
		0.584	-505	112.5	0.010	4	99.7	99.8
		0.974	−485	112.5	0.003	1	99.9	99.9

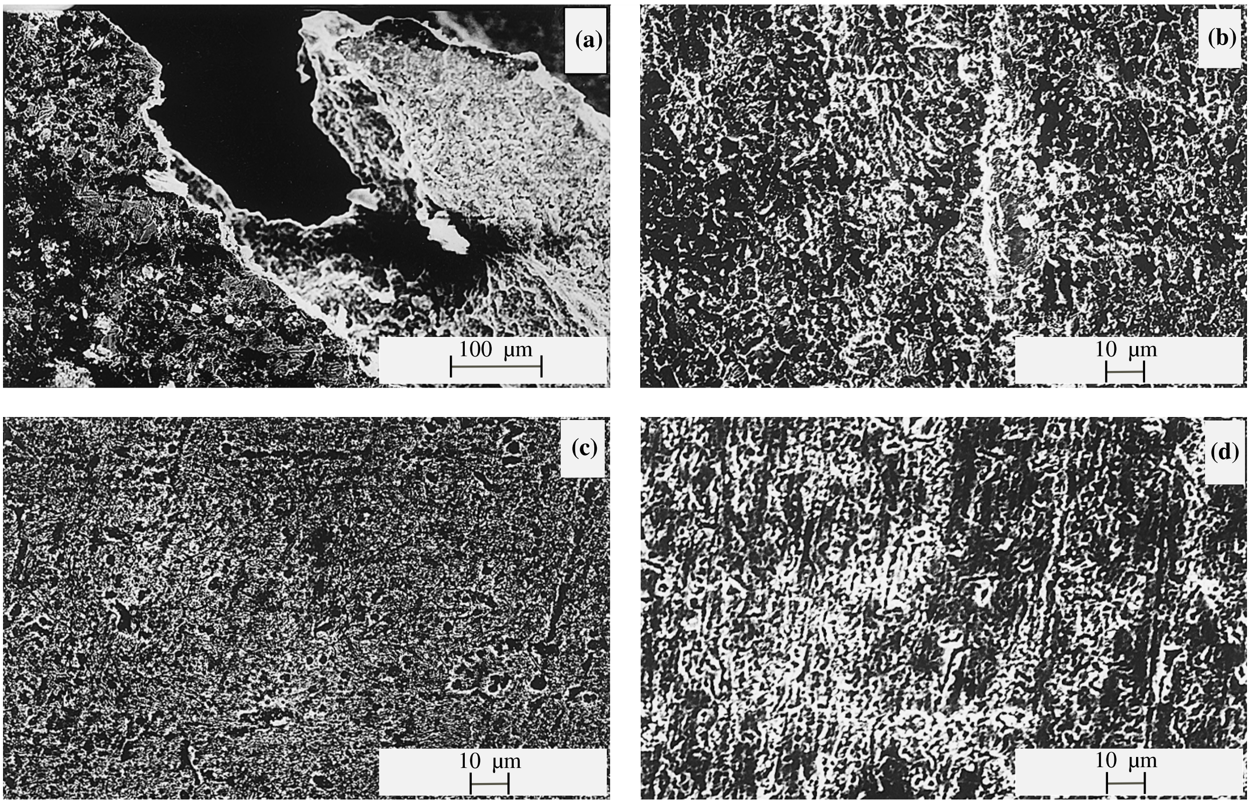


Fig. 3. SEM observation on the surface features of HSLA steel exposed for 72 h to (a) uninhibited 0.5 M H_2SO_4, (b) 0.5 M H_2SO_4 + 4.87 mM benzonitrile, (c) 0.5 M H_2SO_4 + 4.87 mM 3-chlorobenzonitrile, (d) 0.5 M H_2SO_4 + 4.87 mM methylbenzonitrile.

