Effect of inhibitors on the desorption potentials in the anodic dissolution of iron in acid solutions – A review

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Abstract

The desorption potentials of various types of inhibitors in the anodic dissolution of iron in acidic solutions are considered. Literature data on the effect of inhibitor concentration, role of anions, and the presence of heteroatoms on the desorption potentials are summarized. It is shown that the desorption potentials ennoble with an increase in the concentration of inhibitors. For cationic inhibitors, desorption potentials are observed in the presence of halide ions. Desorption potentials are observed in the presence of nitrogen-containing, sulfur-containing and "green" corrosion inhibitors. The specific features of their protective action mechanism are discussed. The main conclusion from the results obtained by various authors is that the range of desorption potentials does not depend on the chemical nature of inhibitors. Therefore, it is determined by the properties of the anodically polarized metal. The interpretation of the results presented in this review is associated with an analysis of the mechanism of anodic dissolution of iron. The analysis of the data obtained in the review was carried out from the standpoint of the cooperative nature of the metal electronic subsystem. Partial depolarization of the anode was assumed to occur during the adsorption and transition of electrons from oxygen atoms of water molecules, halide ions, and other electron-donating inhibitors. It is assumed that at high anodic overvoltages, a two-dimensional quasi-liquid phase is formed on the metal surface, which leads to the desorption of any inhibitors, regardless of their chemical nature.

Key words: *anodic dissolution of iron, inhibition, desorption potential, acid solutions.*

Received: April 25, 2020. Published: June 26, 2020 doi: 10.17675/2305-6894-2020-9-3-4

Introduction

Monographs and reviews [1–3], as well as a large number of original articles, deal with the study of the mechanism of action of metal corrosion inhibitors. According to Rosenfeld [4], inhibitors alter the kinetics of electrochemical reactions that occur during corrosion; therefore, the mechanism of action of inhibitors can be most fully established if the basic laws of electrochemical kinetics in the presence of inhibitors are revealed, as well as the molecular mechanism of their action. In this paper, we consider some features of the effect of inhibitors of various nature on the anodic dissolution of iron and low carbon steel in acid

media. Jofa and Rozhdestvenskaja were the first to show that the anodic reaction on iron in sulfuric acid is inhibited in the presence of iodide ions at low polarizations in the anodic region of potentials, but at higher potentials the anodic current density abruptly increases by several orders of magnitude [5]. Similar results were obtained not only for I^- but also for other halide ions [6–12]. Heusler called the potential at which an abrupt increase in the anodic current density occurred "the potential of unpolarizability" [6]. Kaesche called this potential "the threshold potential" [3]. The reason for the observed phenomenon lies in the desorption of iodide ions that occurs in a narrow range of potentials, as confirmed by X-ray photoelectron spectroscopy [13], therefore, the value of the potential of an abrupt increase in the anodic current is called the desorption potential (E_{des}). This review analyzes the experimental results of studies in which similar phenomena occur not only in the presence of halide ions, but also with other acid corrosion inhibitors of iron and low carbon steel.

Method for determining the desorption potential E_{des}

Two methods are known to determine the desorption potential. In method 1, it was suggested to determine the desorption potential in an inhibited medium by an abrupt increase in the rate of the anodic reaction, *i.e.*, the transition of the anodic process to the non-polarizability state (E_{des} in Figure 1) [3, 5, 6]. Other authors determine the desorption potential by the value of the potential at which the anodic reaction rates in an inhibited and uninhibited acid become equal (method 2, E'_{des} in Figure 1) [14, 15]. In the present work, it was assumed that the desorption potential was determined by method 1. It was found from an analysis of literature data that in some cases the anodic curve in an inhibited solutions after desorption of the inhibitor does not reach the current values in the uninhibited solution (2″), in most cases the curves merge (2′), and in some cases after desorption the current becomes higher than in the uninhibited solution (2‴). We assumed that in all cases (2′, 2″ and 2‴), desorption of the inhibitor begins at E_{des}, while complete desorption may not occur. All the desorption potentials are referred to the normal hydrogen electrode (NHE).

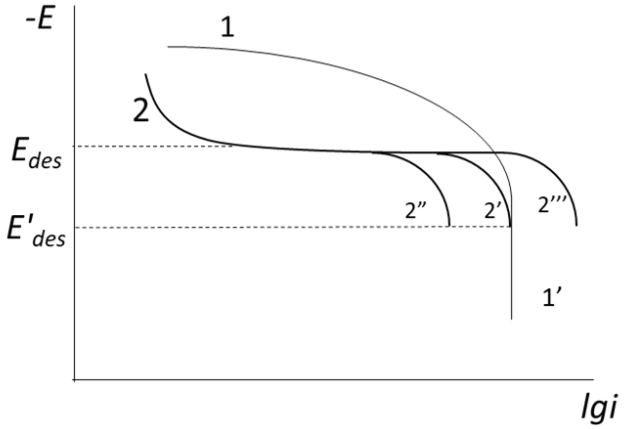

Figure 1. Anodic polarization curves of metal: 1, 1′ – pure medium; 2, 2′, 2″, 2‴ – various options for the effect of the inhibitor on the anodic polarization curve. Explanations are provided in the text.

