Study on Scale and Corrosion Inhibition Performance of Ethane-1,2-diaminium O,O′-dicyclohexyldithiophosphate

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Ethane-1,2-diaminium O,O′-dicyclohexyldithiophosphate (Et-DDD) as novel corrosion and scale inhibitor was successfully synthesized by cyclohexanol ($C_6H_{11}OH$) reaction with phosphorus pentasulfide (P_2S_5) and ethylenediamine ($H_2NCH_2CH_2NH_2$) in toluene ($PhCH_3$), while the corrosion and scale inhibition performance of Et-DDD were studied and evaluated in detailed. Study results show that Et-DDD is a mixed-type inhibitor for Q235 steel (S235) in H_2SO_4 and HCl solution. It can be found that the scale inhibition and corrosion inhibition efficiency increased with Et-DDD concentration increasing. Meanwhile, the scale and corrosion inhibitor also can be act as a surfactant, the surface tension of Et-DDD at critical micelle concentration of 14.15 mmol L^{-1} is 33.47 mN m^{-1}.

1. INTRODUCTION

As we all know, materials corrosion is an important disadvantages in the development and progress of human society. Whenever and wherever materials are used, especially metal materials, corrosion problems are inevitable. This will not only cause economic losses, but also bring safety hazards and pollution problem [1-5]. Up to now, a variety of anti-corrosion technologies have been gradually developed, such as cathodic protection, coating anti-corrosion and so on, according to the metal pickling corrosion, using corrosion inhibitor to slow down the corrosion is a general and effective method for corrosion protection [6-9].

At present, a number of compounds have been reported as corrosion inhibitor [10], such as benzoin, benzoin-(4-phenylthiosemicarbazone), sodium N-1-n-tetradecyl-phthalamate, sodium N-1-n-hexyl-phthalamate, benzyl-(4-phenylthiosemicarbazone), benzimidazole, 1,3-benzothiazole, 1,2-dibenzylbenzimidazole, 3-phenyl-4-amino-5-mercapto-1,2,4-triazole, 3-(heptadeca-8-ene)-4- aryl-5-mercapto-1,2,4-triazole, 2-mercaptobenzimidazole, 2-aminobenzimidazole, 4-amino-5- mercapto-1,2,4-triazole, 2-mercaptobenzimidazole, 3-phenyl-4-amino-5-mercapto-1,2,4-triazole, 2-methyl-benzimidazole, 2-mercaptobenzimidazole, 3,5-dimethylpiperidine, 3-(4-amino-2- methyl-5-pyrimidyl methyl)-4-methylthiazolium chloride, cis-2,6-dimethylpiperidine, 2-(2-pyridyl) benzimidazole, 2-aminomethylbenzimidazole, bis(benzimidazol-2-ylethyl)sulphide, 2-aminomethylbenzimidazole, 3,5-bis(2-thienyl)-1,3,4-thiadiazole, 2-(undecyldimethyl-ammonio) butanol bromide, 3-undecane-4-aryl-5-mercapto-1,2,4-triazole, 2-undecane-5-mercapto-1-oxa-3,4-diazole, 2,4-dibenzyledene aminophenyl-ene, 1-(2-oleylamidoethyl)-2-oleylimidazoline and 1-cinnamylidine-3-thiocarbohydrazide and so on. However, different corrosion inhibitors have different advantages and disadvantages.

To develop novel effective corrosion inhibitor, Et-DDD named ethane-1,2-diaminium O,O′-dicyclohexyldithiophosphate was synthesized. After the synthesis, the corrosion inhibition, surface activity and scale inhibition of Et-DDD were investigated in this paper.

