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Inhibitory activity investigation of a new nitrogen-containing surfactant in an acid medium

In this paper, the results of testing a new nonionic surfactant as a corrosion inhibitor in a 0.5M hydrochloric acid solution are given. The corrosion inhibitor was synthesized by catalytic esterification of maleic anhydride with polyoxyethylene sorbitan and further amidating of the ether with diethanolamine. The structure and composition of the developed inhibitor were characterized by the methods of FT-IR and ^{1}H NMR spectroscopy. Results showed that the reagent MA/Tween-DEA effectively inhibited the corrosion of carbon steel in hydrochloric solution with an optimal inhibition efficiency of 94 % (100 ppm) at 303 K from weight loss test. Thermodynamic parameters such as adsorption heat (ΔH_a), adsorption entropy (ΔS_a) and adsorption free energy (ΔG_{ads}) were obtained from experimental data of the temperature studies of the inhibition process at five temperatures ranging from 303 to 343 K. The thermodynamic parameters of the corrosion process were calculated in the absence and presence of inhibitor and discussed. The mechanism of action of inhibitor protection of a steel plate by a synthesized inhibitor has been studied. Adsorption of MA/Tween-DEA on the carbon surface in 0.5 M HCl follows the Langmuir isotherm model.

Keywords: nonionic surfactant, inhibitor, corrosion protection, inhibition efficiency, temperature, adsorption, thermodynamic, carbon steel.

Introduction

The problem of corrosion and protection of oil and gas equipment in Kazakhstan is becoming actual, which is primarily due to an increasing number of developing oil, gas and gas condensate fields, containing aggressive components, secondly, with increasing work intensity of oilfield equipment. The use of corrosion inhibitors in the oil and gas industry makes it possible to extend the life of equipment and pipelines transporting oil and gas. Nowadays, the oil and gas industry around the world are the largest consumers of corrosion inhibitors [1].

The authors of [2–4] note that organic and polymeric compounds containing polar functional groups, such as nitrogen, sulfur and / or oxygen in the conjugate system, are effective corrosion inhibitors for steel structures. The inhibitory capacity of these substances is associated with the presence of cyclic rings in them and heteroatoms, which are the main active centers of adsorption [5–7]. Adsorption centers help to form complexes with metal ions. The formed complexes are adsorbed on the metal surface to form a barrier film that separates the metal surface from the corrosive agents present in the aggressive solution [8–11]. The purpose of this work is to study the kinetics parameters, inhibition efficiency and mechanism of corrosion in 0.5M HCl solution of carbon steel plates by a new MA/Tween-DEA reagent by weight loss method at various temperatures (303–343 K).

Experimental

Materials

Maleic anhydride (MA), diethanolamine (DEA), polyoxyethylene sorbitan trioleate (Tween-85), pyridine, N,N-dimethylformamide obtained from Sigma Aldrich and used without further purification.

Solutions

The aggressive solutions of 0.5M HCl were prepared by dilution of analytical grade 37 % HCl with distilled water.

FT-IR, NMR analysis

The structure of the synthesized organic inhibitor was confirmed by FT-IR spectrometry on an Agilent Cary 660 spectrometer; by ^{1}H NMR spectroscopy in dimethylsulfoxide on a Bruker Avance 300 Mhz NMR spectrometer; by HPLC with H_2O / CH_3CN / 0.1 % TFA, column: Nucleodur RP C18 10 µm, buffer races: A = 5 % CH_3CN / H_2O / 0.1 HCOOH, B = 100 % CH_3CN / 0.1 HCOOH. Flow rate — 1 ml/min; Pressure — 68 bar; Electrospray — positive ionization (150–900).

Synthesis

Synthesis of a corrosion inhibitor was carried out in two stages. In the first stage, the reaction product was obtained by the catalytic esterification of maleic anhydride and polyoxyethylene sorbitan trioleate. In the second stage, amidation of the ester with diethanolamine was carried out.

A two-necked round bottom flask (50 ml) equipped with a magnetic stirrer and a reflux condenser was charged with maleic anhydride (0.5 g, 0.005 mol) and 5 ml of solvent (DMF). After the maleic anhydride is completely dissolved, Tween-85 (6.5 g, 0.005 mol) and pyridine (0.4 g, 0.005 mol) dissolved in 7.5 ml of DMF are added dropwise. The reaction mixture is heated to 115 ºC and left with stirring and reflux for 5 h. Diethanolamine (0.8 g, 0.005 mol) is added to the mixture and the reaction is continued for another 5 h. After that, the process was stopped, cooled to room temperature and the solvent was removed on a rotary evaporator. The yield of the desired product was 80–85 %.