Desorption potentials of halide ions

The effect of halide ions on the anodic dissolution of iron and low carbon steel has been studied in numerous publications. In a number of papers [6, 7, 9, 11, 12, 16, 18–23], the effect of various concentrations of iodide ions in 0.5 M H_2SO_4 was studied in the absence and in the presence of organic inhibitors of various nature. Data on the desorption potentials of halide ions in 0.5 M H_2SO_4 are given in Table 1.

Table 1. Desorption potentials of halide ions on iron in 0.5 M H_2SO_4 solution in the absence and in the presence of inhibitors.

No.	Inhibitor	Inhibitor concentration (M)	Halide ion concentration (M)	E_{des}, V	Ref.
1			5.5×10^{-4} I^- 5.5×10^{-2} I^-	–0.18 –0.08	6
2			10^{-3} Cl^- 10^{-3} Br^- 0.5×10^{-3} I^-	– –0.18 –0.16	7
	Diphenylamine	10^{-3}	– 10^{-3} Cl^- 10^{-3} Br^- 0.5×10^{-3} I^-	–0.23 –0.19 –0.18 –0.08	7
3			10^{-3} I^- 10^{-2} I^-	–0.22 –0.16	9
4			3×10^{-2} I^-	–0.05	10
5			5×10^{-3} Cl^- 5×10^{-3} Br^- 5×10^{-3} I^-	–0.18 –0.16 –0.06	11
6			10^{-3} I^- 3×10^{-3} I^- 5×10^{-3} I^-	–0.18 –0.16 –0.14	12
	Polyacrylic acid	10^{-3}	10^{-3} I^- 3×10^{-3} I^- 5×10^{-3} I^-	–0.18 –0.15 –0.13	12
7			10^{-1} I^-	–0.15	16
	Cetyltrimethylammonium bromide	7×10^{-6}		–0.13	

No.	Inhibitor	Inhibitor concentration (M)	Halide ion concentration (M)	E_{des}, V	Ref.
8			5×10^{-4} I^- 10^{-3} I^- 2.5×10^{-3} I^- 5×10^{-3} I^-	–0.20 –0.18 –0.16 –0.15	19
	Polyacrylamide	10^{-6}	5×10^{-4} I^- 10^{-3} I^- 2.5×10^{-3} I^- 5×10^{-3} I^-	–0.20 –0.18 –0.16 –0.15	19
9	Amodiaquine	10^{-3}	10^{-2} I^-	–0.04	20
10			10^{-4} I^-	–0.15	21
	Tetrabutylammonium sulphate	10^{-3}	10^{-4} I^-	–0.10	21
11			10^{-1} I^-	–0.15	22
	Cetylpyridinium chloride	10^{-5} 2×10^{-5} 7×10^{-5} 2×10^{-4}		–0.28 –0.25 –0.23 –0.22	22
	Cetylpyridinium chloride	10^{-5}	10^{-1} Cl^- 10^{-1} Br^- 10^{-1} I^-	–0.20 –0.18 –0.14	22
12			10^{-4} KI 5×10^{-4} KI 10^{-3} KI 5×10^{-3} KI 10^{-2} KI 5×10^{-2} KI 10^{-1} KI	–0.17 –0.16 –0.15 –0.10 –0.09 –0.07 –0.07	23
	Propargyl alcohol	10^{-2}	10^{-2} KI	–0.12	23
Desorption potential range, V: –0.22…–0.04					

It can be seen from the data given in Table 1 that the desorption potential is ennobled in the presence of halide ions in the series $Cl^- < Br^- < I^-$, which correlates with the data on the protective action of these anions [10, 11]. In the presence of cationic corrosion inhibitors such as diphenylamine [7], tetrabutylammonium [21], cetylpyridinium [22], the desorption potential of iodide ions shifts to a more positive region compared to the desorption potentials of halide ions at the same concentrations in the absence of organic cations. However, if non-charged or anionic organic polymers act as the organic partners of iodide ions, then the

desorption potentials do not change upon their addition [12, 19]. The same picture is observed in the presence of non-charged propargyl alcohol [23]. With an increase in the concentration of iodide ions, the desorption potential in 0.5 M H_2SO_4 shifts in the positive direction. The range of potentials for the desorption of halide ions is –0.22 to –0.04 V.

Desorption potentials of cationic inhibitors

Quaternary ammonium, pyridinium, imidazolium and phosphonium compounds are known as corrosion inhibitors in hydrochloric and sulfuric acids. Table 2 shows the desorption potentials of organic cations of various nature in the anodic dissolution of iron and low carbon steel in acids of various concentrations, as well as after the addition of various anions.

