

A Selective Organic-Based Corrosion Inhibitors Containing Iodide Ion as Enhancer for Protection of Carbon Steel: A Review

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Abstract. This paper contains a review on the effect of halide ion with a selected inhibitor which is imidazole derivatives on the efficiency of corrosion inhibition. The paper first describes the mechanism of synergistic inhibition effect among halide ions enhancer with inhibitor on the steel surface. Then the paper describes the measured inhibition efficiency and summarizes the synergistic inhibition condition of imidazoline derivatives inhibitor with iodide ions. The characteristic of synergistic inhibition effect and the relationship between the amount of iodide ion consumption and the amount of organic inhibitor consumption are also discussed. It has been shown that, the synergistic effect between imidazole derivative and iodide ion is an effective method to improve the inhibitive performance in different aqueous media.

1. Introduction

Carbon steel is used in wide of industries because of its physical characteristics, such as stiffness and high strength, however they are highly susceptible to corrosion in aggressive solution [1]. Problem attributed to the deterioration of metal by chemical reaction with the environment is called corrosion. Corrosion costs billions of dollars every year and in the middle of 2013 this cost reached more than \$2 trillion or 3-5% of Gross Domestic Product (GDP) in the United States [2]. Studies have found an occurrence of synergistic corrosion inhibition effect when secondary species is added into an organic inhibitor [3]–[7]. Synergistic inhibition effect is an improved performance of organic inhibitors as compared to merely organic inhibitors on the rate of corrosion reaction [8]. It has proven to be an effective way to decrease the amount of organic inhibitor consumption and to expand the application of organic inhibitor in media. Examples of secondary species that added to organic inhibitor are halide ions (Cl⁻, Br⁻, and I⁻), metal ions and organic inhibitor mixtures.[3], [9]–[13]. Since the synergistic inhibition effect of halide ions widely reported in the previous researchers and it has a significant impact on the modern corrosion inhibitor formulation, thus this paper will discuss the effect of iodide ion with a selected inhibitor which is imidazoline derivatives.

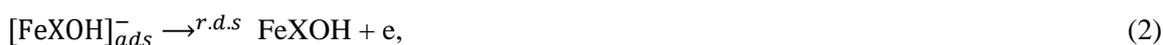
1.1. Synergistic mechanism of halide ions

The addition of halide ions has been found to improve the adsorption of organic inhibitor cations via ion-pair interaction. When halide anions are pre-adsorbed on metal surfaces, they created excess of negative charges on the metal surfaces. Previous studies reported that the pre-adsorption of halide ions on the metal surface has facilitated the adsorption of organic inhibitor cations by forming intermediate bridges between the positively charged metal surface and the positive end of the organic inhibitor. This



promoted a better adsorption mechanism of the organic inhibitor cation on the metal surfaces. The interaction enhanced the inhibition efficiency to a considerable extent [14].

Among halide ions, the synergistic inhibition effect increases in the order of $\text{Cl} < \text{Br} < \text{I}$. This indicates that the radius of halide ions has an important role in determining the adsorption mechanism on metal surface. The largest ionic radius of iodide ion has a higher hydrophobicity property as compared to the other two halide ions. The pre-adsorption of iodide ion onto metal surface will decrease the hydrophilicity of the metal surface. Consequently, adsorption of organic molecules onto the pre-adsorbed metal surface is favoured, instead of water molecules [15]. In the presence of halide ion (X^-), the mechanism for the anodic dissolution is as given in the following equations [16]:



Generally, halide ion will participate in the formation of intermediate. The adsorbed intermediate, $[\text{FeXOH}]_{\text{ads}}^-$ on the metal surface involved in the rate determining step (r.d.s). Organic inhibitor molecules will then combine with the adsorbed intermediate to form a metal-inhibitor complex. The resulting metal-inhibitor complex will either catalyzed or inhibit further metal dissolution depending on its solubility [16]. Two possible models for inhibitor adsorption with the aid of halide ion have been described by Okafor, Liu, & Zheng [9]. The first model is the adsorption of halide ion which then further attracts inhibitor molecule to metal surface (co-operative mechanism). In this co-operative mechanism, the strong chemisorption of halide ion on the metal surface is responsible for the synergistic effect of halide ion in combination with organic molecules. Then, the organic molecules are adsorbed by coulombic attraction at the metal surface, where the halide ion is already chemisorbed. The stabilization of the adsorbed halide ion by means of electrostatic interaction with organic molecules leads to greater surface coverage and thereby greater inhibition efficiency. The second model is the exchange of adsorption site by halide ion and organic ion (competitive mechanism). In competitive adsorption, the anion and cation are adsorbed at different sites on the metal surface. The adsorption of an anion may enhance the adsorption of a cation and vice versa. A combination of both models is also possible [18]. Since the synergistic inhibition effect has a significant impact on the modern corrosion inhibitor formulation, thus this paper will discuss further the effect of iodide ion with three selected inhibitors of imidazoline derivative namely amido-imidazoline (IM), 2-undecyl-1-ethylamino imidazoline (2UEI) and 2-undecyl-1-ethylamino-1-methylbenzyl quaternary imidazoline (2UMQI).

2. Effect of iodide ion on inhibitive action of Imidazoline derivative

A study investigated the inhibition effect of amido-imidazoline (IM) on carbon steel in a 3 wt% sodium chloride and its synergistic effect in the presence of iodide ion (from KI solution) by using an electrochemical impedance spectroscopy technique and a potentiodynamic polarization measurement [19]. In the presence of 2000 mg/L I^- ion (Table 1), the inhibition efficiency, % η showed an increase of 14.8% at 50 mg/L IM when measured via the impedance technique. The increment however was only 1.8% and 2.7% at 75 mg/L IM and 100 mg/L IM, respectively. Similar trend was revealed via the polarization technique. A significant increase of 9.7% at 50 mg/L IM; but only 1.2% and 1.7% at 75 mg/L IM and 100 mg/L IM, respectively. They also found that both the adsorption of IM and IM/KI on carbon steel surface followed the Langmuir adsorption isotherm. In this case, they reported that the co-operative adsorption mechanism dominated over the competitive adsorption mechanism in an IM/KI inhibition system. The co-operative adsorption could stabilize the adsorption of IM on the surface, therefore the inhibition ability improved in the presence of KI. The co-operative adsorption mechanism was also suggested by other researchers in another imidazoline /I study [20].

Another study studied the inhibition effect of 80 mg/L 2-undecyl-1-ethylamino imidazoline (2UEI) on carbon steel in CO_2 -saturated 3 wt% NaCl and its synergistic effect in the presence of I^- ion [17]. According to Table 2, they found that the presence of highly concentrated I^- ions did not show the synergistic inhibition effect with the 2UEI inhibitor. The increase was only 1% and 2.38% at 830 mg/L

and 2000 mg/L I⁻ ion respectively. Without the presence of the I⁻ ions, the inhibition efficiency of the 2UEI inhibitor was very close to 100%. Similar investigation was conducted by using 50 mg/L 2-undecyl-1-ethylamino-1-methylbenzyl quaternary imidazoline (2UMQI) as the inhibitor on carbon steel in 1.0 M H₂SO₄ [18]. Unlike Okafor, Liu, & Zheng [9], they found that the inhibition efficiency increased by about 50% of its initial reading irrespective to I⁻ ion concentrations as obtained in Table 3. Furthermore, when they explored the steel surface through AFM images as shown in Figure 1, they found that the steel surfaces produced the smoothest surfaces under the condition of 50 mg/L 2UMQI+2.5 mM KI. Hence they proved that the 2UMQI/KI system is more effective inhibitor than 50 mg/L 2UMQI alone, without addition of KI.

Table 1. Inhibition efficiency (% η) for carbon steel in 3 wt% NaCl solution at 25°C in the absence and presence of IM and KI from impedance spectroscopy and potentiodynamic polarization [19].

IM (mg/L)	Impedance method (% η)		Polarization method (% η)	
	Without KI	With 2000 mg/L KI	Without KI	With 2000 mg/L KI
0	-	-	-	-
50	76.7	90.1	85.1	94.2
75	91.2	92.9	95.8	97.0
100	91.8	94.3	96.2	97.9

Table 2. Inhibition efficiency for carbon steel in in 3 wt% NaCl saturated with CO₂ at 25°C in the absence and presence of 2UEI and KI using potentiodynamic polarization [17].