2. EXPERIMENTAL

2.1 Materials

All chemicals in this investigation including phosphorus pentasulfide (P_2S_5), ethylenediamine ($H_2NCH_2CH_2NH_2$), cyclohexanol ($C_6H_{11}OH$), toluene ($PhCH_3$), concentrated sulfuric acid (H_2SO_4, 98%) and concentrated hydrochloric acid (HCl, 36%) without further purification. The test samples and working electrode used to study the corrosion inhibition performance of Et-DDD were prepared by Q235 steel (S235).
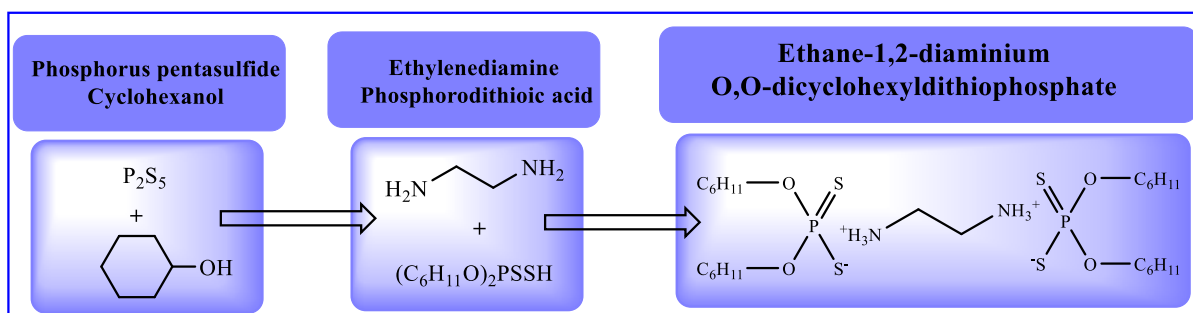
2.2 Synthesis of Et-DDD

Figure 1. Schematic diagram for synthetic reaction of Et-DDD.

The corrosion inhibitor of ethane-1,2- diaminium O,O′- dicyclohexyldithiophosphate (Et-DDD, $[(C_6H_{11}O)_2PS_2^-]_2[H_3N(CH_2)_2NH_3^{2+}]$) is synthesized by cyclohexanol ($C_6H_{11}OH$) reaction with

phosphorus pentasulfide (P_2S_5) and ethylenediamine ($H_2NCH_2CH_2NH_2$) in toluene ($PhCH_3$) solution according to our previous works [3, 4, 11-12], and presented in Figure 1.

2.3 Potentiodynamic polarization measurement

The potential sweep rate for this method was set as 0.5 mV s^{-1}. According to this method, the IE_{C-P} (corrosion inhibition efficiency, %) can be obtained by equation (1) [3, 11, 13-15]. In this equation, i_0 and i_i are the corrosion current densities of electrode in blank corrosion solution (different concentrations HCl/H_2SO_4) and different concentrations HCl/H_2SO_4 with various concentrations of Et-DDD.

$$IE_{C-P} (\%) = \frac{i_0 - i_i}{i_0} \times 100 \qquad (1)$$

2.4 Weight loss measurement

Based on this measurement, the corrosion rate (v_0, v_i) for S235 samples in 1.0 M H_2SO_4 / 1.0 M HCl (blank solution, v_0) and 1.0 M H_2SO_4 / 1.0 M HCl with various concentrations of Et-DDD (v_i) can be obtained and used to calculate the IE_{C-W} (corrosion inhibition efficiency, %) by equation (2) and (3) [4, 12, 16-17].

$$v_i = \frac{m_0 - m_i}{St} \qquad (2)$$

$$IE_{C-W} (\%) = \frac{v_0 - v_i}{v_0} \times 100 \qquad (3)$$

2.5 Surface active and scale inhibition performance measurement

The measure details for surface active and scale inhibition performance measurement of Et-DDD have been reported in our previous work [????].[18]. the IE_S (scale inhibition efficiency, %) can be obtained using equation (4).

$$IE_S (\%) = \frac{V_2 - V_1}{V_0 - V_1} \times 100 \qquad (4)$$

Where, V_0, V_1 and V_2 are the volume of EDTA (V_0) without Et-DDD at the beginning, (V_1) without Et-DDD after incubation and (V_2) with Et-DDD after incubation.

3. RESULTS AND DISCUSSION

3.1 Potentiodynamic polarization measurement

3.1.1 Effect of Et-DDD concentration on IE_{C-P}

The potentiodynamic polarization curves of S235 in 1.0 M HCl and 1.0 M H_2SO_4 with Et-DDD concentrations from 0 mg L^{-1} to 100 mg L^{-1} at 30 °C was presented in Figure 2 (a) and (b). Based on these curves, the corrosion potential (E vs SCE, V), current density (i), anodic and cathodic Tafel

slopes (β_a, β_c) can be obtained, while the corrosion inhibition efficiency (IE_{C-P}, %) can be calculated by equation (1) and listed in Table 1.