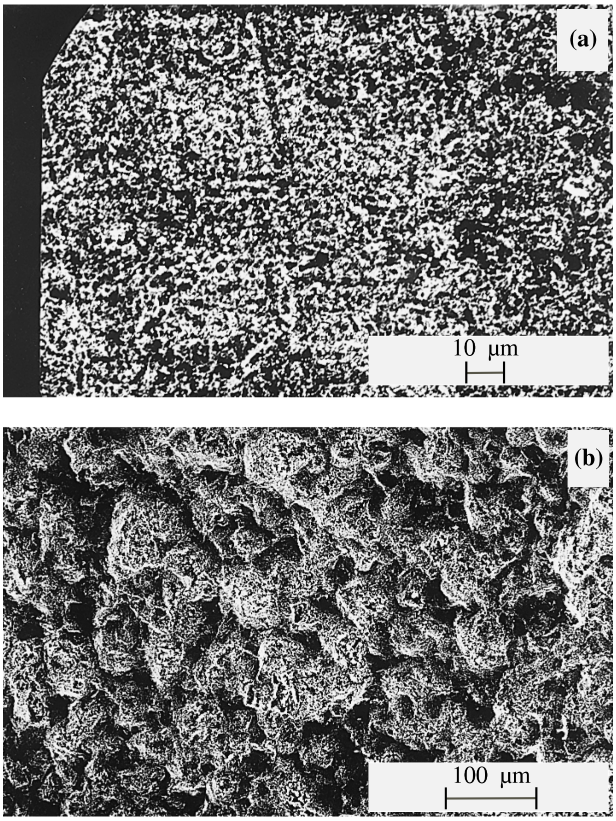


Fig. 4. SEM observations on the surface features of HSLA steel exposed for 72 h to (a) 0.5 H_2SO_4 + 4.87 mM naphthonitrile, (b) 0.5 M H_2SO_4 + 4.87 mM valeronitrile.

the excessive attack which occurred during 72 h of exposure of the steel in 0.5 M H_2SO_4 containing 4.87 mM valeronitrile. Deep pits occur for this compound which has an inhibition efficiency of only 79%.

3.2. *Inhibition of hydrogen evolution reaction*

Since the hydrogen evolution reaction controls the amount of hydrogen liberated at the steel surface, a part of which diffuses into the steel, causing embrittlement, it was of interest to evaluate the effect of nitrile on the hydrogen evolution reaction on HSLA steel exposed to 0.5 M H_2SO_4. Cathodic polarization measurements were used to evaluate h.e.r.

Figures 5 and 6 show the plots of cathodic current density in the presence of the nitriles against inhibitor concentration. It is seen from Fig. 5 that the cathodic current density is drastically reduced with increasing concentration for benzonitrile and naphthonitrile, although the rate of change is different for the two inhibitors. The cathodic current density levels off after decreasing to about 1 mM concentration in the case of valeronitrile. When the derivatives of benzonitrile are considered, the changes in cathodic current densities for 3-chlorobenzonitrile and 4-methyl benzonitrile were similar to that of benzonitrile, but the current densities were an order of magnitude smaller in these cases (Fig. 6). Figure 6 also depicts the change in cathodic current density for two other derivatives, namely, 2-chlorobenzonitrile and 4-chlorobenzonitrile. Here the reduction in cathodic current density is negligible beyond 1 mM concentra-

