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Corrosion inhibition and structure-efficiency relationship study of CTAC and CDHAC

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ABSTRACT

The effect of two cationic surfactants, cetyl-trimethyl ammonium chloride (CTAC) and cetyl-dimethyl-hydroxyethyl ammonium chloride (CDHAC), on the corrosion of mild steel in HCl solution was investigated by using weight loss measurements. The corrosion inhibition efficiency of CDHAC was higher than that of CTAC in any case. And the activation energies of CTAC and CDHAC involved in the corrosion inhibition were calculated and discussed by the relationship of corrosion rate (W_{corr}) and temperature (T) from Arrhenius equation. Most importantly, it was found that the structure-efficiency of these two compounds was associated with these adsorption isotherm and thermodynamics.

Keywords: Cationic surfactant; Quaternary ammonium salt; Corrosion inhibitor; Adsorption; Thermodynamic; Structure efficiency

1. Introduction

Corrosion of stainless steel is a serious problem in liquid supply pipes and storage tanks, ships, bridges and many other constructions. Corrosion of stainless steel has been investigated by many researchers [1–4]. Among the corrosion cases, the acidic corrosion damage is more serious, and corrosion inhibitors are particularly important for metals in such corrosive solutions. Organic compounds as corrosion inhibitors have been evaluated as great significant under various aggressive conditions. Many organic compounds containing hereoatom, for example P, S, N or O e.g., have been widely used as corrosion inhibitors [5]. And cationic organic inhibitors (such as quaternary ammonium salt) and the chloride ions of solution show the synergistic effect of corrosion inhibition [6]. The available data has been provided that most organic inhibitors are physiosorption on the metal surface, while in the presence of non-bonded and *p*-electrons, the inhibitor molecules could undergo chemisorption [7].

At present, there are various types of acid corrosion inhibitors. However, those corrosion inhibitors are short of a systematic structure-efficiency relationship study. Thus, this paper evaluated the corrosion inhibition effect of two cationic surfactants, cetyl-trimethyl ammonium chloride (CTAC) and cetyl-dimethyl-hydroxyethyl ammonium chloride (CDHAC) (Fig. 1), and discussed the effect of structure on the performance by thermodynamics methods.

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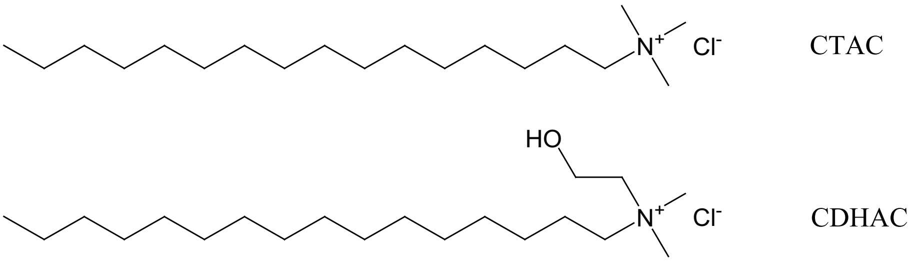

Fig. 1. Structures of CTAC and CDHAC.

2. Experimental

CTAC and CDHAC were purchased from Tianjin Kermel Chemical Reagent Co., Ltd (at AR reagent grade) and were used without further purification. The tested material is A_3 steel plates with the chemical composition of (wtpct) containing 0.02 C, 0.0017 Si, 0.237 Mn, 0.015 P, 0.0016 S, 0.008 Cu, 0.014 Cr, 0.013 Ni, 0.001 Mo, 0.01 Al and Fe balance. The corrosion performance had been carried out on the steel samples using gravimetric method. Firstly, the surface of steel discs was scrubbed with different grades of silicon carbide sandpaper (grade 360-600-1200) to make them bright, and its length, width, and height and small hole diameter were measured by a micrometer. Secondly, the plates were rinsed with a large amount of water, transferred to petroleum ether and immersed with absolute ethyl alcohol to degrease. Finally, they were dried by air blower for later use [8].

Every two steel plates were suspended in 5.0% HCl solution (120 mL), the concentrations of CTAC and CDHAC were from 5 to 70 mg/L, the time of reaction was controlled at 2 h, and the corrosion temperature was ranged from 303 to 343 K at thermostat water bath [9].