According to Figure 2 (a), (b) and Table 1, it can be found that the i_0 of S235 in 1.0 M HCl and 1.0 M H$_2$SO$_4$ at 30 °C are 1835.5 µA cm^{-2} and 2893.8µA cm^{-2}, respectively. However, when the corrosion inhibitor of Et-DDD had been added in 1.0 M H$_2$SO$_4$ and 1.0 M HCl (blank corrosion solution), that the i_i sharply decreased. With the concentration of Et-DDD increases from 20 mg L^{-1} to 100 mg L^{-1}, the i_i decreases from 500.3 µA cm^{-2} to 36.8 µA cm^{-2} (1.0 M H$_2$SO$_4$) and 500.1 µA cm^{-2} to 19.0 µA cm^{-2} (1.0 M HCl).
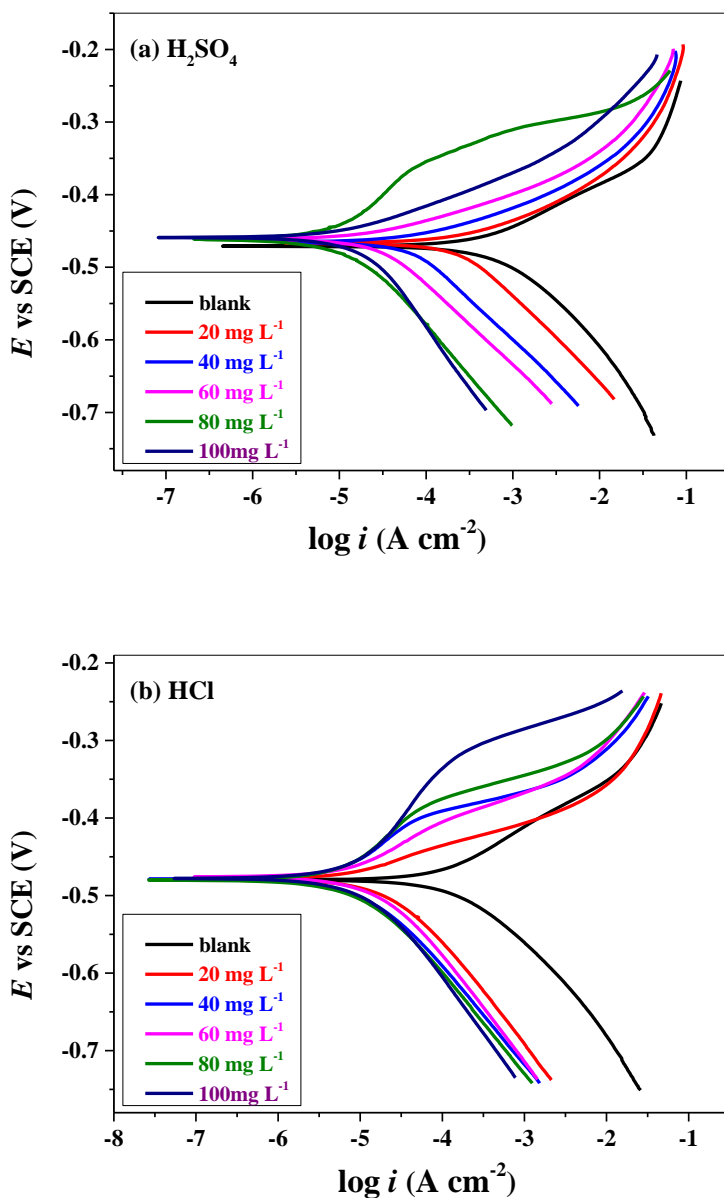

Figure 2. Potentiodynamic polarization curves for S235 in 1.0 M H$_2$SO$_4$ (a) and 1.0 M HCl (b) with Et-DDD concentration from 0 mg L^{-1} to 100 mg L^{-1} at 30 °C.

