The Synergistic Effect of 2-Chloromethylbenzimidazole and Potassium Iodide on the Corrosion behavior of Mild Steel in Hydrochloric Acid Solution

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ABSTRACT

The synergistic effect of 2-chloromethylbenzimidazole (2-CBI) and potassium iodide (KI) for mild steel in 1 M hydrochloric acid solution was investigated by potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS). The results showed that, with the addition of 100 ppm potassium iodide, the inhibition efficiecy (IE) of 100 ppm 2-CBI in 1 M hydrochloric acid had been improved from 91.14% to 96.15%. And synergistic parameter of 100 ppm 2-CBI with different amounts of potassium iodide is always greater than 1. The adsorption of potassium iodide combining with 100 ppm 2-CBI obeys to the Langmuir adsorption isotherm. Thermodynamic adsorption parameters, including ΔG^0_{ads}, ΔH_a and ΔS_a of the adsorption of the combinned inhibitor, as well as the E_a of the mild steel corrosion in 1 M HCl with the combinned inhibitor, were calculated.

Keywords : Mild Steel, 2-Chloromethylbenzimidazole, Potassium Iodide, Synergism, Adsorption

1. Introduction

Mild steel is widely used in diverse fields of industry, and its corrosion is an unavoidable problem. At present, there are many methods for corrosion protection of mild steel, and corrosion inhibitor is one of the most economical and efficient method [1]. The mechanism of corrosion inhibitors can be roughly divided into two categories. One is to interact with ions on the metal surface to form a precipitated film composed of oxides, hydroxides or insoluble salts and adhere to the metal surface to form a protective film. The chromate and phosphate are typical representative of this type. However, they are often harmful to the human and the environment. Therefore, environmentally friendly "green" corrosion inhibitors are more favorable [2]. Most of the organic corrosion inhibitors have the second mechanism, they slow down the corrosion of the metal by forming an adsorption film on the metal surface [3-5]. And adsorption can be the electrostatic interaction between the charged surface of the metal and the charge of the inhibitor [6], or the interaction between the lone pair of electrons or π electrons in the corrosion inhibitor molecule and the empty d-orbitalson of the metal substrate, namely the coordination bonds [7,8].

2-Chloromethylbenzimidazole (2-CBI) is a benzo-heterocyclic compound containing N atom [9], the benzene ring and the N atom bearing the sp^2 electron pair are considered as the "anchoring sites" for molecular adsorption at the metal surface [10-12]. K. F. Khaled [13] studied IE of 2-(aminomethyl)benzimidazole (AB), 2-CBI and 2-(methylthio)benzimidazole (MB) for iron in 1M HNO_3, and AB shows to be the most effective corrosion inhibitor. By using electrochemical impedance spectroscopy (EIS), R. L. Camacho-Mendoza et al. [14] found that 2-CBI has the highest IE among the six heterocyclic compounds. Z.L. Li et al. [15] found that when benzimidazole and its derivatives are used as corrosion inhibitors for mild steel in 1M HCl solution, the corrosion IE shows a 2-chloromethylbenzimidazole(2-

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CBI) > 2Methylmercaptobenzimidazole > benzimidazole, where the corrosion IE of 2-CBI can reach nearly 96% at a concentration of 1.52×10^{-3} mol·L^{-1}. Although 2-CBI has an outstanding IE, it is expensive. In order to expand the application of 2-CBI, to obtain a higher IE with lower 2-CBI concentration is urgent.

Studies [16-18] have found that when a variety of inhibitors were used together, the IE was higher than that of a single inhibitor, and this phenomenon was denoted as synergistic effect. Based on the synergistic effect, one can improve the IE of some inhibitors and reduce the cost of some inhibitors. The mechanism of the synergistic effect was usually ascribed to the interplay between the different inhibitor molecules or the interaction between the corrosion inhibitor and a certain ion existing in the aqueous solution. Researchers have found that chloride ions, bromide ions and iodide ions have better synergistic effects. Among them, due to the largest size and the best polarizability, iodide ions usually has the highest synergistic effect [19-21]. IB Onyeachu et al. [22] found that 5-methyl-1H-benzotriazole (MHB) can inhibit the corrosion of mild steel by 80% in 1 M HCl solution, and the IE of MHB was increased significantly after adding 5 mM potassium iodide into the solution. It was speculated that the iodide anion makes the steel surface negatively charged [23], thereby improving the electrostatic attraction of the protonated MHB on the steel surface. P. Banerjee et al. [24] found that, with an addtion of a very small amount of potassium iodide $(6 \times 10^{-3}$ mol·L$^{-1})$, the IE of palmitic imidazole (PI) increases from 90% to about 98% with its concentration of 1.0×10^{-3} mol·L^{-1}. By using molecular dynamics simulation, they believe the protonated PI may bridge with the previously adsorbed acid anions or iodide anions on the metal surface, thereby reducing the process of H$^+$ gaining electrons and reducing corrosion.