Table 2. Desorption potentials of organic cations on iron in acid solutions.

No.	Acid concentration (M)	Inhibitor	Inhibitor concentration (M)	E_{des}, V	Ref.
1	0.5 M H_2SO_4	*N*,*N*,*N*-Trimethyldodecylammonium bromide	10^{-2}	–0.13	24
2	0.5 M H_2SO_4	Tetrabutylammonium iodide	5×10^{-3}	–0.13	25
3	0.5 M H_2SO_4	Tetrabutylammonium bromide	10^{-2}	–0.16	26
4	0.5 M H_2SO_4	Tetrabutylammonium sulfate	10^{-3} $10^{-3}+10^{-4}$ M I^-	– –0.10	21
5	3 M H_2SO_4	Tetrabutylammonium sulfate	10^{-3} $10^{-3}+10^{-3}$ M I^-	– –0.05	5
6	1 M HCl	Dodecyl pyridinium bromide	1.5×10^{-4}	–0.08	27
7	0.5 M H_2SO_4	Cetylpyridinium chloride	10^{-5} 2×10^{-5} 7×10^{-5} 2×10^{-4}	–0.28 –0.25 –0.23 –0.22	22
8	0.5 M H_2SO_4	1-Octyl-3-methylimidazolium bromide 1-Allyl-3-octylimidazolium bromide	10^{-2} 10^{-2}	–0.18 –0.16	28
9	1 M HCl	1-Vinyl-3-aminopropylimidazolium hexafluorophosphate 1-Vinyl-3-aminopropylimidazolium tetrafluoroborate	8×10^{-4} 8×10^{-4}	–0.09 –0.06	29
10	3 M HCl	3-Oxa-1,5-pentamethylene-bis-(*N*-alkyl-*N*,*N*-dimethylammonium chloride) 12-O-12, R = $C_{12}H_{25}$; 18-O-18, R = $C_{18}H_{37}$	5×10^{-3} 10^{-4}	–0.04 –0.08	30

No.	Acid concentration (M)	Inhibitor	Inhibitor concentration (M)	E_{des}, V	Ref.
11	1 M HCl	Methyltrioctylammonium methylsulfate	2×10^{-4}	–0.08	31
		Trimethyltetradecylammonium methylsulfate	2.7×10^{-4}	–0.08	
12	1 M HCl	Cetylpyridinium bromide	4×10^{-4}	–0.06	32
		Cetyltrimethylammonium bromide	4×10^{-4}	–0.06	
13	1 M HCl	1-(2-(4-Chlorophenyl)-2-oxoethyl)pyridazinium bromide	10^{-3}	–0.08	33
14	0.1 M H_2SO_4	1-Ethyl-3-methylimidazolium dicyanamide	5×10^{-2}	–0.10	34
15	1 M H_2SO_4	2-Undecyl-1-ethylamino-1-methylbenzyl quaternary imidazoline	5×10^{-4}	–0.14	35
			10^{-4}+5 $\times10^{-3}$ I^-	–0.08	
16	1 M HCl	Di(*N*,*N*-diethylphenylammonium bromide ethanoate)polyethylene glycol	10^{-2}	–0.06	36
17	1 M HCl	Poly(4-vinylpyridine-γ-polyethylene oxide), degree of quaternisation 5%	2.5×10^{-8}	–0.06	37
18	0.5 M H_2SO_4	(2-Aminobenzyl) triphenylphosphonium bromide	10^{-2}	–0.18	38
19	0.5 M H_2SO_4	(2–Hydroxyethyl)triphenyl phosphonium bromide	10^{-2}	–0.10	39
20	1 M H_2SO_4	Propargyltriphenylphosphonium bromide	10^{-3}	–0.19	40
21	0.5 M H_2SO_4	Benzyltriphenylphosphonium bromide	10^{-3}	–0.18	41
			10^{-2}	–0.14	
22	0.5 M H_2SO_4	Allyltriphenylphosphonium bromide	10^{-3}	–0.16	42
			10^{-1}	–0.12	
23	0.5 M H_2SO_4	Butyltriphenylphosphonium bromide	10^{-3}	–0.20	43
			10^{-2}	–0.14	
24	0.5 M H_2SO_4	3-(4-Fluorobenzyl)-1-methyl-1*H*-imidazol-3-ium bromide	10^{-2}	–0.08	110
Desorption potential range, V: –0.30…–0.04					

It follows from the data of Table 2 that with an increase in the concentration of cationic inhibitors, the desorption potentials are ennobled [22, 41–43]. In addition, the desorption

potentials of cetylpyridinium cations in sulfuric acid are more negative than in hydrochloric acid [22, 32]. In the absence of iodide ions, the desorption potentials of tetrabutylammonium sulfate are not observed at all, but addition of iodide ions results in a pronounced desorption effect [5, 16]. The desorption potentials of tetrabutylammonium bromide are more negative than those of tetrabutylammonium iodide [5, 14, 25, 26]. For more complex cationic inhibitors such as 2-undecyl-1-ethylamino-1-methylbenzyl quaternary imidazoline, a desorption potential is observed, but upon addition of iodide ions it shifts towards more positive values [35]. Depending on the nature of the acid, the structure of the inhibitor, its concentration and type of the halide ion, the range of desorption potentials of cationic inhibitors ranges from –0.30 to –0.04 V.