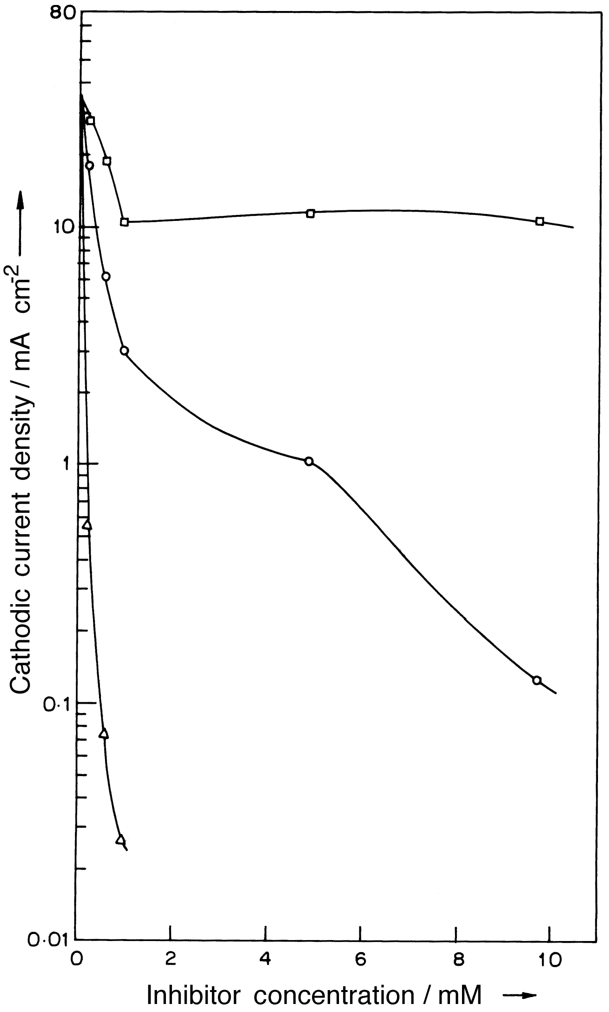


Fig. 5. Variations of cathodic current density at −600 mV of HSLA steel in 0.5 M H_2SO_4 with concentration of benzonitrile (○), Valeronitrile (□), and naphthonitrile (△) at 34 °C ± 2 °C.

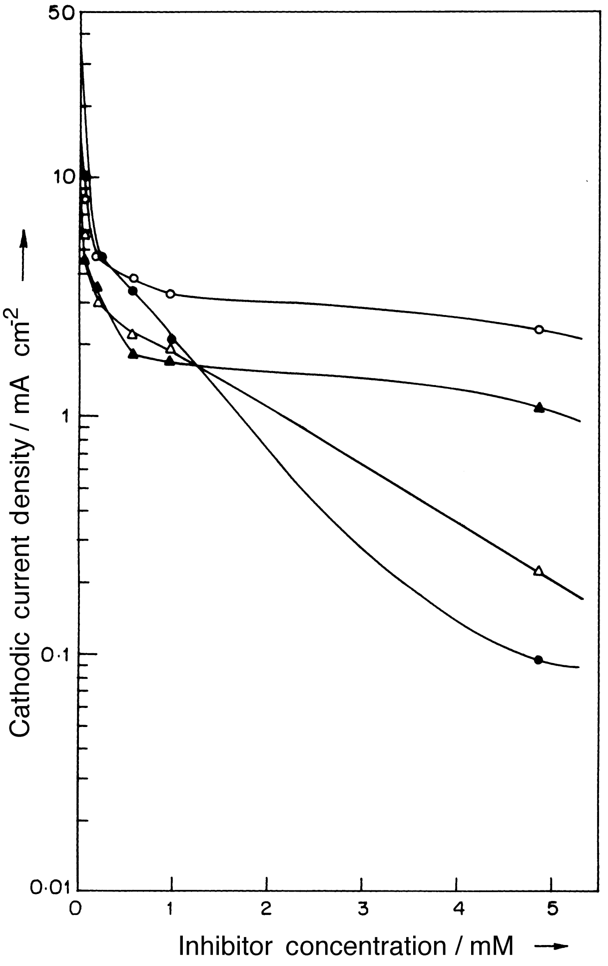


Fig. 6. Variations of cathodic current density at −600 mV of HSLA steel in 0.5 M H_2SO_4 with concentration of 2-chlorobenzonitrile, 3-chlorobenzonitrile, 4-chlorobenzonitrile and 4-methyl benzonitrile at 34 °C ± 2 °C. Key: (○) 2-chlorobenzonitrile; (●) 3-chlorobenzonitrile; (▲) 4-chlorobenzonitrile; (△) 4-methylbenzonitrile at −600 mV.

tion. Cathodic inhibition efficiencies in the Tafel region (−600 mV) were calculated for the nitriles and are given in Table 5. The cathodic inhibition efficiencies for all the nitrile compounds increased with increasing concentration.