Table 1. Polarization parameters of S235 in 1.0 M HCl and 1.0 M H_2SO_4 with various concentrations of Et-DDD at 30 °C.

solution	c (mg L^{-1})	E (mV)	i_i (μA cm^{-2})	β_a (mV dec^{-1})	β_c (mV dec^{-1})	IE_{C-P} (%)
H_2SO_4	0	471	2893.8	140	138	/
	20	465	500.3	81	112	82.7
	40	467	270.1	88	113	90.7
	60	462	153.1	104	115	94.7
	80	461	54.3	121	130	98.1
	100	459	36.8	134	136	98.7
HCl	0	480	1835.5	146	128	/
	20	479	500.1	132	100	72.8
	40	479	221.8	116	111	87.9
	60	476	93.9	93	113	94.9
	80	480	65.7	86	117	96.4
	100	478	19.0	77	121	99.0

The decrease of i_i is determined by the decrease of the corrosion rate of S235 electrode in 1.0 M H_2SO_4 and 1.0 M HCl with different concentration of Et-DDD. This indicates that Et-DDD can effectively inhibit the corrosion behavior of S235 in1.0 M H_2SO_4 and 1.0 M HCl, while the IE_{C-P} for S235 corrosion in 1.0 M H_2SO_4 and 1.0 M HCl with 100 mg L^{-1} Et-DDD at 30 °C are 98.7% and 99.0%, respectively. Additionally, all corrosion potential exhibited in Table 1 shifts less than 12 mV ($\Delta E < 80$ mV), which reveals that Et-DDD is a mixed-type corrosion inhibitor [11,19-20].

3.1.2 Effects of temperature, acid concentration and immersion time on IE_{C-P}

Table 2. Effect of temperature, acid concentration and immersion time on IE_{P-C} for S235 corrosion in H_2SO_4 and HCl solution with Et-DDD at 100 mg L^{-1}.

Solution	T(°C)	IE_{C-P} (%)	C_H(M)	IE_{C-P} (%)	t(h)	IE_{C-P} (%)
H_2SO_4	20	99.4	0.2	99.6	0	98.7
	30	98.7	0.5	99.2	6	98.1
	40	93.3	1.0	98.7	12	97.9
	50	82.2	2.0	96.5	24	97.6
	60	69.1	3.0	89.3	48	97.6
HCl	20	99.0	0.2	99.3	0	99.0
	30	99.0	0.5	99.1	6	98.4
	40	90.2	1.0	99.0	12	98.1
	50	77.2	2.0	93. 1	24	98.2
	60	51.0	3.0	85.1	48	98.3

The effect of temperature, acid concentration and immersion time on IE_{C-P} (%) for S235 in H_2SO_4 and HCl solution with 100 mg L^{-1} Et-DDD were listed in Table 2. Based on this Table, it can be found that the IE_{C-P} decreases with the increase of H_2SO_4, HCl concentration and temperature.

Obviously, Et-DDD exhibited excellent corrosion inhibition at lower temperatures, the IE_{C-P} (%) for S235 in H_2SO_4 and HCl with Et-DDD at 100 mg L^{-1} are 99.4% and 99.0% (20 °C). From Table 2, it can be found that the IE_{C-P} of Et-DDD in HCl solution is lower than that in H_2SO_4 solution at the temperature is higher than 30 °C. With the temperature increase to 60 °C, the IE_{C-P} for S235 in H_2SO_4 and HCl with Et-DDD at 100 mg L^{-1} decrease to 69.1% and 51.0%, respectively.

Based on Table 2, with H_2SO_4 and HCl concentration increases from 0.2 M to 3.0 M, the IE_{C-P} of Et-DDD in H_2SO_4 solution is always higher than that of Et-DDD in HCl solution. When the H_2SO_4 and HCl concentration are higher than 1.0 M, the IE_{C-P} obviously decreases. The IE_{C-P} for S235 in 0.2 M H_2SO_4 and HCl with 100 mg L^{-1} Et-DDD at 30 °C are 99.6% and 99.3%, when the acid concentration increases to 3.0 M, the IE_{C-P} decreases to 89.3% and 85.1%, respectively.