In this contribution, the synergistic effect of 2-CBI/potassium iodide mixture (2-CBI/KI) for mild steel in 1 M HCl was studied. An electrochemical workstation was used to measure the corrosion of mild steel in 1 M HCl solution with different amounts of 2-CBI or 2-CBI/KI with different amounts of potassium iodide. In addition, the adsorption isotherm of 2-CBI/KI on the surface of mild steel was determined, as well as the influence of temperature on the corrosion of mild steel with 2-CBI/KI in the 1 M HCl solution.

2. Experimental

2.1 Materials

2-CBI was purchased from Shanghai Yuanye Biotechnology Co., Ltd.. Potassium iodide and concentrated hydrochloric acid were purchased from Shanghai Runjie Chemical Reagent Co., Ltd., without any further treatment before use. Concentrated hydrochloric acid (37%) was dissolved in distilled water to prepare 1M HCl solution. The chemical composition of the involved mild steel samples is C = 0.193%, Si = 0.272%, Mn = 0.436%, P = 0.033% and S = 0.029%. A cylindrical mild steel sample with a cross-sectional area of 0.785 cm^2 was welded with insulated copper wire and sealed by epoxy resin.

2.2 Characterization

A three-electrode cell containing a mild steel sample as the working electrode, saturated calomel electrode (SCE) as the reference electrode, and platinum electrode as the counter electrode was used. An electrochemical workstation (PARSTAT VersaSTAT3) was used to measure EIS and polarization curve of mild steel in 100 mL electrolyte. Before each measurement, the working electrode was immersed in the electrolyte solution for 30 minutes to achieve a steady state. The scanning range of the polarization curve is -250 mV to 250 mV, relative to the open circuit potential (E$_{oc}$), with a scanning rate at 1 mV·s^{-1}. EIS measurements were carried out at the E$_{oc}$ with the frequency range from 10^5 Hz to 10^{-2} Hz and amplitude of 5 mV. Each experiment was repeated 3 times and representative results or average values are displayed in graphical or tabular form.

3. Results and Discussion

3.1 Electrochemical analysis

We start with the EIS measurments of the mild steel in 1 M HCl at 20ºC with different inhibitors, and the Nyquist plots and Bode diagrams were showed in Fig. 1. The Nyquist plots of mild steel in 1 M HCl with different amount of 2-CBI (Fig. 1a), Potassium Iodide (Fig. 1c) and 2-CBI/KI (Fig. 1e) all show a single depressed capacitive semicircle. The electrical equivalent circuit in Fig. 1a, Fig. 1c and Fig. 1e was used to fit the EIS data and the fitting data were recorded in Table 1, where R_s represents the solution resistance, *CPE* is the double-layer capacitance and
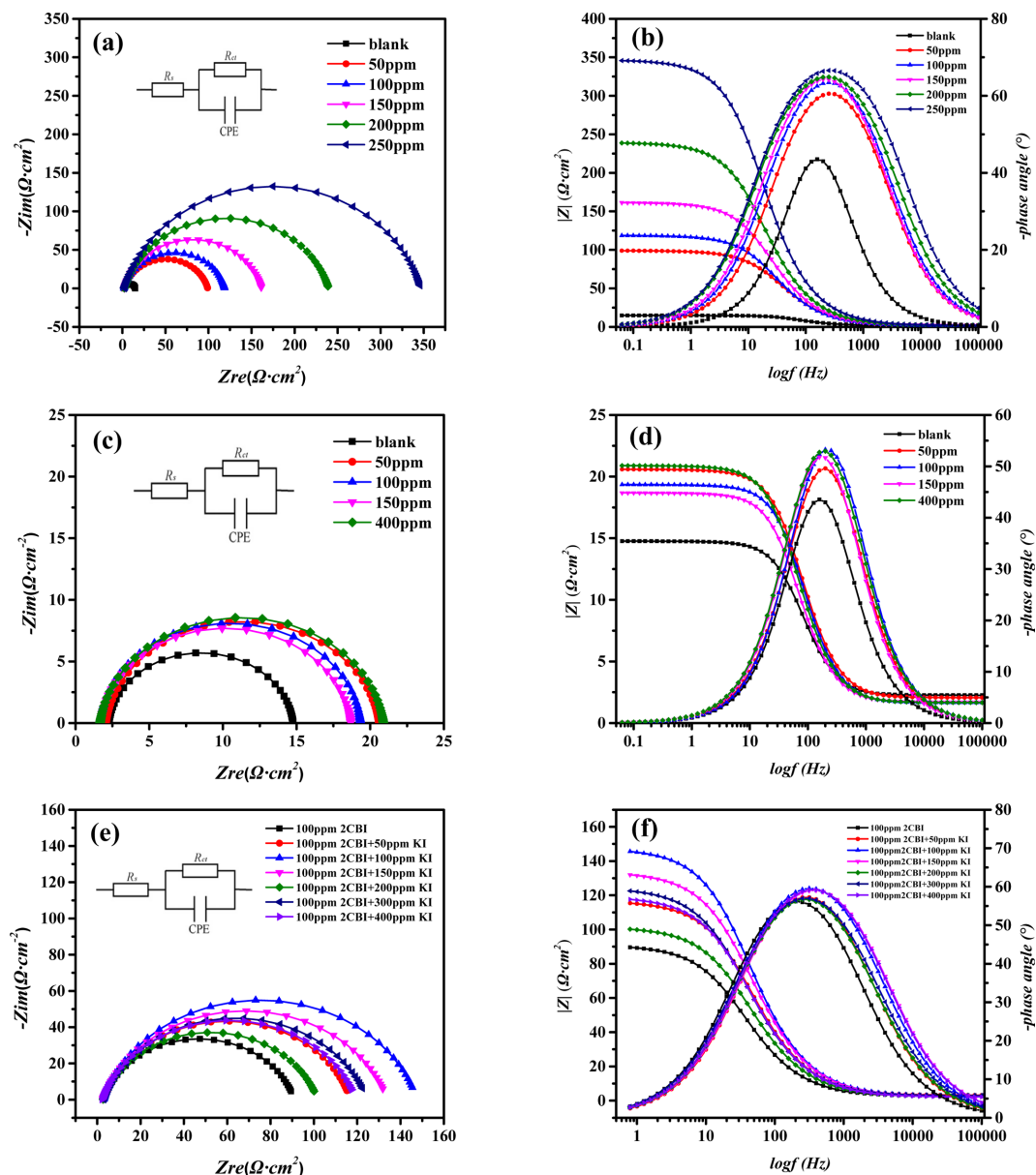
Fig. 1. The EIS results of mild steel in 0.1M HCl with different inhibitors at 20ºC: the Nyquist plots of (a) 2-CBI, (c) Potassium Iodide, (e) 2-CBI+Potassium Iodide; the Bode plots of (b) 2-CBI, (d) Potassium Iodide, (f) 2-CBI+Potassium Iodide