3.3. *Hydrogen embrittlement of HSLA steel in 0.5 M H_2SO_4 and its inhibition*

3.3.1. Hydrogen induced cracking. The crack length and thickness per unit area for an uninhibited hydrogen charged sample were observed to be 0.3989 mm^{-1} and 0.0136 mm^{-1}, respectively. These values decreased in the presence of the nitriles (Table 6.) Average crack inhibition efficiency (average of crack length inhibition efficiency and thickness inhibition efficiency) was calculated. 4-chlorobenzonitrile was found to reduce the crack size ratios to the minimum.

3.3.2. Hydrogen analysis. The amount of absorbed hydrogen measured in separately charged specimens are given in Table 7. The hydrogen content of the sample cathodically charged from uninhibited acid

Table 6. Hydrogen induced cracking in HSLA after 96 h charging

Area measured 50 mm^2, 0.5 M H_2SO_4 Inhibitor concentration 4.87 mM, charging current density 10 mA cm^{-2}

S	*Inhibitor*	*Crack length per unit area* /mm^{-1}	*Crack thickness per unit area** /mm^{-1}	*Average crack inhibition efficiency*† /%
1	Without inhibitor	0.3989	0.0136	–
2	Valeronitrile	0.2935	0.0108	23.5
3	Benzonitrile	0.2929	0.0095	33.3
4	4-methylbenzonitrile	0.3013	0.0087	30.3
5	2-chlorobenzonitrile	0.2343	0.0073	43.6
6	3-chlorobenzonitrile	0.1454	0.0050	63.4
7	4-chlorobenzonitrile	0.1659	0.0033	67.1
8	Naphthonitrile	0.2500	0.0063	45.5

$$* \text{Crack inhibition efficiency} = \frac{(\text{Crack length})_U - (\text{Crack length})_I}{(\text{Crack length})_U}$$

U: uninhibited I: inhibited.

† Average inhibition efficiency = (Crack length inhibition efficiency) + (Crack thickness inhibition efficiency)/2.

Table 7. Hydrogen content in HSLA steel after 96 h

Inhibitor concentration 4.87 mM

S	*Inhibitor*	*Cathodically charged at 10 mA cm^{-2}*	
		Hydrogen concentration /ppm	*Hydrogen inhibition efficiency* /%
1	Without inhibitor	2.65	–
2	Valeronitrile	2.12	20.0
3	Benzonitrile	1.30	50.9
4	4-methylbenzonitrile	2.10	20.8
5	2-chlorobenzonitrile	1.24	53.2
6	3-chlorobenzonitrile	1.19	55.1
7	4-chlorobenzonitrile	1.97	25.7
8	Naphthonitrile	1.59	40.0

for 96 h is 2.65 ppm. Hydrogen content in the steel decreases upon cathodic charging in the presence of nitriles. Under cathodic charging conditions, the hydrogen content approaches a minimum value when 3-chlorobenzonitrile is used as inhibitor.

Based on HIC studies and hydrogen analysis 3-chlorobenzonitrile was found to be the most effective inhibitor.

4. Discussion

4.1. *Inhibition of corrosion*

Inhibition of corrosion of iron and steel in acids has been the subject of numerous investigations [12–15]. Organic molecules are known to inhibit corrosion of these materials by adsorption [8, 16].

Corrosion inhibition of the steel by nitrile compound in H_2SO_4 [17–19] and HCl [20] are well known. As the electron density on the functional group increases, the organic molecule adsorbs strongly on the metal surface. The value of electron density at an atom is measured by the value of Hammett's constant [21]. Positive values of σ are associated with substituents which withdraw electrons from the reaction centre by decreasing its electronic charge density. Negative values of σ are associated with electron-providing substituents, which increase the electronic charge density of the reaction centre. Hammetts constants for some nitriles [22] are shown in Table 8. The higher reactivity of 4-methylbenzonitrile may be inferred from Table 8. It shows better inhibition in comparison to others.

