

Inhibition of hydrogen sulfide corrosion of steel by volatile amines

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Abstract

The protective effect of amines on steel corrosion under simulated conditions of gas condensate fields are studied. It is shown that primary amines are less effective than secondary and tertiary ones in terms of steel protection, especially in vapor phase. The authors also studied the impact of C_{H_2S} , pH, temperature and presence of a hydrocarbon phase on protective effect of chemical compounds considered.

Key words: *corrosion, hydrogen sulfide, carbon steel, volatile amine.*

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Introduction

Development of oil and gas fields today is complicated by several problems associated with corrosion damage of equipment and pipelines [1–4]. High corrosive effect of sour natural gas is caused by the presence of moisture and acid gases (H_2S and CO_2). H_2S is the most dangerous gas because it stimulates general corrosion and forces steel hydrogenation, which leads to loss of its elastic properties and cracking [5].

Experience of oil and gas equipment operation shows that one of the most effective and advanced methods to prevent corrosion is to use inhibitors. It allows the service life and reliability of equipment to be increased without serious interference in the operation process [6,7].

Contact corrosion inhibitors are widely used for corrosion protection of oil and gas equipment. However, they will have protective effect in vapor phase only provided that they preliminarily form a coating on the surface. But such coatings are not able to recover if their integrity is disturbed, for example, by gas flow. Volatile corrosion inhibitors (VCIs) exhibit this property and are able to penetrate into gaps and slots of complex metallic structures [8]. As opposed to contact inhibitors, they have a sufficient vapor pressure (p_s) to be volatile, saturate the gas-vapor phase and are adsorbed on the steel surface creating a self-organizing protective layer. However, there is not much information on development

of new VCIs for steel protection against hydrogen sulfide corrosion (HSC) [9–12]. In view of this, we studied the possibility of steel HSC inhibition by volatile amines and the impact of various media properties on it.

Experimental

Corrosive behavior of steel was studied on low-carbon (St.3, St.20, 08ps, SV08A) and high-carbon steel samples (70S2KhA). Their composition is given in Table 1. NACE solution (0.5% NaCl, 0.25 g/l CH₃COOH, pH 3.6) simulated a corrosion medium in a gas condensate field. Tests were performed for different H₂S concentrations. H₂S content was monitored by standard iodometric titration. In some cases tests were carried out in the presence of a hydrocarbon phase (white spirit); the hydrocarbon–water ratio was 1:10, excess pressure $P_{N_2} = 1$ atm.

Table 1. Steel sample composition (mass %).

Element	C	Mn	Si	P	S	Cr	Ni	Cu	As
Steel									
St.3	0.18	0.5	0.21	0.04	0.05	–	–	–	–
St.20	0.21	0.5	0.27	–	–	0.25	–	–	–
SV08A	0.1	0.47	0.03	0.03	0.03	0.12	0.25	–	–
08ps	0.08	0.5	0.11	0.035	0.04	0.1	0.25	0.25	0.08
70S2KhA	0.7	0.52	1.52	–	–	0.3	–	–	–

Impact of inhibitors on steel corrosion was studied by gravimetric method on steel plates with the area (S) 8.4 cm² and 18 cm² for St.08ps and St.70C2KhA correspondingly. The samples were weighed on analytical balance with an accuracy of 10⁻⁶ g. The test duration was from 1.5 to 240 hrs. Corrosion rate (K) was evaluated by mass losses (Δm), averaged by data on three (liquid phase) and six (gas phase) samples for the given period of time (τ):

$$K = \frac{\Delta m}{S \cdot \tau} \quad (1)$$

Inhibitor protective effect (Z) was calculated by the formula:

$$Z(\%) = \frac{K_0 - K_{in}}{K_0} \cdot 100, \quad (2)$$

where K_0 and K_{in} are the corrosion rates in non-inhibited and inhibited media, respectively.

Corrosion tests were performed in cylindrical glass vessels 280×15 mm in size with ground-in stoppers (1.5 h) and in 2 litre plastic vessels at 20 ± 2°C. Steel samples were put

into the vessel in such a manner that one part of them was fully immersed in the corrosive solution, while the other part was in a vapor phase above the solution. pH before and after the tests was determined by a pH analyzer.