The effect of immersion time on IE_{C-P} for S235 in 1.0 M H_2SO_4 and HCl with 100 mg L^{-1} Et-DDD at 30 °C was presented in Table 2. It can be found that the IE_{C-P} changed slightly with immersion time increasing. With the immersion time was up to 48 hours, that the IE_{C-P} for S235 in 1.0 M H_2SO_4 and HCl with 100 mg L^{-1} Et-DDD at 30 °C are 97.6% and 98.3%, respectively.
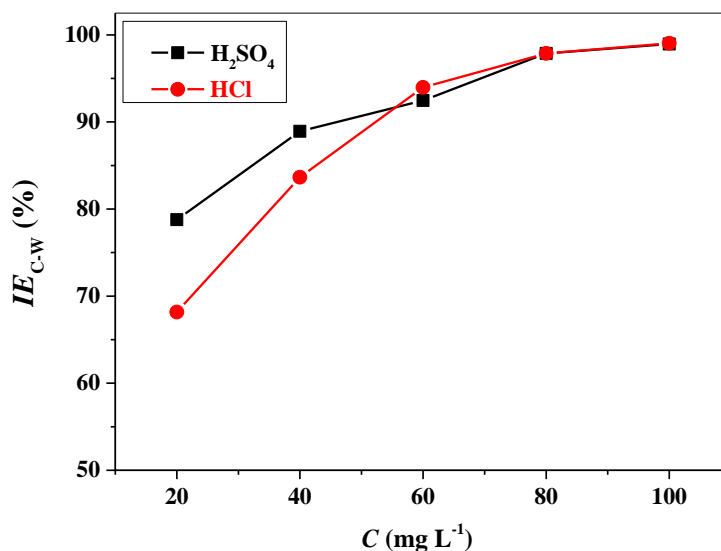
3.2 Weight loss measurement

Figure 3. The effect of Et-DDD concentration on IE_{C-W} for S235 in 1.0 M H_2SO_4 and 1.0 M HCl with Et-DDD by weight loss measurement.

The IE_{C-W} (corrosion inhibition efficiency, %) of S235 in 1.0 M H_2SO_4 and 1.0 M HCl with different concentrations of Et-DDD at 30 °C by this method was presented in Figure 3. With Et-DDD concentration lower than 40 mg L^{-1}, the IE_{C-W} for S235 in 1.0 M H_2SO_4 higher than it in 1.0 M HCl at

30 °C, when Et-DDD concentration is 20 mg L^{-1}, the $IE_{C\text{-}W}$ are 78.8% and 68.2%, respectively. When the concentration of Et-DDD increases to 100 mg L^{-1}, the $IE_{C\text{-}W}$ tends to be stable, which are both 99.0% for S235 in 1.0 M H$_2$SO$_4$ and 1.0 M HCl at 30 °C, which higher than the $IE_{C\text{-}W}$ of hydroxyethyl ammonium O,O'-diphenyldithiophosphate(97.83%)[4], S-4-methylbenzyl-O,O'-di(phenyl) dithiophosphate (92.05%)[12], S-4-methyl benzyl-O,O'-di(4-bromophenyl)dithiophosphate (73.98%)[12] and S-benzyl-O,O'-bis(2-naphthyl)dithiophosphate (97.92%)[3]. The high $IE_{C\text{-}W}$ indicates that Et-DDD can be used as the excellent corrosion inhibitor.
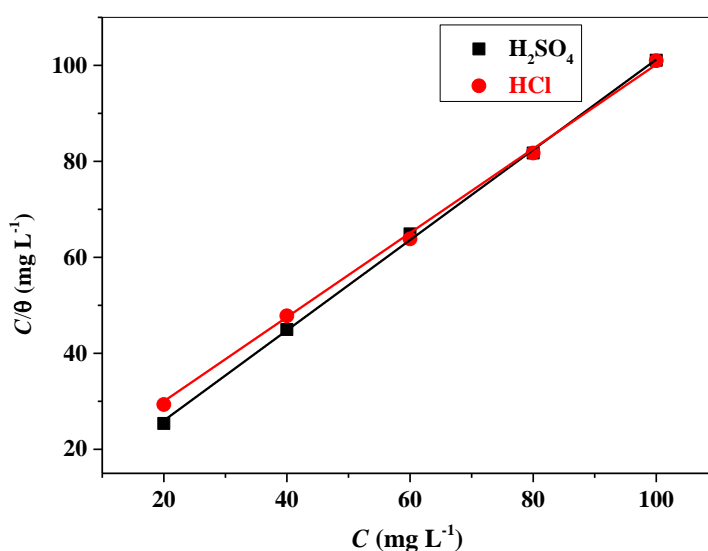
3.3 Adsorption isotherms

Figure 4. The plots of Langmuir adsorption isotherm for Et-DDD on S235 surface in 1.0 M H$_2$SO$_4$ and 1.0 M HCl at 30 °C.