In the weight loss method, the mass loss is determined after removing corrosion products from the metal surface, and the corrosion rate is calculated by the following relation (1):

$$W_{corr} = \frac{\Delta m}{St} \tag{1}$$

where Δm represents the weight loss, S represents the exposed area of sample, t is the time of reaction.

The values of inhibition efficiency (E_w%) and the corrosion rate (W_{corr}) are calculated by the following relationship (2):

$$E_w\% = \frac{W_{corr} - W'_{corr}}{W_{corr}} \times 100 \tag{2}$$

where W_{corr} and W_{corr}' are the corrosion rates of the A_3 steel discs in absence and presence of the inhibitors, respectively.

3. Results and discussion

3.1. Effect of concentration

The values of inhibition efficiency (E_w%) and corrosion rate (W_{corr}) at 303 K were calculated by Eq. (1) and are summarized in Table 1. We could see that both CTAC and CDHAC had an inhibitory effect on the plates at 303 K. And as the concentration of inhibitors (CTAC and CDHAC) increased, the values of E_w were also increasing. This indicated that the number of inhibitors adsorbed over the surface of plates increased with the concentration increased. And CDHAC as a inhibitor was more effective for the plates in 5.0% HCl solutions at the same temperature and concentration.

Table 1
Corrosion rate and inhibitor efficiencies for various concentrations of CTAC and CDHAC in 5.0% HCl at 303 K

Inhibitor	Concentrations (mg·L^{-1})	W_{corr} (g·m^{-2}·h^{-1})	E_w (%)
Blank	0	2.9	/
CTAC	5	1.1	57.9
	10	0.8	67.8
	20	0.8	68.8
	50	0.8	69.6
	70	0.8	71.0
CDHAC	5	1.2	52.2
	10	0.8	67.9
	20	0.6	75.2
	50	0.6	78.4
	70	0.5	81.8

3.2. Effect of the temperature

The effect of temperature on the inhibition efficiency of CTAC and CDHAC (20 mg·L^{-1}) was studied, and the temperature was arranged at 303–343 K. The corresponding data are listed in Table 2. As the temperature rose, the values of W_{corr} increased, but the values of E_w increased first and then decreased. And the value of E_w for the additives (CTAC and CDHAC) was the highest at 323 K, reached 88.7% for CTAC and 89.9 % for CDHAC, respectively. The ln W_{corr} vs. $1/T$ can be represented as a straight-line function in Fig. 2. All of the linear regression coefficients (R^2) were almost equal to 1, which manifested that the adsorption process of the additives of CTAC and CDHAC on the steel samples in acid solution complied with the Arrhenius adsorption [11].

The apparent activation energy (E_a) during dissolution of the steel sheets could be evaluated from the Arrhenius equation [10] (3):

Table 2
Effect of the temperature on the steel in 5.0% HCl at different temperature in the present of 20 mg·L^{-1} CTAC and CDHAC

Inhibitor	T (K)	W_{corr} (g·m^{-2}·h^{-1})	E_w(%)
Blank	303	2.6	/
	323	17.1	/
	343	57.6	/
CTAC	303	0.8	68.8
	323	1.9	88.7
	343	7.6	86.9
CDHAC	303	0.6	75.2
	323	1.7	89.9
	343	6.7	88.4

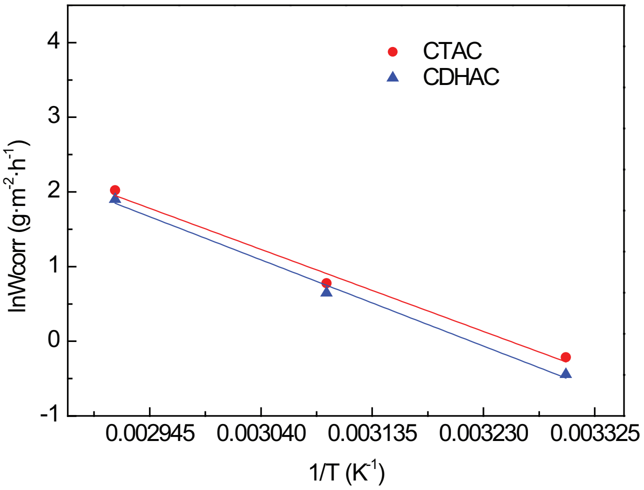

Fig. 2. Arrhenius plots of the steel in 5.0% HCl with 20 mg/L. CTAC and CDHAC at different temperature.

$$W_{corr} = K\exp\left(-\frac{E_a}{RT}\right) \tag{3}$$

where K is the rate constant of the metal dissolution reaction, E_a is the apparent activation energies for the corrosion, T is the absolute temperature in Kelvin, R is the universal gas constant. The logarithm of corrosion rate of the steel plates could be represented as straight-lines function of 1/T (Arrhenius equation) in Fig. 2.