Desorption potentials of nitrogen-containing inhibitors

Table 3. Desorption potentials of nitrogen-containing inhibitors.

No.	Acid concentration	Inhibitor	Inhibitor concentration (M)	E_{des}, V	Ref.
1	0.1 M $HClO_4$	Piperazine	10^{-2}	–0.23	44
2	0.1 M HCl	2-[(1,3-Benzothiazol-2-ylamino)methyl]-1-naphthol 2-{[(6-methyl-1,3-benzothiazol-2-yl)amino]methyl}-1-naphthol	10^{-3} 10^{-3}	–0.13 –0.12	45
3	0.1 M HCl	1,3-Bis [2-(2-hydroxy-benzylidenamino)phenoxy]propane	10^{-4}	0.14	46
4	0.1 M HCl	Hypoxanthine	10^{-2}	–0.19	47
5	2 M H_2SO_4	Polytriazole derivative + $5\cdot10^{-3}$ M KBr + $5\cdot10^{-3}$ M KI	2.4×10^{-1}	–0.06 –0.04	48
6	1 M HCl	(*E*)-2-((2,3-Dimethylphenyl)-amino)-*N*′-(4-methylbenzylidene) benzohydrazide (*E*)-N′-Benzylidene-2-((2,3-dimethylphenyl)amino)benzo-hydrazide (HDZ-3)	10^{-3} 10^{-3}	–0.09 –0.09	50
7	1 M HCl	5-Penthylaminomethyl-8-hydroxyquinoline	10^{-4} 10^{-3}	–0.16 –0.13	51
8	1 M HCl	1,1′-(Pyridine-2,6-dihylbis(methylene))bis(5-methyl-1-*H*-pyrazole-3-carboxylic acid)	10^{-3}	–0.13	52
9	1 M HCl	5-(((4-hydroxybenzylidene) amino)methyl)quinolin-8-ol	10^{-3}	–0.16	53

No.	Acid concentration	Inhibitor	Inhibitor concentration (M)	E_{des}, V	Ref.
10	1 M HCl	5-(4-Dimethylaminobenzylidene) rhodamine	10^{-4}	–0.12	54
11	1 M HCl	5′-Phenyl-2′,4′-dihydrospiro [indole-3,3′-pyrazol]-2(1*H*)-one	3.6×10^{-5}	–0.20	55
12	1 M HCl	Piperidine, 4-methyl-piperidine	10^{-2}	–0.11	56
13	1 M HCl	2-Benzylidenemalononitrile	10^{-3}	–0.11	57
14	1 M HCl	6-Benzylaminopurine	2.0×10^{-3} 4.0×10^{-3}	–0.14 –0.13	58
15	1 M HCl	6-Benzylquinoline	10^{-3}	–0.06	59
16	0.1 M H_2SO_4 0.1 M HCl	Adenine Adenine Adenine Adenine	10^{-2} 10^{-2} + 5×10^{-3} I^- 10^{-2} 10^{-2} + 5×10^{-3} I^-	–0.22 –0.16 –0.19 –0.16	60
17	0.5 M H_2SO_4	Amodiaquine	10^{-3}+10^{-2} I^-	–0.11	18
18	0.5 M H_2SO_4	8-Hydroxyquinoline	10^{-3} + 10^{-2} NaCl 10^{-2} + 10^{-2} NaCl	–0.14 –0.10	61
19	1 M HCl	Tinidazole	2.3×10^{-3}	–0.11	62
20	1 M HCl	1-Ethyl-3-methylquinoxalin-2(1*H*)-one	10^{-3}	–0.11	63
21	1 M HCl	Pyrazole	10^{-2}	–0.06	64
22	1 M $HClO_4$	1-Hydroxybenzotriazole	5×10^{-3}	–0.11	65
23	1 M HCl	1-Methylpyrazole	5×10^{-3}	–0.14	66
24	1 M HCl	Phenanthroline	1.4×10^{-3}	–0.14	67
25	1 M HCl	2,5-Bis(2-pyridyl)-1,3,4-oxadiazole 2,5-Bis(2-hydroxyphenyl)-1,3,4-oxadiazole	3×10^{-4} 3×10^{-4}	–0.10 –0.12	68
26	0.5 M HCl	4-Nitro-2-methoxyphenyl-*N*-salicylidine	10^{-3}	–0.14	76
27	1 M HCl	4-(Pyridin-4-yl)thiazol-2-amine	2×10^{-4}	–0.11	115
Desorption potential range, V: –0.30…–0.04					