Table 3. Fitting results of Langmuir adsorption isotherm for Et-DDD on S235 in 1.0 M H$_2$SO$_4$ and 1.0 M HCl at 30 °C.

Solution	Isotherms	Pearson's R^2	Equation ($y = a + b*x$)
H$_2$SO$_4$	Langmuir	0.99905	y = 0.94048 * x + 7.18135
HCl	Langmuir	0.99672	y = 0.87702 * x + 12.47521

Figure 4 shows the Langmuir adsorption isotherm for Et-DDD on S235 surface in 1.0 M H$_2$SO$_4$ and 1.0 M HCl at 30 °C, and the obtained parameters by Langmuir adsorption isotherm fitting results was presented in Table 3. Based on the fitting results show that R^2 is very close to 1 (R^2 =0.99905, 0.99672), which indicates that the adsorption of Et-DDD on S235 surface belongs to Langmuir adsorption isotherm. Meanwhile, the ΔG (adsorption free energy) for Et-DDD on S235 surface in 1.0 M HCl and 1.0 M H$_2$SO$_4$ at 30 °C can be obtained by equation (5) to (8) [3, 12, 21]. According to

fitting results presented in Table 4, The ΔG of Et-DDD on S235 surface in 1.0 M H_2SO_4 and 1.0 M HCl at 30 °C are -33.07 kJ mol^{-1} and -37.47 kJ mol^{-1}, which also shows that the adsorption processes of Et-DDD on 235 QS surface in H_2SO_4 and HCl solution both are physi- and chemisorption [3, 12, 21].

$$\theta = (v_0 - v_i)/v_0 \qquad (5)$$
$$c/\theta = 1/K_0 + c \qquad (6)$$
$$\Delta G = -8.314T\ln(55.5K_1) \qquad (7)$$
$$K_1 = 10^3 * M_r * K_0 \ (\text{mol L}^{-1}) \qquad (8)$$

Table 4. Fitting parameters of Et-DDD on S235 surface in 1.0 M H_2SO_4 and 1.0 M HCl at 30 °C.

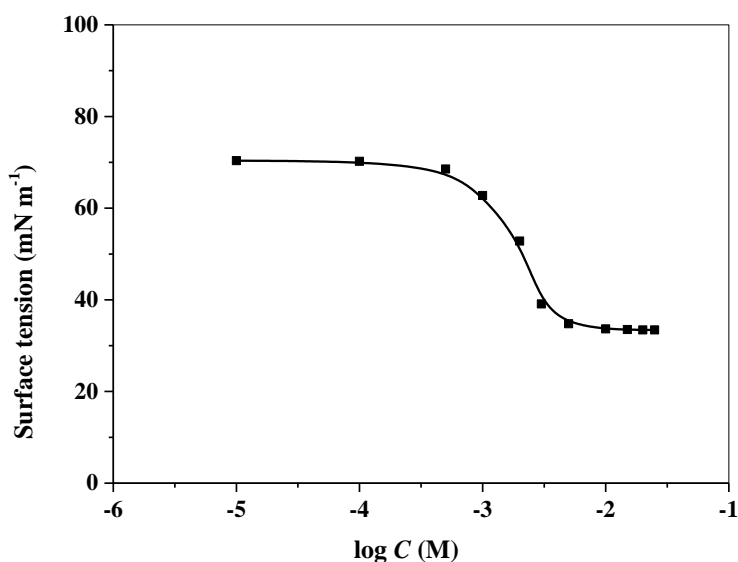| Solution	Mr	$1/k_0$ (mg L^{-1})$^{-1}$	k_1(mol L^{-1})$^{-1}$	ΔG(kJ mol^{-1})	Adsorption
H_2SO_4	649	7.18	9.04×10^4	-33.07	Physi- and chemisorption
HCl	649	12.48	5.20×10^4	-37.47	Physi- and chemisorption

3.4 Surface active properties

Figure 6. Variations in surface tension with Et-DDD concentrations in double distilled water at 30 °C.