The activation energy could be determined from the Arrhenius plots of the steel samples as shown in Fig. 2. The activation energy (E_a) of the additives could be calculated from Eq. (3), E_a = 48.1 kJ·mol^{-1} for CTAC and E_a = 50.5 kJ·mol^{-1} for CDHAC, respectively. The increase of apparent activation energy could be interpreted as physical adsorption that occurs in the first stage. The increase of activation energy could be expressed as a significant reduction in the amount of adsorption of the inhibitor on the surface of the steel samples. Because the adsorption and desorption process of inhibitor were an opposite equilibrium state, the desorption of inhibitor molecule decreased as the adsorption decreased. The apparent activation energy of CDHAC was larger than that of CTAC, indicating that the desorption of CDHAC on the surface of the steel samples was more difficult than that of CTAC. Therefore, under the same conditions, the corrosion rate in CDHAC solution is lower than that of CTAC. As the desorption of the inhibitor molecules increases at higher temperatures, the rate of corrosion increases with increasing temperature [12].

3.3. Adsorption isotherm

In order to confirm the adsorption of CTAC and CDHAC on the steel surface, adsorption isotherms were studied. The efficiency of the molecule as a sustainable corrosion inhibitor was primarily determined to adsorb on the steel plates by their capacity. And their adsorption capacity is mainly associated with their lone pair of electrons of heteroatoms (e.g. atoms of N, O, S, etc.), π-electrons [13–15]. The presence of isolated electrons of O-atoms in the corrosion inhibitor is beneficial to the greater adsorption of the corrosion inhibitor on the steel plate [16]. The process of corrosion inhibition was the organic molecule at the corroding interface instead of water molecules, which effectively prevented the corrosion of hydrogen ions on the steel plate.

It is necessary to obtain the value of the surface coverage (θ) as a function of the inhibitor concentration in order to achieve the isotherm. The interaction between the organic molecules and the metal surface was obtained from various isotherms. The surface coverage (θ) of the additives at different concentrations in 5% HCl solution is determined by the following equation:

$$\theta = \frac{W_{corr} - W'_{corr}}{W_{corr}} \tag{4}$$

According to the Langmuir adsorption isotherm, the surface coverage (θ) is related to inhibitor concentration (c) by the following equation:

$$\frac{c}{\theta} = \frac{1}{K_{ads}} + c \tag{5}$$

where K_{ads} is the equilibrium adsorption constant of the adsorption process.

As can be seen from Fig. 3, the plots of c/θ vs. c yield straight lines. Furthermore, all of the linear regression coefficients (R^2) are close to 1. Therefore, the adsorption processes of CTAC and CDHAC on the steel surface in 5% HCl conform to the Langmuir adsorption isotherm model [17].

3.4. Thermodynamics study

In order to study and calculate thermodynamics, such as the Gibbs free energy of adsorption (ΔG_{ads}), the standard entropy of adsorption (ΔS) and the heat of adsorption (ΔH), the values of adsorption equilibrium constant (K_{ads}) were first calculated through the weight loss measurements in 5.0% HCl solution at different temperature and optimum concentrations. The values of K_{ads} of the inhibitors on the steel immersed in HCl at different temperature were calculated by Eq. (5) and are summarized in Table 3. The relatively high values of K_{ads} for CTAC and CDHAC proved that