Weight loss measurements

Chemical composition of the steel St3. is given in Table 1. Carbon steel samples (5×2.5×0.2 cm) were abraded with a series of emery papers (grade 500–800–1200) and then washed with distilled water and acetone. After weighing accurately, the specimens were immersed in a 250 mL beaker containing 250 mL 0.5M HCl solution with and without addition of different concentrations of MA/Tween-DEA. After 5 h the specimens were taken out, washed, dried, and weighed accurately. In order to get good reproducibility experiments were carried out in triplicate. The average weight loss of three parallel sheets was obtained. The tests were repeated at different temperatures.

The corrosion rate V_{cor} (mg/cm^2×h) is calculated by the formula:

$$V_{cor} = \frac{W}{S \cdot \tau},$$

where W — is the average weight loss of three parallel St3 sheets; S — is the total area of one specimen and τ — is the immersion time.

The inhibition efficiency (IE) was calculated as follows:

$$IE\% = \frac{V_0 - V_1}{V_0} \cdot 100,$$

where V_0 and V_1 — are the values of the corrosion rate without and with addition of the inhibitor, respectively.

Table 1

Chemical composition of the steel (%)

C	Si	Mn	Ni	S	P	Cr	N	Cu	As	Fe
0.14	0.15	0.4	0.3	0.05	0.04	0.3	0.0008	0.3	0.08	other

Results and discussion

A new chemical compound was prepared by the catalytic esterification of maleic anhydride with Tween-85 and further amidation of the ester acid with diethanolamine. IR and NMR spectroscopy methods were used to study the composition.

Figure 1 shows the FT-IR spectra of MA/Tween-DEA, in which the band at 3382 cm^{-1} refers to the vibrations of the OH group, bands at 2921 and 2878 cm^{-1}, respectively, to aliphatic –CH_2 asymmetric and symmetrical vibrations, a band in the region of 1724 cm^{-1} to the stretching vibrations of the C=O bond of the ester, 1640 cm^{-1} refers to the amide bond (N–C═O, amide I). The band at 1168 cm^{-1} can be attributed to the asymmetric vibration of C–O–C in the ester bond (O–C=O).

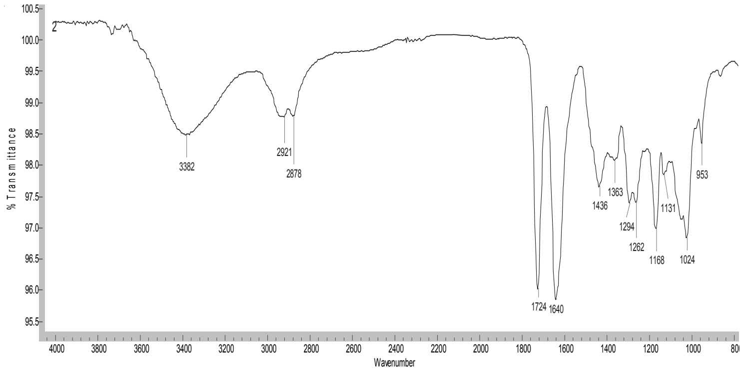


Figure 1. The FT-IR spectra of MA/Tween-DEA

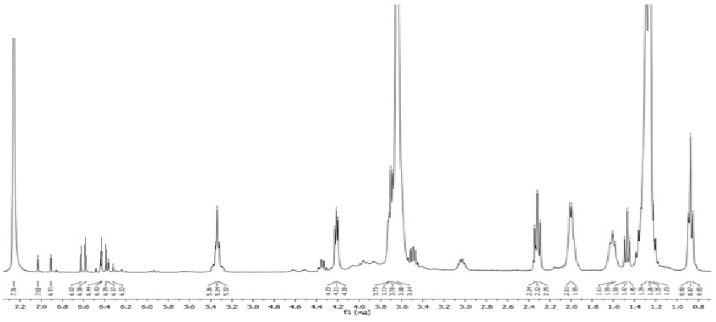
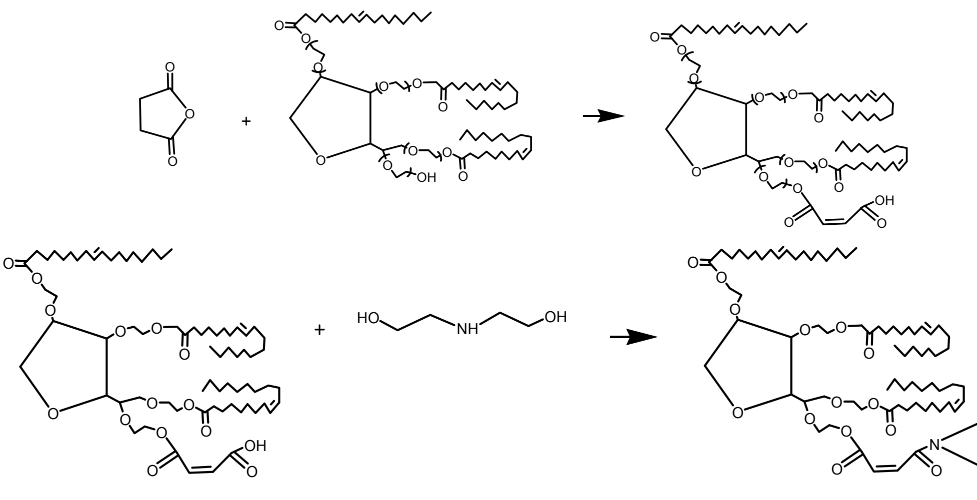