Tests with wet H_2S were carried out in Drexel cells on St.20 samples ($S = 24.8 \text{ cm}^2$) and wire made from SV08A steel ($L = 11 \text{ cm}$). Hydrogen sulfide was passed through the cell for 5 hours. Primarily the system was deaerated by nitrogen (30 min). The cells were half filled with NACE base solution (Fig. 1). VCIs were injected into the liquid phase. Steel samples were put into both liquid and vapor phases above the solution. Tests under increased temperature were performed in the same way, but the cells were put into a water bath with automatic thermal control.

Impact of repeated wetting was studied on a wheel type unit ($w = 80 \text{ r.p.m}$, $t = 20^\circ\text{C}$, $\tau = 5 \text{ h}$) on St.3 samples ($S = 10 \text{ cm}^2$). After all the tests, corrosion products were removed by a washing solution containing 880 ml of distilled water, 66 ml of concentrated H_2SO_4 , 100 g of citric acid, and 10 g of thiourea.

Plasticity of SV08A steel was estimated with an NG-1-3M unit by the number of sample bends ($L = 11 \text{ cm}$) until its destruction in the initial state (n_0) and after testing in the inhibited solution (n). Residual plasticity of steel (P , %) was determined by the formula:

$$P = (n/n_0) \cdot 100\% \quad (3)$$

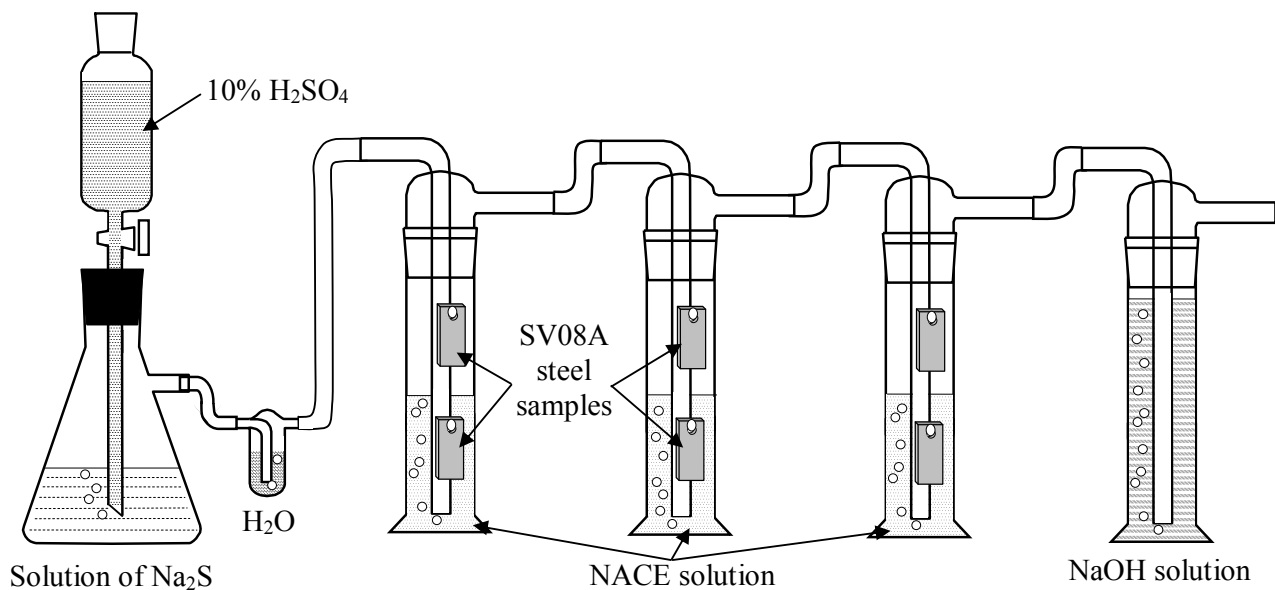


Fig. 1. Chart of experiment under steady wet H_2S flow conditions.