It follows from the data in Table 3 that there is no significant difference in the desorption potentials of nitrogen-containing inhibitors in solutions of sulfuric, perchloric and hydrochloric acids. With an increase in the concentration of inhibitors, the desorption potential is ennobled [51, 58, 61]. Addition of iodide ions results in an increase in the

desorption potentials [48, 60]. In general, the desorption potentials of nitrogen-containing inhibitors are in the range of –0.30...–0.04 V.

Desorption potentials of sulfur-containing inhibitors

Table 4. Desorption potentials of sulfur-containing inhibitors.

No.	Acid concentration (M)	Inhibitor	Inhibitor concentration (M)	E_{des}, V	Ref.
1	1 M HCl	Methyl [6-(propylthio)-1*H*-benzoimidazol-2-yl]carbamate	4×10^{-4}	–0.08	49
2	1 M HCl	Cimetidine	2×10^{-3}	–0.11	69
3	1.4 M HCl	5-(2-Hydroxyphenyl)-1,2,4-triazole-3-thione	5×10^{-4}	–0.16	70
4	0.1 M H_2SO_4	Thiourea	10^{-3}	–0.16	71
5	1 M HCl	*N*,*N*′-((2*E*,2′*E*)-2,2′-(1,4-phenylenebis(methanylylidene)) bis(hydrazinecarbonothioyl))bis(2-oxo-2*H*-chromene-3-carboxamide)	5×10^{-4}	–0.16	72
6	0.5 M H_2SO_4	3-[(2-Hydroxy-benzylidene)-amino]-2-thioxo-thiazolidin-4-one	10^{-3}	–0.12	73
7	0.5 M HCl	5-((*E*)-4-Phenylbuta-1,3-dienylideneamino)-1,3,4-thiadiazole-2-thiol	10^{-3}	–0.04	74
8	0.5 M $HClO_4$ 1 M $HClO_4$	4-(*N*,*N*-Dimethylamino-benzylidine)-3-mercapto-6-methyl-1,2,4-triazin-(4*H*)-5-one	10^{-3} 10^{-3}	–0.14 –0.12	75
9	1 M HCl	4-Salicylideneamino-3-phenyl-5-mercapto-1,2,4-triazole	1.6×10^{-3}	–0.06	77
10	0.1 M HCl	*N*-(2-Thiophenyl)-*N*′-phenylthiourea	4×10^{-4}	–0.11	78
11	1 M HCl 2 M HCl 0.5 M H_2SO_4 1 M H_2SO_4	3-{[8-(Trifluoromtthyl)quinilin-4-yl]thio}-*N*′-(2,3,4-trihydroxybenzylidene) propanohydrazide	10^{-3} 10^{-3} 10^{-3} 10^{-3}	–0.08 –0.06 – –0.13	79
12	1 M HCl	Cephamycin	7.5×10^{-4}	–0.10	80
13	1 M HCl	5,5′-((1*Z*,1′*Z*)-(1,4-Phenylene-bis(methanylylidene))bis-(azanylylidene))bis(1,3,4-thiadiazole-2-thiol)	5×10^{-3}	–0.13	81

No.	Acid concentration (M)	Inhibitor	Inhibitor concentration (M)	E_{des}, V	Ref.
14	1 M HCl	1,3-Dibenzylthiourea 1-Benzyl-3-diisopropylthiourea 1,3-Dibenzylurea	2×10^{-4} 2×10^{-4} 2×10^{-4}	–0.10 –0.08 –0.12	82
15	0.01 M HCl	*N*-(Furfuryl)-*N*′-phenylthiourea	4×10^{-4}	–0.16	83
16	0.1 M H_2SO_4 + 0.25 M Na_2SO_4	Thiourea	6.5×10^{-3}	–0.16	84
17	1 M HCl	3-Pyridinecarbozalde thiosemicarbazone	1.5×10^{-3}	–0.14	85
18	0.5 M H_2SO_4 1 M HCl	*p*-Hidroxyisopropylphenylseleno-(methoxy)methane	Saturated solution	–0.14 –0.08	86
19	1 M HCl + 3% ethanol	Dibenzylthiourea Dibenzylthiourea + 2-hydroxypropyl-α-cyclodextrin	5×10^{-5} 5×10^{-5}	–0.10 –0.10	87
20	0.5 M H_2SO_4	Cysteine	1.3×10^{-2}	–0.05	88
21	1 M HCl	Allyl-thiourea	$4\cdot10^{-3}$	–0.11	89
22	0.5 M H_2SO_4	Benzenemethanethiol	5×10^{-3} 10^{-2}	–0.11 –0.06	90
23	0.5 M HCl	3-Amino-1,2,4-triazole-5-thiol	10^{-2}	–0.06	91
24	1 M $HClO_4$	*N*-Naphtyl-*N*′-phenylthiourea	2.5×10^{-4}	–0.06	92
25	1 M $HClO_4$	2-Mercapto-1-methylimidazole	2.5×10^{-3}	–0.01	93
26	2 M HCl	5,5′-[Butane-1,4-diylbis(sulfanediyl)bis(4-amino-4*H*-1,2,4-triazole-3-thiol)]	10^{-3}	–0.15	94
27	1 M HCl	1,3-Diisopropyl-2-thiourea	5×10^{-3}	–0.08	95
28	0.1 M HCl	Pyridine-2-thiol	10^{-3}	–0.16	96
Desorption potential range: –0.16…–0.01					