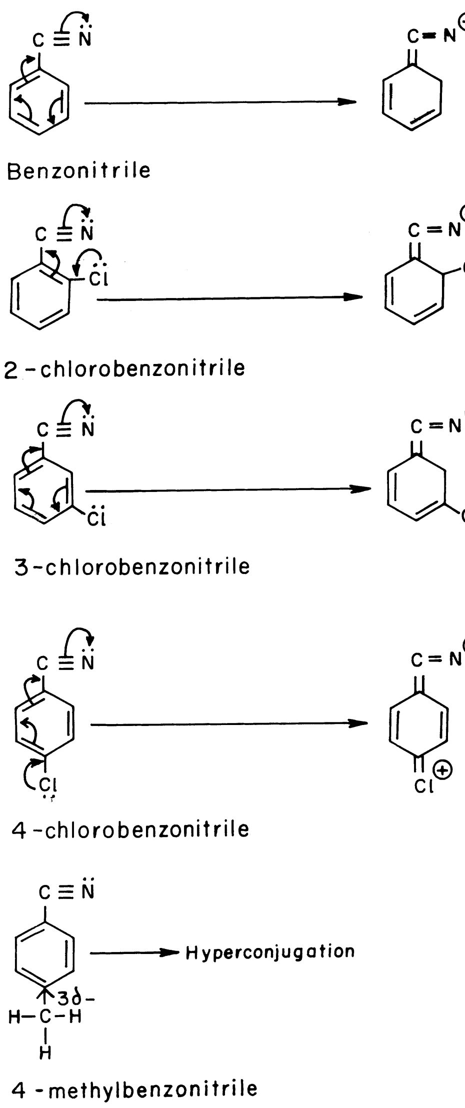


Fig. 7. Delocalization of electrons in nitrile compounds.

The reactivity of nitriles is also affirmed by the delocalization of electrons in these compounds (Fig. 7), where the nitrogen atom of benzonitrile has a high electron density which helps it to adsorb better on the steel surface. Benzonitrile gives an inhibition efficiency ranging between 52% and 98.5%. Inhibition characteristics of benzonitrile are influenced differently when the Cl atom is present at different positions. In the case of 2-chlorobenzonitrile the efficiency decreases due to the presence of the Cl atom at the ortho position, which gives a steric interaction with the nitrogen atom and reduces its electron den-

Table 8. Variation of corrosion data according to Hammett's constant value

S	*Compound*	*Hammett's constant* (*e*)	*Corrosion inhibition efficiency* /%	*Wt. loss polarization*	*HER inhibition efficiency* /%
1	Benzonitrile	−0.02	97.7	96.2	97.1
2	4-methylbenzonitrile	−0.16	99.4	99.1	99.4
3	2-chlorobenzonitrile	+0.20	81.5	94.7	96.9

sity. When Cl is present at the meta position, it enhances the efficiency due to presence of a greater negative charge on the nitrogen atom as well as on the Cl atom. Parasubstituted benzonitrile has a more negative character than ortho substituted benzonitrile. There is no steric hinderance in the case of 4-chlorobenzonitrile, which thus gives higher efficiency than 2-chlorobenzonitrile.

In the case of 4-methylbenzonitrile the C-atom of the CH_3 group attains $3\delta^-$ charge due to hyperconjugation. But it is not strong enough to take part in the delocalization of electrons. As a result, nitrogen possesses a higher electron density [19] (Table 8) and adsorbs strongly as compared to benzonitrile.

Naphthonitrile undergoes mesomerization and hence a higher electron density will be present on the N-atom, whereas there is no possibility of electron shifting in the case of the aliphatic molecule i.e. valeronitrile.

The higher molecular weight of naphthonitrile gives it higher inhibition efficiency than the low molecular weight valeronitrile and benzonitrile [23]. Their inhibition efficiency may be graded as naphthonitrile > benzonitrile > valeronitrile.

To evaluate the adsorption characteristics of nitriles the inhibition efficiency (surface coverage, θ) was plotted against inhibitor concentration using the four common adsorption isotherms, namely, Langmuir, Frumkin, Temkin and Bockris, Devanathan and Muller isotherms. The best fit was obtained for the Temkin isotherm in all cases.