2UEI (mg/L)	Polarization method (% η)		
	0 mg/L KI	830 mg/L KI	2000 mg/L KI
0	-	-21.8	-51.0
80	95.0	96.0	97.4

Table 3. Inhibition efficiency for carbon steel in 1 M H₂SO₄ at 25°C in the absence and presence of 2UMQI and KI using impedance spectroscopy and potentiodynamic polarization [18].

2UMQI (mg/L)	Impedance method (% η)				Polarization method (% η)			
	0 mg/L KI	166 mg/L KI	166 mg/L KI	415 mg/L KI	0 mg/L KI	16.6 mg/L KI	166 mg/L KI	415 mg/L KI
0	-	93.6	96.5	98.1	-	88.2	93.2	96.6
50	61.6	98.6	99.5	99.6	63.4	97.5	98.2	98.9

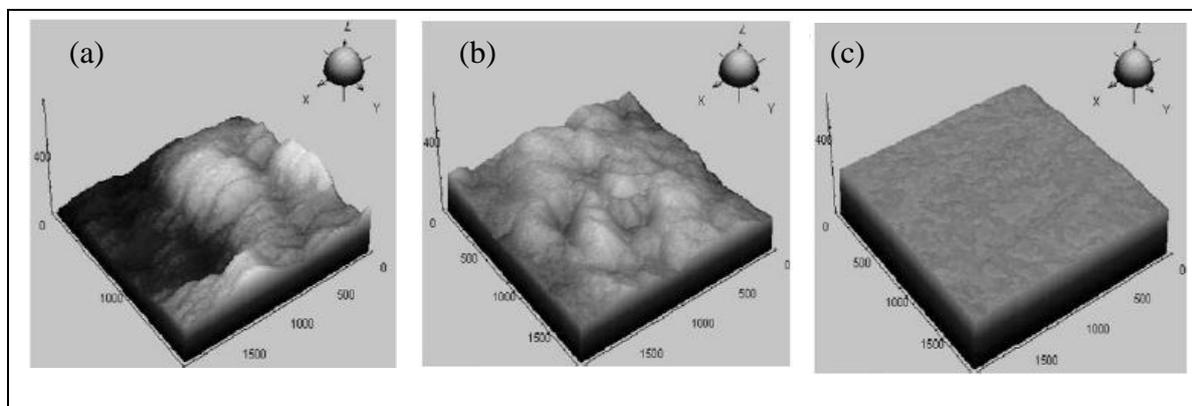


Figure 1. AFM images of carbon steel immersed in 1.0 M H₂SO₄ (a) without inhibitor (b) containing 50 mg/L 2UMQI and (c) containing 50 mg/L 2UMQI + 2.5 mM KI after 1 hour of immersion at 25 °C [18].

Figure 2 is plotted in order to observe the effect of I^- ion at different concentrations of inhibitor systems. Heydari & Javidi [19] studied at a fixed amount of I^- ion, Okafor, Liu, & Zheng [17] and Okafor & Zheng [18] studied at varies amount of I^- ion. It is observed that a more evident increment of the inhibition efficiency between inhibitor-only system and inhibitor/ I^- system, particularly when the inhibitor is presence at low concentration. According to Figure 2, without the presence of I^- ion, the inhibition efficiency is 63.4% and 85.1% for 50 mg/L 2UMQI inhibitor and 50 mg/L IM inhibitor, respectively. In the presence of 50 mg/L 2UMQI + 16.6 mg/L I^- ion, the inhibition efficiency is 97.5%. While in the presence of 50 mg/L IM + 2000 mg/L I^- ion, the inhibition efficiency is 94.2%. The inhibition efficiency remains at a value close to 100% at increasing I^- ion.