It is evident from the data in Table 4 that the desorption potentials of thiourea and its derivatives depend on the presence of substituents. In the series comprising thiourea [71, 84], allylthiourea [89], dibenzylthiourea [82, 87] and naphthylphenylthiourea [92], the desorption potentials become more negative. Moreover, the desorption potential shifts towards positive potentials with an increase in the inhibitor concentration [90]. The desorption potentials of sulfur-containing inhibitors are in the range of -0.16 ... -0.01 V.

Desorption potentials of "green" corrosion inhibitors

Table 5. Desorption potentials of "green" corrosion inhibitors.

No.	Acid concentration (M)	Inhibitor	Inhibitor concentration	E_{des}, V	Ref.
1	1 M HCl	Extract from *Aniba rosaeodora*	200 mg/L	–0.04	97
2	1 M HCl	Piper Longum	300 mg/L	–0.18	98
3	0.5 M H_2SO_4 0.5 M HCl	*Ziziphus mauritiana* leaves extracts	2800 ppm	– –0.13	99
4	1M HCl	1,1′-(2,2′-(2,2′-Oxybis(ethane-2,1-diyl) bis(sulfanediyl))bis(ethane-2,1-diyl))diazepan-2-one	10^{-3} M	–0.11	100
5	1 M HCl	*Zingiber officinale* oil	2 g/L	–0.11	101
6	0.5 M H_2SO_4 0.5 M HCl	Tetratriethanolamine trioleate	100 ppm	–0.11 –0.04	102
7	0.5 M HCl	*N*-(1*H*-Indol-3-yl-methylene)-nicotinamide	500 ppm	–0.11	103
8	1 M HCl	*Mucuna pruriens* seed extract	1 g/L	–0.16	104
9	1 M HCl	*Gongronema latifolium* extract	1 g/L	–0.16	105
10	5% NH_2SO_3H	*Myrtus communis* extract	250 ppm	–0.16	106
11	1 M HCl	Podocip	100 ppm	–0.16	107
12	1 M HCl	*Artemisia judaica* herbs extract	300 ppm	–0.06	108
13	0.5 M H_2SO_4	Iota-carrageenan Inulin	1000 ppm 1000 ppm	–0.09 –0.06	109
14	1 M HCl	*Eriobotrya Japonica* (Thunb.) leaf extract	500 mg/L	–0.12	110
15	1 M HCl	Atenolol	300 ppm	–0.06	111
16	1 M HCl	Coffee ground extracts	400 mg/L	–0.11	112
17	1 M HCl	*Euphorbia falcata* extract	3 g/L	–0.14	113
18	1 M HCl	Date extract	1.5 V/V%	–0.11	114
19	0.5 M H_2SO_4	Loquat (*Eriobotrya japonica* Lindl.) leaves extract	saturated	–0.16	116
20	0.5 M HCl	Vitamin B1	10^{-5} M	–0.06	117
21	0.5 M HCl 1 M HCl	*Pimenta dioica* leaf extracts	0.13% 0.13%	–0.10 –0.08	118
22	1 M HCl	*Michelia alba* leaves extract	1.7 g/L	–0.16	119
Desorption potential range: –0.18…–0.04 V					

In recent years, many publications have appeared where natural extracts were studied as "green" acid corrosion inhibitors. Table 5 shows that desorption processes are also observed in the inhibition of anodic reaction with inhibitors based on natural compounds. The same compounds in sulfuric acid do not exhibit desorption phenomena at all but manifest them in hydrochloric acid [99]. The desorption potential in hydrochloric acid is more positive than in sulfuric acid [102]. The desorption potentials of "green" inhibitors range within –0.18...–0.04 V.