Results and discussion

Impact of VCIs Chemical Structure on Their Inhibiting Properties

It is known [7, 9–12] that steel HSC inhibitors are usually represented by nitrogen-containing organic compounds. In order to be a VCI they should have a vapor pressure not less than 10^{-6} mmHg [8]. That is why we studied aliphatic and aromatic amines as HSC volatile inhibitors. Their p_s values were calculated by the method proposed in [13, 14]. This method is based on the linear energy relationship principle.

First of all we studied the ability of considered compounds to protect steel against HSC in the liquid phase in short-term (1.5 h) corrosion tests in NACE solution saturated by H_2S (2 g/l) (Tables 2–4). Corrosion rate of high-strength 70S2KhA steel in this media without inhibitor was estimated at $0.856 \text{ g}/(\text{m}^2 \cdot \text{h})$.

Table 2. Protective HSC effects of primary amines (steel 08ps and 70S2KhA) in vapor gas (numerator) and liquid (denominator) phases after 1.5 h and 240 h tests in NACE solution saturated by 2 g/l H_2S .

Substance	M , g/mol	$\lg P$	p_s , mmHg	$\tau = 1.5 \text{ h}$ $C_{in} = 1 \text{ g/l}$ St.70S2KhA Z_{liq} , %	$\tau = 240 \text{ h}$		
					C_{in} , g/l	St. 08ps Z , %	St.70S2KhA Z , %
PRIMARY AMINES							
Allylamine (AA)	57	-0.12	57.8	95.4	–	–	–
<i>tert</i> -Butylamine	73	0.67	77.2	52.4	–	–	–
Cyclohexylamine	99	1.52	3.2	82.6	3.0	<u>12.0</u>	
						83.0	
Benzylamine (BA)	107	1.44	0.5	88.2	1.0	<u>20.0</u>	
						90.3	
					3.0	<u>23.0</u>	
						87.3	
Heptylamine	115	2.59	1.1	94.0	2.0	<u>50.0</u>	<u>54.1</u>
						73.2	99.0
Mixture of primary amines $C_{10} - C_{13}$ (MPA)	~180	5.13	0.013	95.7	1.0	<u>45.6</u>	<u>80.5</u>
						94.4	98.0

As expected, protective effect of primary amines (Table 2) increases along with the growth of hydrophobic properties of their hydrocarbon radical, and consequently the surface activity of the inhibitor itself. Allylamine is the only exception. It has hydrophilic properties ($\lg P < 0$)¹ and ensures high-grade protection. It seems that due to multiple bond

¹ Here P is the distribution ratio of a compound in the system of two immiscible liquids, octanol–water. It helps to identify its hydrophobicity value, which increases along with $\lg P$ [15].

in the allyl radical this amine reacts with hydrogen sulfide and generates surfactants that are adsorbed on steel better than the amine itself.

Benzene ring in the primary amine reduces inhibitor's protective effect. Thus, benzylamine and heptylamine have the same number of carbon atoms (C_7) and almost the same molecular mass. However in the liquid phase aliphatic amine demonstrates the better corrosion protection properties. This can be explained by the fact that heptyl is more hydrophobic than benzyl. *tert*-Butylamine provides the lowest steel protection among the studied primary amines ($Z = 52.4\%$). This can be explained by the branched *tert*-radical that creates space limits for inhibitor adsorption.

If samples are exposed for 10 days, steel corrosion rate in the liquid phase will decrease to $K = 0.28 \text{ g}/(\text{m}^2 \cdot \text{h})$. This is caused by formation of a corrosion film (ferric sulfides) that has some protective properties. Effectiveness of steel protection against HSC by amines in the liquid phase does not differ much as compared to short term tests ($\pm 2\%$). Even if the inhibitor concentration (C_{in}) increases threefold (benzylamine and cyclohexylamine), the situation remains similar.

Corrosion rate for 10 day exposure in vapor gas phase is slightly higher: $K = 0.35 \text{ g}/(\text{m}^2 \cdot \text{h})$, and Z value for primary amines is by 2–4 times lower than in a liquid phase. The mixture of primary amines C_{10} – C_{13} (MPA) is the best inhibitor in this case. It provides less than 50% corrosion protection for 08ps steel and 80.5% protection for 70S2KhA steel. Unfortunately, MPA injection into solution causes strong solution foaming even for $C_{\text{in}} < 1.0 \text{ g/l}$, which restricts application of this VCI. In both short and long tests heptylamine demonstrated lower protection properties in the liquid phase as compared to MPA ($Z_{\text{gas}} < 60\%$). Other primary amines were even less effective in short tests (as compared to heptylamine), that is why they were not studied further.