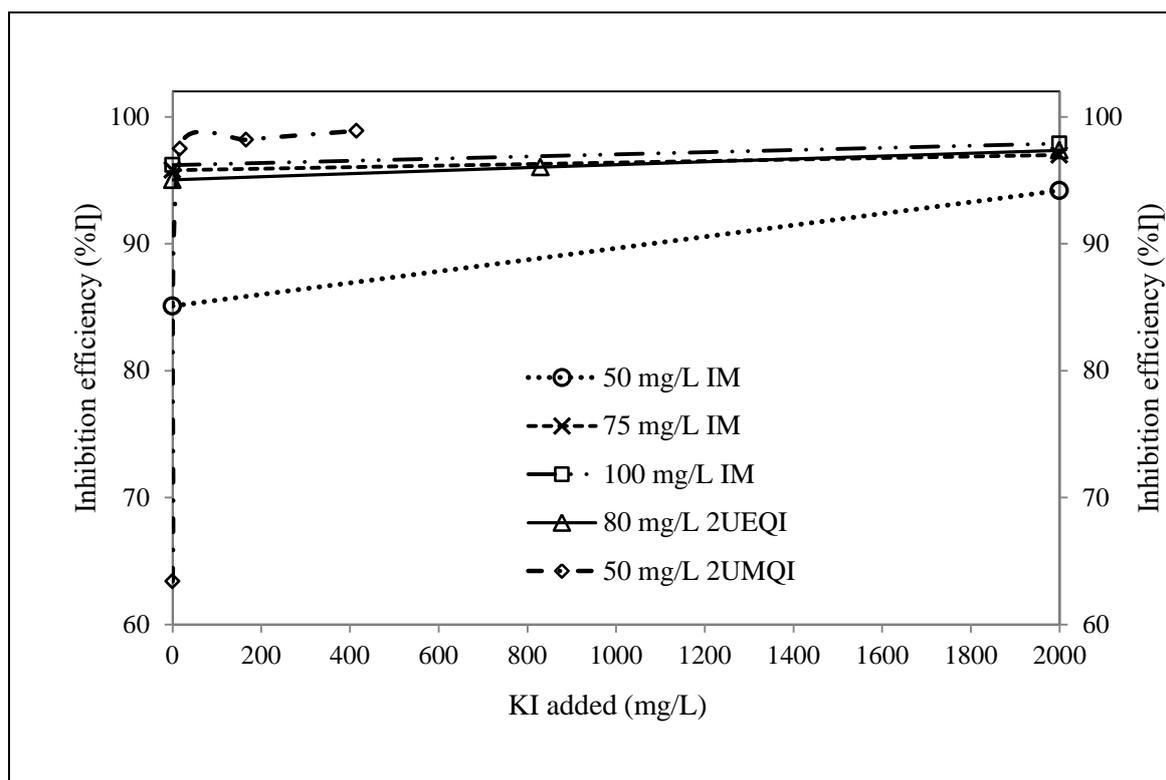


Figure 2. Effects of $[I^-]$ ion on inhibition efficiency (% η) in different inhibitor systems at 25°C [17]–[19].

This means that there is a synergistic inhibition effect of the I^- ion in the imidazoline derivative inhibitors. However, only a slight increase of inhibition efficiency has occurred when inhibitors are presence at high concentrations. This is shown from the potentiodynamic polarization measurements of 75 mg/L and 100 mg/L IM systems and 80 mg/L 2UEQI systems. The inhibition efficiencies are already close to 100% despite no I^- ion is present. In this case, it is concluded that the synergistic inhibition effect of the I^- ion is predominant in a low concentration inhibitor system. This will become a benefit to manufacturing industries since they will be able to reduce corrosion related problem issues at lower operation costs. This is possible when they use enhancer such as iodide ion together with a small amount of corrosion inhibitor.

3. Conclusions

It has been shown that synergistic effect between organic inhibitors and iodide ion is an effective method to improve the inhibitive performance for metals in different aqueous media. The results from a series of investigations revealed that the adsorption of organic inhibitors was stabilized by the presence of iodide ion (I^-) in the solutions and enhanced the inhibition efficiency significantly due to synergistic effect. The synergistic effect increases with increases in KI concentration in the mixture. It has proven to be an effective way to decrease the amount of organic inhibitor consumption.

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