Discussion

In [6], the origins of the inhibitory effect and desorption of iodide ions and CO were interpreted from the standpoint of the "catalytic" mechanism of anodic dissolution. Since exactly similar effects arise from adsorption of both neutral carbon monoxide molecules and charged iodide ions, it appears unlikely that the effects may be ascribed to any significant changes in the potential in the diffuse part of the double layer. The observed effects of iodide ions or carbon monoxide may arise from one or more of the following reasons:

- the activation energy of the dissolution reaction can be increased (without specifying the reason – my comment);
- the concentration of adsorbed hydroxyl ions, and hence of the catalyst, may be diminished;
- the frequency of finding an active metal atom contiguous to a catalyst site may be reduced.

However, the reason for the desorption of inhibitors is not explained. The review [3] showed that the same phenomena are observed in the presence of phenylthiourea as in the presence of iodide ions and CO. The adsorption of inhibitors such as thiourea derivatives, as well as carbon monoxide and iodide ions, is due to a covalent chemical bond with the metal. According to the author, desorption occurs for the same reasons that organic compounds and iodide ions are desorbed from mercury at potentials that are more negative or positive than the zero-charge potential. The same point of view is shared by Z.A. Iofa [21] who believes that the desorption of tetrabutylammonium cations in the presence of iodide ions from the surface of iron is due to electrostatic reasons. With an increase in the concentration of inhibitors, the adsorption potential is ennobled; this effect was studied, in particular, using of iodide ions as an example in the work by Heusler [6] and in other publications [7, 9, 11, 12, 18–23]. The results of other authors are similar both in the character of the dependence of E_{des} on the concentration of anions and in the absolute values of the desorption potentials (Figure 2).

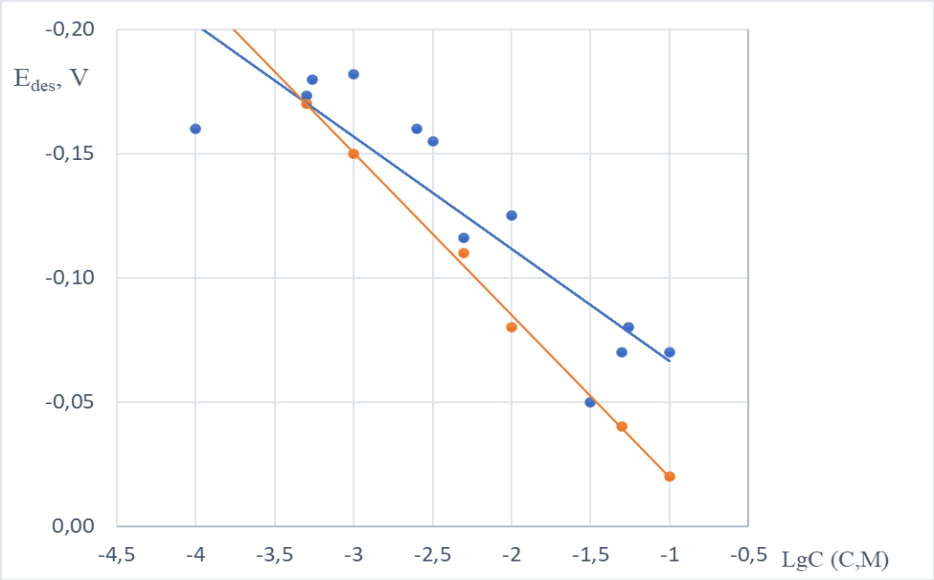

Figure 2. Dependence of iodide ion desorption potentials on concentration during anodic dissolution of iron in 0.5 M H_2SO_4 according to [6] (blue line); according to [7, 9, 11, 12, 16–23] (orange line).

As follows from the data presented in the review, acid corrosion inhibitors of various nature – halide ions, cationic inhibitors in the presence of halide ions, nitrogen-containing and sulfur-containing compounds, as well as "green" inhibitors of various compositions – are desorbed in the same range of potentials. Therefore, the desorption potentials are independent of the nature of inhibitors. It can be assumed that they are determined by the properties of the anodically polarized metal. All the inhibitors listed in the review are capable of adsorption on the metal surface due to chemical forces, similarly to the above iodide ions, CO, and phenylthiourea. Cationic inhibitors that do not have electron-donating properties are not adsorbed in the anodic region of potentials in the absence of halide ions [17]. It is known that halide ions increase the adsorption of cationic inhibitors [130]. From the results of this review it follows that in the presence of organic cations such as tetrabutylammonium, halide ions are desorbed at more positive potentials than in their absence [5, 21]. In the framework of the proposed model of anodic dissolution, this is due to the fact that cations located on top of the layer of chemisorbed anions block the process of desorption of the anodic dissolution products, *i.e.*, metal cations, which increases the potential region in which anions are able to have a depolarizing effect on the anodic process.