Increase in steel protection along with the growth of molecular mass is typical of secondary amines as well (Table 3). All studied secondary amines demonstrated good corrosion protection during short-term tests ($Z > 89\%$).

As for long-term tests (240 h) protective effect of secondary amines increased in the liquid phase ($Z \geq 95\%$). This can be explained by the fact that inhibitors form a stronger protection film with time. Diisoamylamine with the highest hydrophobicity ($\lg P = 3.83$) is effective in both phases. Even at $C_{\text{in}} = 0.5 \text{ g/l}$, it ensures good protection of 08ps steel in gas vapor phase ($Z = 81.7\%$), and it almost stops the corrosion at 2 g/l ($Z = 99.1\%$).

During long-term tests in the liquid phase, benzylcyclohexylamine (BCHA) dramatically decreases the HSC even at 0.1 g/l , and at $C_{\text{in}} \geq 0.5 \text{ g/l}$ corrosion process almost stops. However, BCHA is less effective in the gas vapor phase ($Z < 60\%$). It demonstrates lower HSC inhibition properties than diisoamylamine and dibutylamine. This is probably because of its lower volatility as compared to these amines (Table 3). A further increase in C_{in} caused sedimentation, and this did not allow to study cases with more concentrations of the inhibitor.

Table 3. Protective HSC effects of secondary amines (steel 08ps and 70S2KhA) in vapor gas (numerator) and liquid (denominator) phases after 1.5- and 240-hour tests in NACE solution saturated by 2 g/l H₂S.

Compound	<i>M</i> , g/mol	lg <i>P</i>	<i>p_s</i> , mmHg	$\tau = 1.5 \text{ h}$ <i>C_{in}</i> = 1 g/l St.70S2KhA <i>Z_{liq}</i> , %	$\tau = 240 \text{ h}$		
					<i>C_{in}</i> , g/l	St. 08ps <i>Z</i> , %	St.70S2KhA <i>Z</i> , %
SECONDARY AMINES							
Dipropylamine	101	1.67	12.3	89.1	–	–	–
					0.5	$\frac{81.7}{97.3}$	$\frac{70.2}{76.1}$
Diisoamylamine (DIAA)	157	3.83	0.3	90.6	1.0	$\frac{82.5}{99.3}$	$\frac{89.0}{91.3}$
					2.0	$\frac{99.1}{99.7}$	$\frac{92.1}{96.1}$
					1.0	$\frac{68.3}{98.4}$	$\frac{98.5}{98.9}$
Dibutylamine (DBA)	129	2.75	1.2	90.2	1.5	$\frac{80.5}{99.3}$	$\frac{93.5}{99.1}$
					2.0	$\frac{73.7}{94.3}$	$\frac{96.8}{98.8}$
					3.0	$\frac{54.3}{94.8}$	$\frac{44.3}{98.1}$
					0.1	$\frac{12.0}{98.2}$	$\frac{6.0}{98.4}$
Benzylcyclohexylamine (BCHA)	189	3.38	$3 \cdot 10^{-3}$	99.4	0.5	$\frac{24.8}{99.6}$	$\frac{17.0}{99.9}$
					1.0	$\frac{58.5}{99.7}$	$\frac{28.4}{99.9}$

As for tertiary amines (Table 4), the more is their molecular mass, the better protective effect they provide for different time periods of sample exposure. Even in short-term tests dimethylbenzylamine (DMBA), the less effective tertiary amine, is better than all studied primary and secondary amines in terms of steel protection against HSC. Only BCHA is better than DMBA. Finally, tributylamine demonstrated the best inhibitor properties among all the amines studied.

Table 4. Protective HSC effects of tertiary amines (steel 08ps and 70S2KhA) in vapor gas (numerator) and liquid (denominator) phases after 1.5- and 240-hour tests in NACE solution saturated by 2 g/l H₂S.