R_{ct} corresponds to charge tranfer resistance.

The IE (η%) was calculated by using the following equations [25]:

$$\eta = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \times 100\% \tag{1}$$

where R_{ct}^0 and R_{ct} are the charge tranfer resistance values in the absence and presence of the inhibitors, respectively.

It can be seen from Fig. 1a that the radius of impedance arc increases with the increasing of 2-CBI amount. From the data in Table 1, it can be seen that as the concentration of 2-CBI increases, the charge transfer resistance R_{ct} increases, indicating that the

Table 1. The parameters from EIS for mild steel in 0.1M HCl with different inhibitors at 20ºC

Inhibitor	C(ppm)	$R_s(\Omega \cdot cm^2)$	$R_{ct}(\Omega \cdot cm^2)$	η	θ
		2.256	12.51	/	/
	50	2.081	96.99	87.1%	0.871
Blank 2-CBI	100	1.738	117.10	89.3%	0.893
	150	2.221	159.30	92.1%	0.921
	200	2.072	237.40	94.7%	0.947
	250	2.126	344.70	96.4%	0.964
	0	2.796	88.22	85.8%	0.858
	50	3.129	113.70	89.0%	0.890
100ppm 2-CBI + Potassium Iodide	100	2.890	144.80	91.4%	0.914
	150	2.494	131.40	90.5%	0.905
	200	2.688	98.99	87.4%	0.874
	300	2.883	121.80	89.7%	0.897
	400	2.182	117.20	89.3%	0.893

addition of 2-CBI can form a dense molecular layer on the metal surface and retard the charge transfer process, and thus slow down the corrosion of the metal. From Fig. 1c, one can find that the addition of potassium iodide did not significantly change the radius of the impedance arc. Therefore, it can be deduced that potassium iodide has almost no inhibition effect for the corrosion of mild steel in 1 M HCl at 20ºC. However, after adding potassium iodide into 1 M HCl solution with 100 ppm 2-CBI, the radius of the impedance arc changes. It can be seen from Fig. 1e that, with the increasing of potassium iodide amount, the IE of 2-CBI/KI mixture (the concentration of 2-CBI fixed at 100 ppm) increases first and then decreases. And all IE of the 2-CBI/KI mixture are higher than that when 100 ppm 2-CBI was used only.

The Bode diagrams (Fig. 1b, Fig. 1d and Fig. 1f) at low-frequency range confirms the changes of IE with increasing of inhibitor concentration, which depended on the adsorption of the inhibitor on the surface of mild steel [26,27]. It can be seen from the bode phase plot that only one time constant is shown in the figure. Therefore, fitting the EIS data by using the electrical equivalent circuit in Fig. 1a, Fig. 1c and Fig. 1e are reasonable.