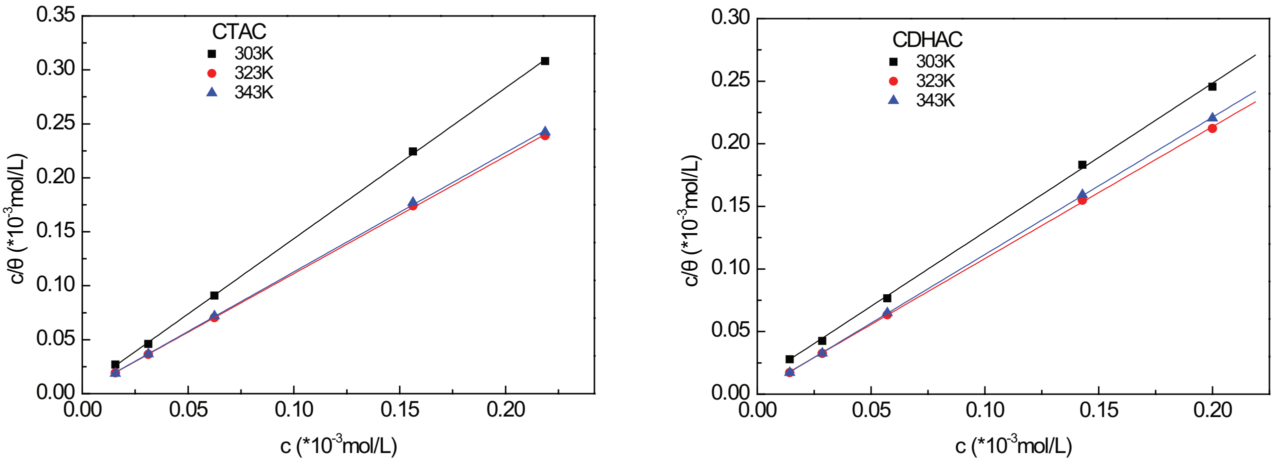

Fig. 3. Langmuir's adsorption plots for steel in 5% HCl containing different concentrations of CTAC and CDHAC at different temperature.

Table 3
Adsorption equilibrium constant (K_{ads}) of CTAC and CDHAC on the steel surface immersed in 5.0% HCl at different temperature

Inhibitor	T(K)	R-Square	Slope	K_{ads}(L·mol^{-1})
CTAC	303	0.9998	1.40	248139.0
	323	0.9998	1.09	336700.4
	343	0.9997	1.10	411522.6
CDHAC	303	0.9992	1.19	92850.5
	323	0.9998	1.05	202020.2
	343	0.9999	1.10	512820.5

Table 4
Activation parameters ΔG, ΔH and ΔS of CTAC and CDHAC during the Absorption on steel in 5.0% HCl at different concentrations

Inhibitor	T (K)	ΔG (kJ·mol^{-1})	ΔH (kJ·mol^{-1})	DS (J·mol^{-1}·K^{-1})
CTAC	303	–41.41	10.96	172.8
	323	–44.96	10.96	173.1
	343	–48.32	10.96	172.8
CDHAC	303	–38.93	37.00	250.6
	323	–43.59	37.00	249.5
	343	–48.95	37.00	250.6

there was stronger adsorption capacity of the molecules on the steel surface in HCl solution. In Table 3, the values of K_{ads} for each inhibitor increased as the temperature increased, which manifested that the additives capacity of adsorption increased with the temperature increased, and K_{ads} is a function of temperature.

The value of K_{ads} is related to the Gibbs free energy of adsorption (ΔG_{ads}) by the following equations:

$$\Delta G_{ads} = -RT\ln(55.5K_{ads}) \tag{6}$$

where K_{ads} is K, R is the universal gas constant and T is the absolute temperature and the value "55.5" is the molar concentration of water solution in mol·L^{-1} [18].

The values of K_{ads} are listed in Table 3. The Gibbs free energy of adsorption values could be calculated from the K_{ads} value and Eq. (6), which are summarized in Table 4. The results showed that all of the ΔG_{ads} values were negative and their absolute values were close to 40 kJ·mol^{-1}, which confirmed that the adsorption reactions of the additives were spontaneous reaction. It has generally been accepted that if the ΔG_{ads} values reach –20 kJ·mol^{-1}, the type of adsorption is physical adsorption (because of the electrostatic interaction between the charged molecules and the charged metal surface), while if the ΔG_{ads} values are in about –40 kJ·mol^{-1}, the type of adsorption is deemed to be chemically absorption (because of charge sharing or charge transferring from the inhibitor to the metal surface to form a covalent bond) [19–21]. Therefore, the calculated adsorption type of the inhibitors was closer to chemical adsorption. And the absolute value of Gibbs free energy increases with increasing temperature.