Substance	M , g/mol	$\lg P$	p_s , mmHg	$\tau = 1.5 \text{ h}$ $C_{in} = 1 \text{ g/l}$ St.70S2KhA Z_{liq} , %	$\tau = 240 \text{ h}$		
					C_{in} , g/l	St. 08ps Z , %	St.70S2KhA Z , %
TERTIARY AMINES							
Dimethyloctylamine	157	3.31	0.876	96.8	0.5	$\frac{20.0}{99.3}$	$\frac{0.0}{97.6}$
					1.0	$\frac{37.0}{97.7}$	$\frac{0.0}{98.2}$
					1.5	$\frac{40.4}{93.0}$	$\frac{0.0}{99.2}$
					3.0	$\frac{42.8}{97.5}$	$\frac{0.0}{99.8}$
Dimethylbenzylamine (DMBA)	135	1.56	0.576	95.7	1.0	$\frac{0.0}{95.3}$	$\frac{0.0}{95.8}$
					3.0	$\frac{43.7}{92.7}$	$\frac{21.1}{95.9}$
Tributylamine (TBA)	185	4.23	$8 \cdot 10^{-2}$	97.7	0.5	$\frac{73.9}{98.5}$	$\frac{92.4}{99.2}$
					1.0	$\frac{74.0}{98.3}$	$\frac{98.7}{99.8}$
					2.0	$\frac{77.7}{99.8}$	$\frac{96}{100}$
					3.0	$\frac{89.1}{100.0}$	$\frac{94.2}{100}$
					4.0	$\frac{98.7}{99.9}$	$\frac{99.7}{100}$

In the gas phase, the protective effect increases in the following series: DMBA < dimetyloctylamine < tributylamine. The latter provides a high level of steel protection against HSC in vapor gas phase and is inferior only to diisoamylamine. This means that its volatility is sufficient to form a protective layer. That is why at $C_{in} \geq 2.0$ g/l, tributylamine can ensure steel protection in H₂S-containing media. However, it has some drawbacks. At such C_{in} , sedimentation in the solution is inevitable.

Impact of Corrosive Medium Composition on HSC Process and its Inhibition

As it was shown above, secondary and tertiary amines are much better than primary ones in terms of ability to protect steel from HSC in vapors. That is why we have chosen two VCIs (secondary – SA and tertiary – TA) to study inhibitor protection in the gas phase (Table 5), as they are able to ensure effective protection of steel against steel corrosion in H₂S-containing media ($Z > 90\%$).

As it was mentioned earlier [16], $C_{\text{H}_2\text{S}}$ determines the protective properties of HSC inhibitors. Indeed, without VCI the K value of 08ps steel appropriately increased along with $C_{\text{H}_2\text{S}}$ both in liquid (0.071, 0.098, 0.23 g/(m²·h)) and in vapor phases (0.145, 0.155, 0.455 g/(m²·h)) for $C_{\text{H}_2\text{S}} = 0.5, 1.0$ and 2.0 g/l, respectively. The same situation happened for 70S2KhA high strength steel: $K_{\text{liq}} = 0.162, 0.41, 0.43$ g/(m²·h), $K_{\text{gas}} = 0.118, 0.161, 0.417$ g/(m²·h). The more is the $C_{\text{H}_2\text{S}}$ value, the more effective are the amines. This is most evident in gas vapor phase. For example, at $C_{\text{in}} = C_{\text{H}_2\text{S}} = 2.0$ g/l TA, the protection efficiency for 08ps and 70S2KhA steels is $Z_{\text{gas}} = 95.7$ and 93.4% , respectively, and 94.2 and 98.9% for SA. At the same C_{in} and $C_{\text{H}_2\text{S}} = 1.0$ g/l, TA efficiency decreases to $Z_{\text{gas}} = 58$ and 42.5% and that of SA to $Z_{\text{gas}} = 63.4$ and 66.6% (Table 5). If $C_{\text{H}_2\text{S}}$ decreases to 0.5 g/l, Z_{gas} for SA remains at 60 – 75% , whereas TA stimulates corrosion ($Z_{\text{gas}} < 0$). As expected, a decrease in C_{in} by half caused a significant reduction in protection efficiency of amines, $Z_{\text{gas}} < 0$ for $C_{\text{H}_2\text{S}} = 0.5$ – 1.0 g/l.