Fig. 2 shows the Tafel polarization curves of mild steel in 1 M HCl solutions with different corrosion
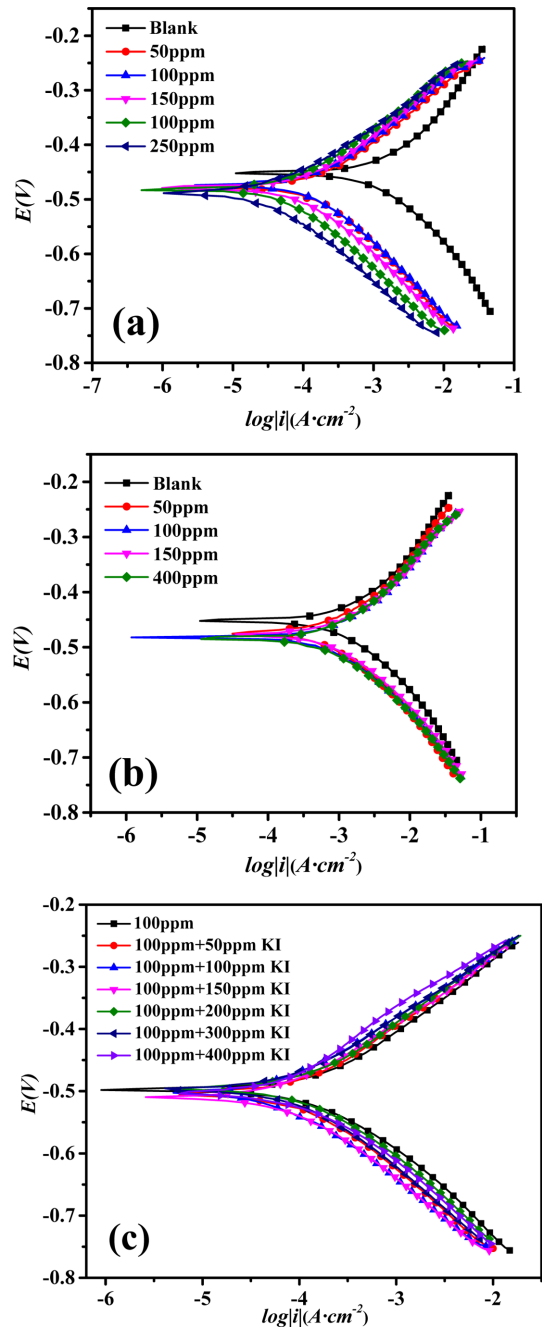
Fig. 2. The polarization curves for mild steel in 0.1M HCl with different inhibitors at 20ºC: (a) 2-CBI, (b) Potassium Iodide, (c) 100ppm 2-CBI+ Potassium Iodide

inhibitors. Corrosion current density (i_{corr}) had been determined by extrapolating the cathode and anode curves to meet the corrosion potential (E_{corr}). And the

Table 2. The relevant parameters from polarization curves with different concentration inhibitors

Inhibitor	C (ppm)	E_{corr} (mV)	i_{corr} (μA cm^{-2})	β_c (mv dec^{-1})	β_a (mv dec^{-1})	θ	η
		-453.299	1683.000	168.501	166.372	/	/
	50	-476.960	164.753	134.473	103.697	0.9021	90.21%
Blank	100	-473.348	149.066	129.254	103.000	0.9114	91.14%
2-CBI	150	-480.454	99.305	121.643	100.450	0.9410	94.10%
	200	-481.698	60.521	119.894	93.831	0.9640	96.40%
	250	-488.312	31.599	109.729	85.723	0.9812	98.12%
	50	-504.800	110.388	128.514	114.059	0.9344	93.44%
100ppm	100	-501.826	64.821	119.251	100.763	0.9615	96.15%
2-CBI	150	-510.112	77.056	119.797	107.174	0.9542	95.42%
+ Potassium	200	-495.234	126.487	127.052	114.728	0.9248	92.48%
Iodide	300	-496.674	87.931	122.512	106.984	0.9478	94.78%
	400	-501.517	85.837	114.478	121.413	0.9490	94.90%

Tafel slopes of the cathode (β_c) and anode (β_a) were determined. All the parameters obtained from Talfel polarization were listed in Table 2, as well as the surface coverage θ and the IE (η%) calculated by using equation 2 and equation 3 [28,29] respectively:

$$\theta = \frac{i_{corr}^0 - i_{corr}}{i_{corr}^0} \qquad (2)$$

$$\eta = \frac{i_{corr}^0 - i_{corr}}{i_{corr}^0} \times 100\% \qquad (3)$$

where i_{corr} and i_{corr}^0 are the self-corrosion current density of carbon steel with and without corrosion inhibitor.