In earlier studies [3, 6, 21], the anodic polarization curves are presented in a narrow range of potentials near the corrosion potential. In most of the papers cited in this review, polarization curves in a wide range of potentials are given. Using the effect of halide ions on the anodic dissolution of iron in sulfuric acid as an example [11], it can be seen that desorption begins in the region of potentials in which the transition of the anodic process from the Tafel region to the region where limiting currents occur (or occurred) in non-inhibited solutions (Fig 3). It was previously shown that the routes of anodic dissolution in the Tafel region and in the region of limiting currents are different [121–123].

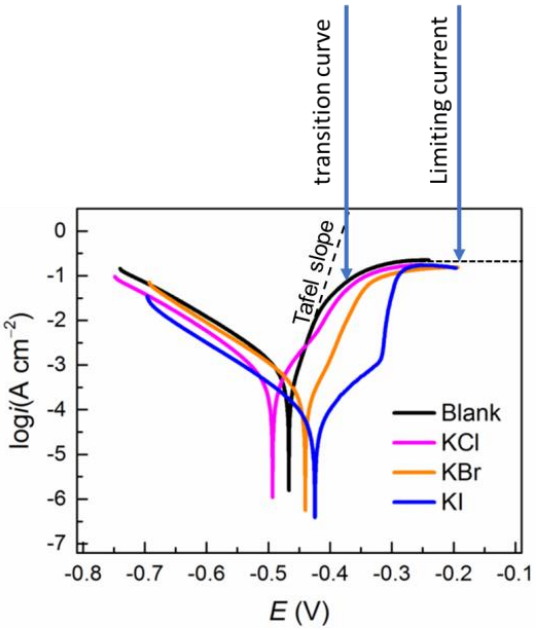

Figure 3. Potentiodynamic polarization curves for mild steel in 0.5 M H_2SO_4 in the absence and presence of 5×10^{-3} M KX (X = Cl, Br, I). Reproduced with permission from L. Guo *et al*. [11].

Therefore, the approach to the interpretation of the results presented in this review is associated with an analysis of the mechanism of anodic dissolution of iron. All valence electrons in metals are shared to form a common subsystem of quasi-free electrons at the Fermi level [124]. The change in the Fermi-level energy of electrons through the change in electrode potential that is the principal origin of the effects of electrode potential on the electron charge-transfer rates in electrochemical reactions [125]. With anodic polarization of a metal, a decrease in the Fermi level occurs [126]. Studies of the electronic subsystem of crystalline iron showed that each metal atom in the crystal lattice transfers three electrons to the Fermi level [127]. For this reason, the activation barrier associated with the transfer of the first and second electrons from a surface Fe^s atom to the metal conduction band during anodic dissolution is absent. The act of depolarization of the $[Fe_n]^{p+}$ anode as a cooperative system with a lower Fermi level due to polarization (p+ is the conditional charge of a polarized anode) consists of the transfer of an ion leaving the metal to the near-surface electrolyte layer [122, 123]:

$$[Fe_nFe^s]^{p+} + mH_2O \rightarrow [Fe_n]^{(p-2)+} + [Fe(H_2O)_m]^{2+} \quad (1)$$

Another method of partial depolarization of the anode is by adsorption and transition of electrons of the oxygen atoms of water molecules [126], halide ions and other electron-donating inhibitors described in this work, which, due to the electron-donating properties of heteroatoms or multiple bonds, decrease the anodic polarization. One can see from Figure 2 that the adsorption and protective effect of halide ions on the anodic dissolution of iron increases in the series $Cl^- < Br^- < I^-$ [11], which coincides with the data in Table 1 on the change in the desorption potentials of halide ions. The desorption potentials of halide ions and other inhibitors are in the region of potentials in which the transition of the anodic

process from the Tafel region to the region of limiting currents occurs in uninhibited solutions (Figure 2). It was shown earlier [123] that a decrease in the density of surface electronic states with an increase in the anodic polarization can lead, at sufficiently large anodic overvoltages, to complete delocalization of atoms in the first surface layers of crystals in contact with a liquid phase. A special structurally disordered quasi-liquid state of this layer appears with a short-range order that is characteristic of a two-dimensional adsorption layer in an electrolyte [128]. During the electroreduction of metals at one of the stages, a liquid rapidly crystallizing phase of the metal was discovered [129]. Under the conditions where a two-dimensional quasi-liquid phase is formed from the metal surface, desorption of any inhibitors occurs regardless of their chemical nature, as shown in the analysis of Tables 1–5.

Conclusion

In the present work, the desorption processes of iron acid corrosion inhibitors in the anodic potential region are analyzed. The main conclusion from the results obtained by different authors is that the range of desorption potentials does not depend on the chemical nature of inhibitors. Therefore, it is determined by the properties of the anodically polarized metal. The analysis of the data obtained in the review was carried out from the standpoint of the cooperative nature of the metal electronic subsystem. For a deeper understanding of the patterns identified here, it is advisable to continue the accumulation of experimental material and perform a theoretical analysis of results using quantum-chemical and statistical methods for studying metal-corrosive environment-inhibitor systems.

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