Variations in surface tension with Et-DDD concentrations in double distilled water at 30 °C were presented in Figure 5. Meanwhile, the surface tension (γ_{cmc}) of Et-DDD was measured for a range of concentrations above and below the critical micelle concentration (*cmc*), which are 33.47 mN m^{-1} at

14.15 mmol L^{-1}. And the π_{cmc} (maximum surface pressure) of Et-DDD can be calculated by $\pi_{cmc} = \gamma_0 - \gamma_{cmc}$, where γ_0 is 70.42 mN m^{-1}, and the π_{cmc} is 36.72 mN m^{-1}, which higher than the π_{cmc} of hydroxyethyl ammonium O,O'-diphenyldithiophosphate (35.29mN m^{-1}) in double distilled water at 30 °C [4]. This result shows that Et-DDD also can use to be an excellent surfactant.

3.5 Scale inhibition properties

Figure 6 presented the effect of Et-DDD concentration on IE_s (scale inhibition efficiency, %) for against calcium sulfate (CaSO$_4$) and calcium carbonate (CaCO$_3$) scale. From Figure 6, we can found that the IE_s increased with the increasing of Et-DDD concentration. With Et-DDD concentration reaches a certain value, the IE_s gradually tends to be stable. Furthermore, with the concentration of Et-DDD increased from 60 mg L^{-1} to 100 mg L^{-1}, that the IE_s for against CaCO$_3$ scale and CaSO$_4$ scale increased from 45.33% to 49.39% and 49.55% to 58.44%, respectively. From Figure 6, by comparing the performance of Et-DDD for against CaCO$_3$ and CaSO$_4$, it can be seen that Et-DDD was more effective in inhibiting CaCO$_3$ at low concentration and CaSO$_4$ at high concentration.
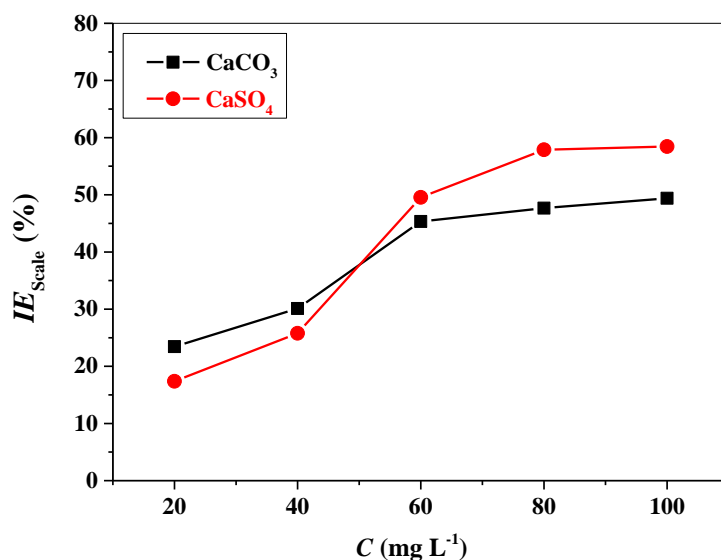

Figure 6. The effect of Et-DDD concentration on IE_s against CaCO$_3$ and CaSO$_4$.

4. CONCLUSIONS

Ethane-1,2-diaminium O,O'-dicyclohexyldithiophosphate (Et-DDD) as corrosion and scale inhibitor was successfully synthesized by cyclohexanol reaction with phosphorus pentasulfide and ethylenediamine in toluene solution. The corrosion inhibition evaluated show that Et-DDD is a mixed-type effective corrosion inhibitor for Q235 steel (S235) corrosion in H$_2$SO$_4$ and HCl solution. It can be found that the scale inhibition efficiency and corrosion inhibition efficiency increased with Et-DDD concentration increasing. Meanwhile, the scale and corrosion inhibitor also can be used as an excellent

surfactant, the surface tension of Et-DDD at critical micelle concentration of 14.15 mmol L^{-1} is 33.47 mN m^{-1}.

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