Such behavior of amines upon $C_{\text{H}_2\text{S}}$ decrease is probably associated with reduction of H₂S content in the gas phase. This also prevents formation of sulfide film, which can have some protection functions and facilitate adsorption of amines. Besides, the corrosion behavior can change in vapor gas phase in this case and corrosion is mainly accompanied by oxygen depolarization. This is not a mere coincidence that steel samples exposed to vapor phase above the base solution or TA-containing solution at $C_{\text{H}_2\text{S}} = 0.5$ g/l manifested dark brown and red corrosion products similar to rust that forms upon atmospheric steel corrosion (ferric oxides and hydroxides).

There is no doubt that a change in the solution pH is an important factor that influences the protection of steels by amines. The distribution diagram for H₂S acid composed on the basis of its $\text{p}K_{\text{a}}^{\text{I}} = 7.02$ and $\text{p}K_{\text{a}}^{\text{II}} = 14$ is presented in [17]. The following pH were selected for the studies: 3.6, 6.0 and 8.4. The content of volatile molecular form [H₂S] was 99.96, 91.30 and 4.00 mol.%, respectively. When pH was increased, the corrosion rate of 08ps and 70S2KhA steels decreased correspondingly in gas vapor phase (g/(m²·h)): 0.455, 0.43, 0.188 and 0.417, 0.36, 0.141, and in liquid phase: 0.23, 0.126, 0.035 and 0.433, 0.058, 0.016 for pH 3.6, 6.0, 8.4 (Table 6).

Table 5. Protective effects of amines in vapor (numerator) and liquid (denominator) phases after 10-day tests in NACE solution saturated by 0.5, 1 and 2 g/l H₂S, $p_{N_2} = 1$ atm.

VCI	C_{in} , g/l	C_{H_2S} , g/l	St. 08ps Z, %	St. 70S2KhA Z, %	pH before the test	pH after the test
SA	0.5	2.0	$\frac{56.5}{97.9}$	$\frac{61.8}{98.1}$	4.88	5.04
		0.5	$\frac{-60.0}{87.6}$	$\frac{-78.0}{86.4}$	6.39	6.43
	1.0	1.0	$\frac{-8.6}{80.5}$	$\frac{16.5}{97.4}$	6.05	6.25
		2.0	$\frac{64.3}{93.3}$	$\frac{23.7}{94.1}$	5.62	6.02
	2.0	0.5	$\frac{60.6}{83.4}$	$\frac{75.1}{90.4}$	7.48	10.21
		1.0	$\frac{63.4}{76.9}$	$\frac{66.6}{92.4}$	6.69	7.89
		2.0	$\frac{94.2}{97.2}$	$\frac{98.9}{98.1}$	6.23	6.47
		2.0	$\frac{94.2}{97.2}$	$\frac{98.9}{98.1}$	6.23	6.47
TA	0.5	2.0	$\frac{34.0}{93.3}$	$\frac{7.0}{98.2}$	4.54	4.70
		0.5	$\frac{-172}{76.5}$	$\frac{-141}{86.0}$	6.10	6.26
	1.0	1.0	$\frac{-23.0}{88.3}$	$\frac{-25.0}{95.0}$	5.78	5.85
		2.0	$\frac{49.6}{98.7}$	$\frac{34.4}{96.9}$	5.64	5.81
	2.0	0.5	$\frac{-131}{97.8}$	$\frac{-32.0}{97.3}$	7.14	9.15
		1.0	$\frac{58.0}{95.7}$	$\frac{42.5}{98.8}$	6.67	8.95
		2.0	$\frac{95.7}{97.5}$	$\frac{93.4}{98.9}$	6.25	6.56
		2.0	$\frac{95.7}{97.5}$	$\frac{93.4}{98.9}$	6.25	6.56

Impact of pH on protective properties of amines is more complicated. If we compare test results for initial solution with pH 3.6 (Table 5) and 6.0 (Table 6), we will see that in the second case corrosion inhibition in the liquid phase remains at a high level ($Z_{gas} > 90\%$). However in gas vapor phase efficiency of protection of low-carbon steel by amines

decreases, though TA protects 70S2KhA steel against HSC better than in acid environment.