Among other things, the heat of adsorption (ΔH) is calculated by the Van't Hoff equation:

$$\ln K = -\frac{\Delta H}{RT} + constant \tag{7}$$

The plots of ln K vs. $1/T$ (K^{-1}) yielded a straight line in Fig. 4. The slope of these straight lines was equal to $-\Delta H/R$. The ΔH values of the inhibitors are listed in Table 4. An endothermic adsorption process ($\Delta H > 0$) belongs definitely to chemisorption, while an exothermic adsorption process ($\Delta H < 0$) can relate to physisorption, chemisorption or a mixed adsorption of both [22]. In Table 4, the values of ΔH for CTAC and CDHAC are 11.0 and 37.0 kJ·mol^{-1}, respectively. So the adsorption of the inhibitors was endothermic chemisorption. With a higher ΔH, CDHAC could absorb on the steel surface more tightly than that of CTAC, which leaded to the higher corrosion inhibition.

The standard entropy of adsorption (ΔS), the last one of thermodynamic parameters, is obtained by following the thermodynamic basic equation:

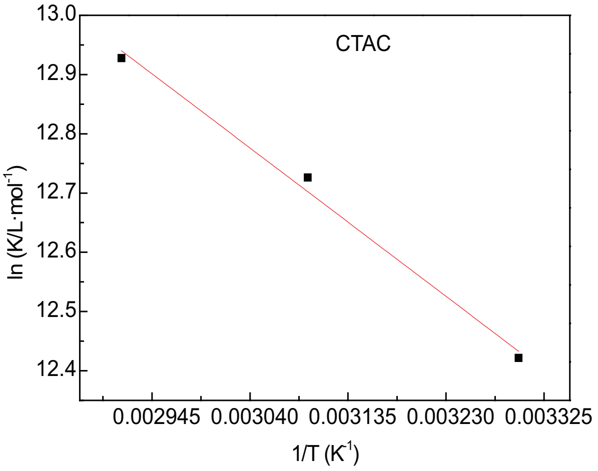

Fig. 4. Plots of 1/T versus ln*K* for adsorption of CTAC and CDHAC on the steel.

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{8}$$

Table 4 shows that all of ΔS were positive, which interpreted that more water molecules desorbing from the metal surface led to an increase in the disorder of the system disorder [23].

3.5. Inhibition mechanism

The mechanism of corrosion inhibitor in acidic solution has been extensively studied. It is generally accepted that the phase-forming theory suggests that the metal surface generates an insoluble complex, which is the product of the ionic interaction between the metal corrosion inhibitor and the corrosive medium, covering the surface of the metal to play a protective role. Since the chloride ions have a small degree of hydration, they should be adsorbed on the metal surface firstly according to the following reaction:

$$Fe + Cl^- \rightleftharpoons (FeCl^-)_{ads}$$

The large negative charge generated by the adsorption of a large amount of chloride ions causes the steel sheet to be negatively charged [24]. Based on negatively charged steel surface, the positively charged molecules (A^+) are adsorbed on the surface of the steel plate by electrostatic action to form a protective film $(FeCl^- A^+)_{ads}$ that separates the medium from the metal surface and acts as a protective metal [25]. The adsorption model is shown in Fig. 5.

In addition to the electrostatic interaction, the interaction between hydroxyl of CDHAC and free electron pairs with the metal surface enhanced the adsorption of CDHAC on steel plate, and further enhanced the corrosion inhibition effect of CDHAC.

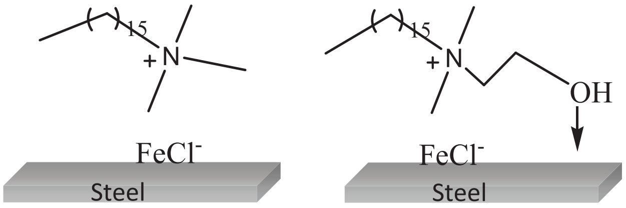

Fig. 5. Adsorption of CTAC and CDHAC on the steel surface.

4. Conclusions

In this work, the effects of CTAC and CDHAC as corrosion inhibitors on low carbon steel were studied and discussed in 5.0% HCl solution from the aspects of thermodynamics and dynamics. The weight loss measurements showed that the corrosion inhibition efficiency of CDHAC was higher than that of CTAC in any case.

Through the thermodynamic study of the two corrosion inhibitors, it was found that the better corrosion inhibition effect of CDHAC than CTAC was consistent with the results of structure-efficiency studies.

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