4.2. *Inhibition of h.e.r.*

Many workers have reported that the hydrogen evolution reaction is slowed down by addition of inhibitors like BTA, tolyltriazole and piperidine [22, 24, 25]. However, the mechanism of hydrogen evolution remains unchanged. The present results also show that nitriles reduce the hydrogen evolution rate on HSLA. This is clearly seen from Table 5 which shows the h.e.r. inhibition efficiencies (cathodic inhibition at −600 mV) for the nitriles investigated. Naphthonitrile reduces h.e.r. most efficiently while valeronitrile is least effective. However, the cathodic Tafel slope is the same for HSLA steel in the absence and presence of these organic inhibitors. This indicates that the inhibition of the h.e.r. by nitriles on uninhibited steel in 0.5 M H_2SO_4 is the same. The action of the inhibitor is due to blocking of the metal surface, which enhances cathodic polarization and diminishes cathodic current density.

4.3. *Inhibition of hydrogen embrittlement*

It is known that when hydrogen is introduced it damages steels. This damage may be reduced by the use of inhibitors [16, 26, 27]. Bockris *et al.* [17] have shown earlier that the addition of valeronitrile, benzonitrile and naphthonitrile to 0.5 M H_2SO_4 solution decreases the rate of hydrogen permeation because of the vertical adsorption of these compounds on the surface of the metal, which hinders the discharge of hydrogen ions. This reduces the θ_H, that is, lowers the permeation rate of hydrogen. Hence, it reduces hydrogen embrittlement of the metal. An increase in overvoltage is expected [28] on pushing the hydrogen through the adsorbed organic layer. This agrees with the cathodic polarization result (Table 5).

Comparison of inhibition efficiencies for corrosion, h.e.r., HIC and hydrogen entry (Tables 5, 6 and 7) shows benzonitrile and its derivatives (4-methylbenzonitrile, 3-chlorobenzonitrile) to be the most promising inhibitors. However, their capabilities to suppress HE differ widely. Based on their overall efficiencies to inhibit corrosion, h.e.r. and HE, these compounds may be graded in decreasing order of efficiency as follows: 3-chlorobenzonitrile > 4-chlorobenzonitrile > 4-methylbenzonitrile.

4.4. *Model for the inhibition of hydrogen embrittlement of steel*

Hydrogen embrittlement of steel depends essentially on the amount of hydrogen present within the steel and the ease with which it can move. The amount of hydrogen introduced into the steel depends upon the surface conditions which are controlled by both metallurgical and environmental factors. For a particular steel, the metallurgical conditions may remain the same but the environmental conditions change by the addition of inhibitors, cathodic charging etc.

Organic substances may prevent hydrogen embrittlement of a steel by [17, 29]:

(i) blocking the active cathodic sites and preventing the discharge of hydrogen into the metal leading to reduction in the h.e.r.
(ii) vertical adsorption of the organic molecule on the surface hindering the approach of hydrated hydrogen ions from the solution to the metal surface.
(iii) the hydrogen ions discharged at the metal surface covered with a coating of the organic molecules may be tied up at the organic compound layers due to a hydrogenation reaction of hydrogen ions with the organic molecules.

According to these mechanisms, HE decreases while corrosion and h.e.r. inhibition efficiencies increase in some compounds because of the adsorption of the organic compound at the most active cathodic sites. The uncovered or weak sites have low Fe–H bond energies which permit the entry of hydrogen into the metal.

The compounds which inhibit both h.e.r. and HE may absorb vertically on the steel surface forming thick layers. These layers prevent hydrogen entry into the metal by reactions with the organic compound.

5. Conclusion

The following conclusions may be drawn from the present study:

(i) 3-chlorobenzonitrile, 4-chlorobenzonitrile, 4-methylbenzonitrile and benzonitrile are found to be good inhibitors for the inhibition of corrosion and hydrogen embrittlement of HSLA steel in 0.5 M H_2SO_4.

(ii) These inhibitors behave as mixed inhibitors as they shift both cathodic and anodic polarization curves to lower current densities. These inhibitors adsorb on HSLA steel following the Temkin adsorption isotherm. Nitriles do not affect the mechanism of hydrogen evolution reaction.

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