It can be seen from Fig. 2a that, after adding 2-CBI into the 1 M HCl solution, the cathode and anode curves shift to the left obviously, and the corrosion current density decreases greatly. From the data in Table 2, one can find that the IE increases with the increasing of 2-CBI concentration. The results shown in Fig. 2a and Table 2 consist with the results presented in Fig. 1a and Table 1 well, it is easy to say that 2-CBI is an efficient inhibitor in HCl solution solution. After adding different amounts of potassium iodide into the 1 M HCl (Fig. 2b), as indicated in Fig. 1c, the cathode and anode curves have no change, which means potassium iodide has no inhibition effect for mild steel in 1 M HCl. However, as shown in Fig. 2c, both the cathode and anode curves shift to the left after adding different amounts of potassium

iodide into the 1 M HCl solution with 2-CBI fixed at 100 ppm. As presented in Table 2, when the potassium iodide concentration is 100 ppm, the corrosion current density decreases from 149.07 μA·cm^{-2} to 64.82 μA·cm^{-2}, and IE increases from 91.14% to the maximum value of 96.15%. Based on the EIS and Tafel polarization results, it is easy to say, although potassium iodide have no inhibition effect for mild steel in 1 M HCl, but it can enhance the IE of 2-CBI.

According to S.A. Umoren [30], when the halide ions and other molecules were combined and used as inhibitor, there are two mechanisms for their adsorption on the metal surface. One is that the ion pair firstly formed in the solution and then adsorbed to the metal surface. The other is that the halide ions adsorbed onto the metal surface firstly, and then the other molecules were attached by the adsorbed halide ions. Based on the existing researches [31,32], the enhanced IE of 2-CBI by potassium iodide would be ascribed to the following reason that, with potassium iodide in the solution, the first adsorbed I$^-$ makes 2-CBI easier to adsorb onto the mild steel surface, and forming a denser molecular layer to protect the mild steel.

Nevertheless, with the increasing of the potassium iodide concentration, the IE 2-CBI/KI mixture reaches the maximum when the potassium iodide concentration is 100 ppm, and then the IE decreases. This probably due to the reason that, as the concentration of potassium iodide further increased, the

Table 3. Synergy parameter of 2-CBI and Potassium Iodide

Inhibitor concentration (ppm)	Synergy parameters (S)
100ppm 2-CBI + 50ppm Potassium Iodide	1.44
100ppm 2-CBI + 100ppm Potassium Iodide	2.43
100ppm 2-CBI + 150ppm Potassium Iodide	2.06
100ppm 2-CBI + 200ppm Potassium Iodide	1.27
100ppm 2-CBI + 300ppm Potassium Iodide	1.79
100ppm 2-CBI + 400ppm Potassium Iodide	1.86

adsorption of 2-CBI and I⁻ on the metal surface changed from staggered adsorption to overlapping competitive adsorption, thus resulting in a desorption of 2-CBI [33,34].

In a word, combining 2-CBI with potassium iodide in 1 M HCl can induce a higher IE than that of 2-CBI itself, it is safe to say, there is a synergy effect bewteen 2-CBI and potassium iodide when they were used together as inhibitor for mild steel in 1 M HCl. Here, the synergy parameters (S) were calculated by using the following equation [35]:

$$S = \frac{1 - \theta_A - \theta_B + \theta_{AB}}{1 - \theta_{AB}} \qquad (4)$$

Where θ_A and θ_B are the surface coverage of 2-CBI and potassium iodide on the metal surface, respectively, and θ_{AB} is the surface coverage of the mixture of 2-CBI and potassium iodide. If S> 1, it indicates synergy, if S <1, it indicates antagonism between 2-CBI and potassium iodide [36]. It can be seen from Table 3 that synergy parameter of 2-CBI/ KI mixture are always greater than 1, no matter the concentration of potassium iodide is.

3.2 Adsorption isotherm

The adsorption isotherm can provide information about the interaction between adsorbed molecules and the electrode surface [37]. In order to leran more about how the 2-CBI/KI mixture adsorb on the surface of mild steel, various adsorption isotherm models (such as Temkin, Langmuir and Frumkin models) were used to fit the data. It was found that, for 2-CBI and 2-CBI/KI mixture, the Langmuir adsorption isotherm is working. The calculation results were fitted by the following formulae [38]:

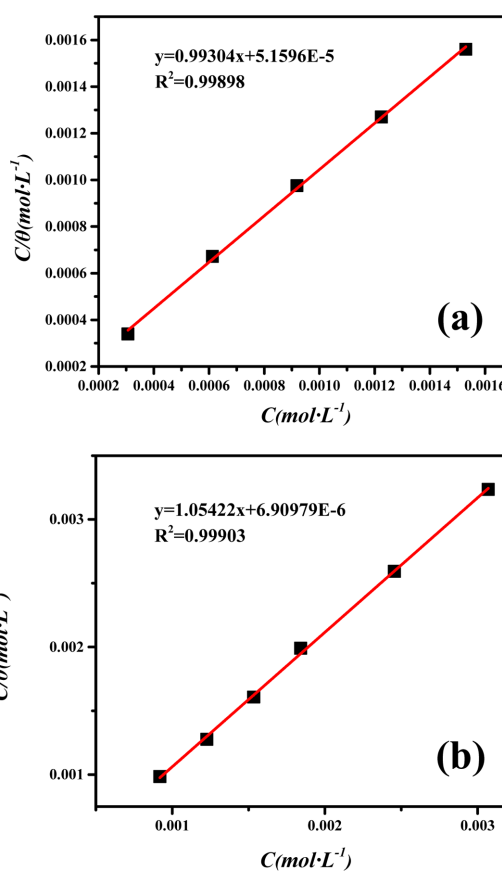$$\frac{\theta}{1 - \theta} = C \cdot K_{ads} \qquad (5)$$