Injection of 2.0 g/l SA in the initial alkaline medium significantly slows down steel corrosion ($Z_{liq} \geq 88.9\%$). However, such pH increase to protect steel in gas vapor phase has negative consequences. It even leads to serious stimulation of low carbon steel corrosion in SA containing environment, whereas TA provides very weak protection ($Z_{gas} < 30.2\%$).

Table 6. Impact of pH on protective effects of amines ($C_{in} = 2$ g/l) and steel plasticity in vapor (numerator) and liquid (denominator) phases. $C_{H_2S} = 2$ g/l, $p_{N_2} = 1$ atm. Test period is 10 days.

VCI	St. 08ps Z, %	St. 70S2KhA Z, %	pH after the test
pH 3.6			
SA	$\frac{94.2}{97.2}$	$\frac{98.9}{98.1}$	6.47
TA	$\frac{95.7}{97.5}$	$\frac{93.4}{95.7}$	6.56
pH 6.0			
SA	$\frac{51.9}{90.5}$	$\frac{66.1}{97.4}$	7.29
TA	$\frac{87.4}{99.5}$	$\frac{92.4}{90.8}$	6.92
pH 8.4			
SA	$\frac{-28.0}{96.6}$	$\frac{10.6}{88.9}$	10.84
TA	$\frac{6.7}{96.8}$	$\frac{30.2}{91.4}$	10.2

Effect of VCI in wet H₂S flow deserves attention (Table 7), as this medium better determines inhibitor behavior under dynamic conditions. Tests were carried out in accordance with the procedure described earlier. The corrosion rate of St.20 was 1.19 and 1.53 g/(m²·h) in gas vapor phase above base solution, and 0.6 and 3.6 g/(m²·h) at 20 and 80°C in liquid phase, correspondingly. The Z value of amines increased appropriately with C_{in} growth. An increase in temperature up to 80°C deteriorated the corrosion protection properties of SA at all the C_{in} studied, and those of TA at C_{in} = 0.5 g/l. The protective properties of TA increased to 95.0–97.4% at C_{in} = 1–2 g/l. The enhancement of TA effectiveness can be explained by increase of steel corrosion rate in non-inhibited media and intensification of amine volatility with an increase in temperature. In liquid phase the protective properties of amines improved at C_{in} > 1.0 g/l. Residual plasticity of SV08A carbon steel after 5-hour tests without VCI was 44 and 25% in gas and liquid phase at

20°C and 33% in both phases at 80°C. Injection of amines at 20°C significantly improved the ductile properties of steel wire. In some cases they amounted to 100% for both phases. In most cases, an increase in temperature caused a change in plasticity, which is similar to above mentioned impact on steel protection by amines. The concentration of C_{H_2S} (Table 7) in solutions estimated after the tests indicated that the liquid phase was saturated with H_2S to the maximum possible limit (under given conditions).

Table 7. Protective effects of amines and residual steel plasticity after 5 hours of continuous blowing by wet H_2S (preliminary deaeration for 30 min) at 20 and 80°C. The numbers in the numerator indicate the vapor phase, those in the denominator – the liquid phase.

VCI	C_{in} , g/l	20°C			80°C		
		St. 20 Z, %	St. SV08A P, %	C_{H_2S} , mg/l	St. 20 Z, %	St. SV08A P, %	C_{H_2S} , mg/l
SA	0.5	$\frac{46.2}{82.3}$	$\frac{44.0}{75.0}$	3400	$\frac{12.9}{79.7}$	$\frac{55.0}{42.0}$	893
	1.0	$\frac{76}{87.2}$	$\frac{44.0}{100}$	3700	$\frac{56.9}{92.7}$	$\frac{92.0}{100}$	840
	2.0	$\frac{90.3}{89.0}$	$\frac{100}{100}$	3400	$\frac{85.1}{96.5}$	$\frac{100}{100}$	850
TA	0.5	$\frac{62.4}{92.6}$	$\frac{100}{44}$	3315	$\frac{5.0}{64.4}$	$\frac{72.0}{36.0}$	730
	1.0	$\frac{90.3}{88.1}$	$\frac{100}{100}$	3500	$\frac{95.0}{96.2}$	$\frac{95.0}{89.0}$	725
	2.0	$\frac{96.6}{98.5}$	$\frac{100}{100}$	3200	$\frac{97.4}{97.9}$	$\frac{100}{100}$	740

As compared to static tests, results of tests performed under dynamic conditions are closer to reality in terms of effectiveness of steel protection, especially in gas vapor phase.