Fig. 3. The Langmuir adsorption isotherm of (a) 2-CBI, (b) 2-CBI/Potassium Iodide on mild steel surface in the 1M HCl solution at 20ºC

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad (6)$$

Among them, K_{ads} is the constant of the adsorption-desorption process that occurs on the metal surface, C is the corrosion inhibitor concentration (mol·L⁻¹), and θ is the surface coverage.

Table 4. The relevant thermodynamic parameters for mild steel from Langmuir adsorption

Inhibitor	$K_{ads} \times 10^3$ (L mol^{-1})	ΔG^0_{ads} (kJ mol^{-1})
Blank	/	/
2-CBI	19.4	-34.41
2-CBI/ Potassium Iodide	144.7	-39.39

The Langmuir adsorption isotherm of 2-CBI and 2-CBI/KI mixture are shown in Fig. 3, respectively. It can be observed that, for the adsorption of 2-CBI or 2-CBI/KI mixture onto mild steel, the correlation coefficient (R^2) and slope value are near unity indicating Langmuir adsorption isotherm works very well [39]. The value of K_{ads} was obtained from the intercept of isotherm plot Fig. 3. The calculated values of K_{ads} are displayed in Table 4. The higher the value of K_{ads}, the greater the adsorption capacity and the better the corrosion inhibition effect [40]. The free energy of adsorption ΔG^0_{ads} can be calculated by K_{ads}, with the following equation [41]:

$$\Delta G^0_{ads} = -RTln(55.5 \cdot K_{ads}) \qquad (7)$$

Among them, R is the gas constant, T is the Kelvin temperature, and the value 55.5 represents the molar concentration of water in the acid solution (mol·L^{-1}).

Table 4 shows the K_{ads} and ΔG^0_{ads} values of 2-CBI and 2-CBI/KI mixture. The negative sign of ΔG^0_{ads} indicates that the corrosion inhibitor is spontaneously adsorbed onto the metal surface. Studies have reported that the larger the absolute value of ΔG^0_{ads}, the better the adsorption ability of the corrosion inhibitor [42]. Generally, the value of ΔG^0_{ads} between -20 kJ·mol^{-1} and -40 kJ·mol^{-1} means the the adsorption is a physical and chemical mixed process. When the value close to -40 kJ·mol^{-1}, it means the chemisorption is dominant [43, 44]. In this experiment, the ΔG^0_{ads} of 2-CBI and 2-CBI/KI mixture are -34.41 kJ·mol^{-1} and -39.39 kJ·mol^{-1}, respectively. Those values indicate that, with the addition of potassium iodide, the interaction between inhibitor and the surface of mild steel towards to chimisorption more. We propose here that, with the 2-CBI alone, 2-CBI ionized into cations in water and arrived the metal surface through the physical adsorption of electrostatic attraction and the chemical adsorption of forming coordination bonds. It is known to all that the mild steel surface charges positive in acid solution [45]. After potassium iodide was added, I$^-$ ions adsorbed onto the mild steel surface first and they created an excess negative charge toward the solution [46,47] and favor more adsorption of the cations. Also, they changed the distribution of the electron cloud of the N atom in 2-CBI [48], and thus promoted the interacation between the lone pair of electrons or π electrons in the 2-CBI and the empty Fe d-orbitals in on the mild steel surface.

3.3 Effect of temperature

The effect of temperature [49] on the corrosion of mild steel with inhibitors in the acid solution is very complicated. For example, the anode or cathode reaction, the rapid etching and desorption of the cor-

Table 5. Electrochemical parameters extrapolated from the polarization curves in Figure 3

Inhibitor	T(ºC)	E_{corr}(mv)	i_{corr}(μA cm^{-2})	β_c(mv dec^{-1})	β_a(mv dec^{-1})	θ	η	S
2-CBI	20	-476.675	127.717	121.864	103.533	0.9241	92.41%	
	25	-473.297	270.161	143.209	111.027	0.8910	89.10%	
	30	-456.448	614.749	160.406	123.212	0.7753	77.53%	
	35	-448.274	1268.000	169.709	140.756	0.7318	73.18%	
	40	-439.952	1531.000	164.968	128.795	0.7220	72.20%	
2-CBI/ Potassium Iodide	20	-471.459	111.326	126.393	106.302	0.9339	93.39%	1.14723
	25	-464.710	224.088	136.222	116.995	0.9096	90.96%	1.2056
	30	-461.314	307.508	138.333	118.702	0.8876	88.76%	1.99913
	35	-469.223	439.441	148.306	126.205	0.9070	90.70%	2.88548
	40	-464.225	596.297	151.998	129.543	0.8917	89.17%	2.56751

rosion inhibitor and the decomposition of corrosion inhibitor itself. In order to learn more inhibition mechanism of 2-CBI/KI mixture for mild steel in 1 M HCl, the effect of temperature on electrochemical parameters of mild steel with 100 ppm 2-CBI and 2-CBI/KI mixture (100 ppm 2-CBI + 100 ppm potassium iodide) was performed, the temperature ranging from 20ºC to 40ºC. Fig. 4 shows Tafel polarization curves of mild steel with 100 ppm 2-CBI and 2-CBI/KI mixture (100 ppm 2-CBI + 100 ppm potassium iodide) in 1 M HCl at different temperatures, and the relevant electrochemical parameters are listed in Table 5.

From Fig. 4 and Table 5, it can be seen that the IE of 2-CBI and 2-CBI/KI mixture both decreases with increasing of the temperature. However, the IE of 2-CBI and 2-CBI/KI mixture response to temperature differently. For 2-CBI, with temperature increasing from 20 to 40ºC, the IE decreases from 92.41% to 72.20%. While for 2-CBI/KI mixture, the IE decreases from 93.39% to 89.17%. The smaller IE reduction with temperature increasing indicates that the 2-CBI/KI mixture molecule film has the higher stability than that of 2-CBI alone.

Further, the activation energy of the corrosion process was calculated by using Arrhenius and transition state equation [50-52]:

$$Ini_{corr} \;=\; lnA - \frac{E_a}{RT} \tag{8}$$

$$ln\frac{i_{corr}}{T} \;=\; ln\frac{R}{Nh} + \frac{\Delta S_a}{R} - \frac{\Delta H_a}{RT} \tag{9}$$

Among them, A is the pre-exponential factor, R is the gas constant, h is the Plank constant, N is the Avogadro number, E_a is the apparent activation energy, ΔS_a is the entropy of activation, and ΔH_a is the enthalpy of activation respectively.

The plots (Arrhenius plots and transition state plots) for mild steel in 1M HCl solution witout inhibitor or with different inhibitors are shown in Fig. 5 and the relevant data are listed in Table 6. One can find that, without any inhibitor, the value of E_a is 45.991 kJ·mol⁻¹, while with 2-CBI or 2-CBI/KI mixture as inhibitor, the value of E_a is 99.615 kJ·mol⁻¹ and 61.632 kJ·mol⁻¹ respectively. According to the exsiting researches, the increasing of E_a means the interaction between the inhibitor and the metal surface more inclined to physical adsorption, while the decreasing of E_a is more inclined to chemical
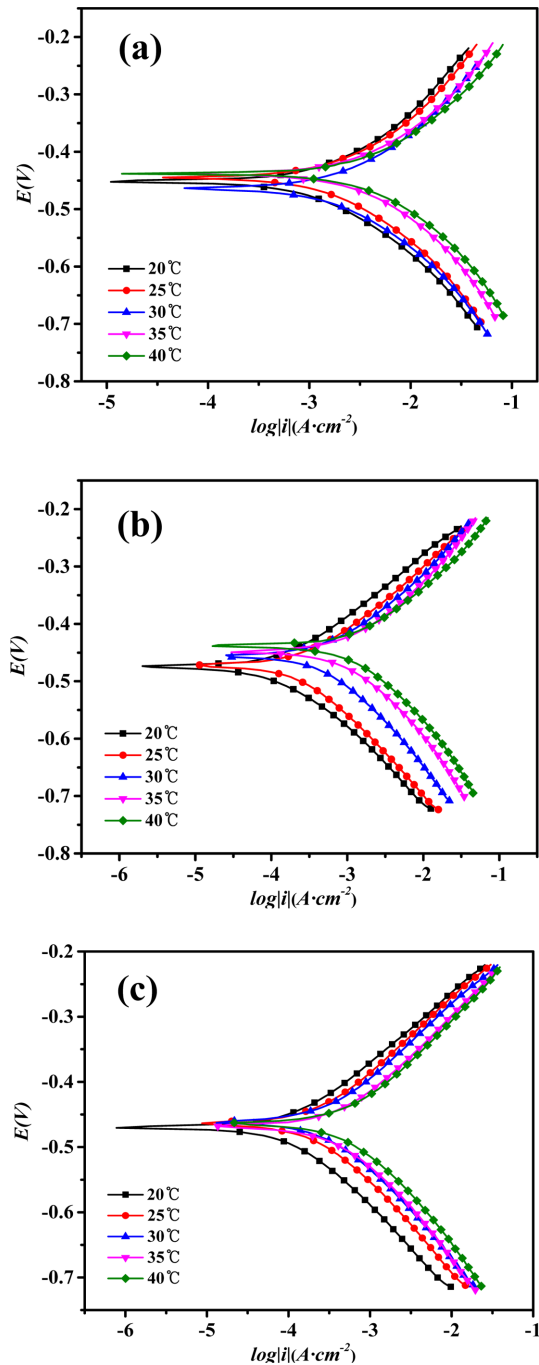