The important feature of VCI inhibitors is that they are able to protect steel surface in the area of periodic wetting that is usually studied in a wheel type unit. Protective properties of amines were examined on St.3 samples for 5 hours under such conditions (Fig. 2). The corrosion rate without a VCI and both without and with the hydrocarbon phase was $K = 4.68$ and $3.5 \text{ g/m}^2 \cdot \text{h}$, correspondingly. The protective effect of both VCIs continued to grow along with an increase in their concentration in the wetting fluid and finally almost approached the value of $Z = 90\%$ at $C_{in} = 2.0 \text{ g/l}$. Hydrocarbon phase increased Z value of amines at $C_{in} = 0.5 \text{ g/l}$. However, at $C_{in} \geq 1.0 \text{ g/l}$, the Z value slightly decreased. This happens because hydrocarbons reduce the corrosiveness of the media approximately by 1/3. Protection effectiveness of amines remains at a high level.

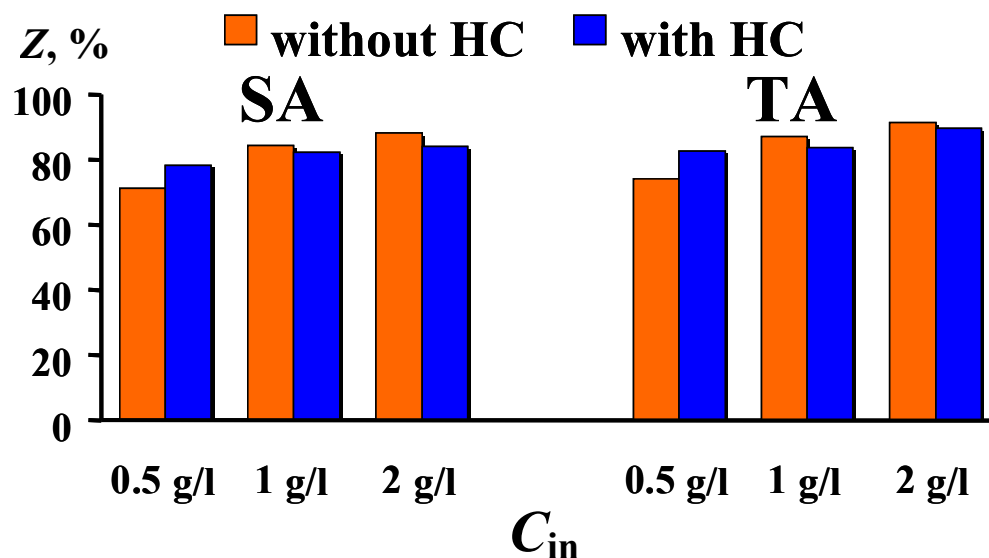


Fig. 2. Protective effects of amines against HSC under periodic wetting in a wheel-type unit with and without hydrocarbon phase, $\tau = 5$ h. $C_{H_2S} = 2$ g/l.

Conclusions

1. The results obtained prove a basic possibility of inhibition of steel HSC in a vapor phase by volatile amines.
2. Secondary (SA) and tertiary amines (TA) are able to ensure effective steel protection against hydrogen sulfide corrosion (HSC) in vapor phase above the solution containing $C_{H_2S} = 2$ g/l with pH 3.6 providing strong protection $Z_{gas} = 94.2$ – 98.9% at $C_{in} = 2$ g/l.
3. The chemical compounds studied (SA and TA) effectively inhibit HSC both under periodic wetting conditions (Z up to 90%), also in the presence of a hydrocarbon phase, and under wet H_2S flow conditions ($Z_{gas} = 90.3$ – 96.6%).

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