Fig. 4. The polarization curves of mild steel in 1M HCl with or without inhibitors at different temperatures: (a) Blank, (b) 2-CBI, (c) 2-CBI+ Potassium Iodide

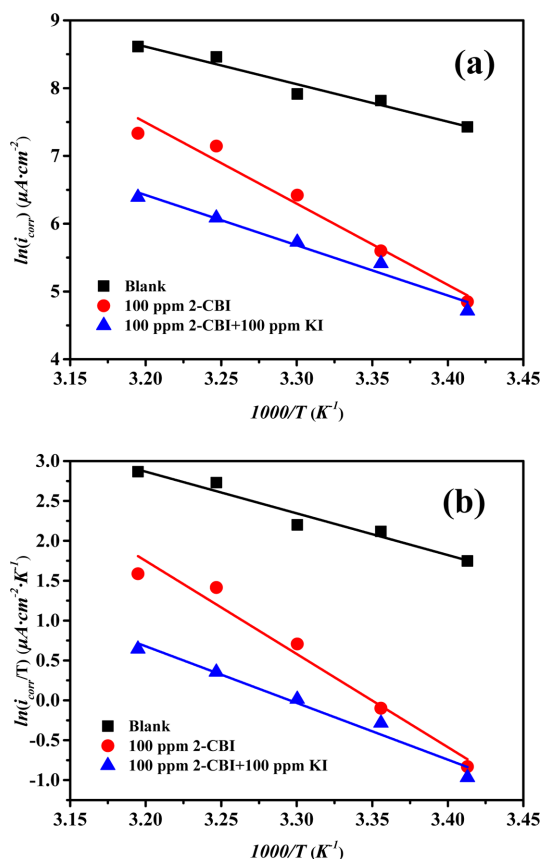adsorption [53,54]. Those results can also confirm the fact that, potassium iodide can promote the

Fig. 5. Arrhenius plots (a) and transition state plots (b) for mild steel in 1M HCl solution without and with different inhibitors

Table 6. Activation parameters for mild steel in 1 M HCl solution without and with different inhibitors.

Inhibitor	E_a (kJ/mol)	ΔH_a (kJ/mol)	ΔS_a (J·K^{-1}·mol^{-1})
Blank	45.991	43.474	-34.901
2-CBI	99.615	97.107	127.272
2-CBI/Potassium Iodide	61.632	59.114	-3.203

chemisorption of 2-CBI on the mild steel surface in 1 M HCl.

In Fig. 5 and Table 6, there is a good linear relationship between $\ln i_{corr}$ and 1000/T as well as $\ln (i_{corr}/T)$ and 1000/T. It can be observed from Table 6 that the E_a has the same trend with ΔH_a, which can be explained by the equation, $\Delta H_a = E_a - RT$. In addition, the apparent entropy change (ΔS_a) with 2-CBI as

inhibitor is greater than that of the control. And this phenomenon can be ascribed to the the competitive adsorption of water molecules and corrosion inhibitors. However, the addition of potassium iodide reduces the value of ΔS_a sharply, which probably means that potassium iodide promoted the chemisorption of 2-CBI on the surface of mild steel and thus form a more stable2-CBI film to ptotect the mild steel [55].

4. Conclusions

The synergistic effect of 2-CBI and potassium iodide for mild steel in 1 M hydrochloric acid solution was proved to be effective by electrochemical test. Although potassium iodide have no inhibition effect for mild steel in 1 M HCl, but it can enhance the IE of 2-CBI and the synergistic parameter of 2-CBI/KI mixture (100 ppm 2-CBI with different amount of potassium iodide) is always greater than 1.

Langmuir adsorption isotherm is working in this experiment, the ΔG_{ads}^0 of 2-CBI and 2-CBI/KI mixture are -34.41 kJ·mol^{-1} and -39.39 kJ·mol^{-1}, respectively. Without any inhibitor, the value of E_a is 45.991 kJ·mol^{-1}, while with 2-CBI or 2-CBI/KI mixture as inhibitor, the value of E_a is 99.615 kJ·mol^{-1} and 61.632 kJ·mol^{-1} respectively.

Based on the adsorption isotherm results and the effect of temperature, it is easy to say, after adding potassium iodide, the interaction between inhibitor and the surface of mild steel changes from physical adsorption to chemisorption. With potassium iodide in the solution, the first adsorbed I$^-$ makes 2-CBI easier to adsorb onto the mild steel surface, and forming a denser molecular layer to protect the mild steel.

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