Figure 2. The ^{1}H NMR spectrum of MA/Tween-DEA

Figure 2 shows the NMR spectrum of the MA / Tween-DEA reagent. ^{1}H-NMR (300 MHz, D_2O, ppm): $\delta = 0.85–0.9$ (t, 6 H, $-2 \times CH_3$, alkyl chain), 1.1–1.4 (m, 36 H, $-2 \times (CH_2)_{14}$, alkyl chain), 1.51–1.71 (m, 4 H, $-2 \times NCH_2CH_2-$), 3.01 (s, 12 H, $-2 \times N+(CH_3)_2$), 3.61 (s, 4 H, $-2 \times CH_2O$), 4.21 (s, 4 H, $-2 \times N+CH_2$), 6.39–6.67 (m, CH = CH).

Based on the results obtained by FT-IR and NMR spectroscopy, the structure of the new compound was presented as follows:



Analyzing the structure of the synthesized compound, it is assumed that the new reagent can exhibit the properties of a corrosion inhibitor. The corrosion rate and inhibition efficiency for St3 steel in 0.5M hydrochloric solution at 30, 40, 50, 60 and 70 ºC in the absence and presence of MA/Tween-DEA are given in Table 2. The study of the temperature range on the inhibition effectiveness is important for clarifying the mechanism and kinetics of their action and, ultimately, for the correct selection of these inhibitors for specific practical purposes.

Table 2

Corrosion parameters obtained from weight loss of carbon steel in 0.5 M HCl solution containing various concentrations of MA/Tween-DEA at different temperatures

Temperature, K	Concentration, ppm	Inhibition efficiency (IE), %	Corrosion rate (V_{cor}), (mg/cm^2×h)
303	Blank		0.3870
	50	60	0.1548
	100	72	0.1084
	150	85	0.0581
	200	94	0.0232
313	Blank		0.4310
	50	58	0.1810
	100	67	0.1422
	150	79	0.0905
	200	89	0.0474
323	Blank		0.5220
	50	54	0.2401
	100	61	0.2036
	150	73	0.1409
	200	89	0.0574
333	Blank		0.6130
	50	51	0.3004
	100	58	0.2575
	150	69	0.1900
	200	79	0.1287
343	Blank		0.6750
	50	49	0.3443
	100	53	0.3173
	150	61	0.2633
	200	75	0.1688

Data analysis on temperature effect on corrosion rate show that with increasing temperature from 303 K to 343 K corrosion rate increases, which corresponds to the regularity of the temperature effect from the Arrhenius equation. Thus, at the temperature of 303 K, the corrosion rate of the uninhibited medium is 0.3870 mg/cm^2×h, and the introduction of the inhibitor, even in a minimum amount of 50 ppm decrease the corrosion rate by two times and a half and V_{cor} is 0.1548 mg/cm^2×h, 200 ppm decreases V_{cor} in 16 times to 0.0232 mg/cm^2×h. A similar pattern was found for the temperature range studied from 313 to 343 K. The effectiveness of inhibitory protection in the temperature range under study increases with increasing consumption of the inhibitor, but decreases with increasing temperature. Thus, at the temperature of 303 K, the effectiveness of inhibitor protection increases from 60 % at a reactant consumption of 50 ppm to 94 % at 200 ppm. However, with an increase in temperature to 343 K, inhibitor protection achieves lower values from 49 % at a reagent consumption of 50 ppm to 75 % at 200 ppm.

The relationship between the corrosion rate (mg/cm^2×h) of the steel plate in a neutral medium and the temperature can be described using the *Arrhenius* equation [9]:

$$V_{cor} = \lambda \exp\left(-\frac{E_a}{RT}\right),$$

where E_a — is activation energy, kJ/mol; λ — is pre-exponential factor; R — is universal gas constant, J/mol×K; T — is the absolute temperature, K.

Figure 3 shows plots of lnV_{cor} from 1/T at various concentrations of the reagent and without the introduction of an inhibitor, where extrapolation to the y-axis gives lnλ, and extrapolation to the abscissa value ($-E_a/R$).

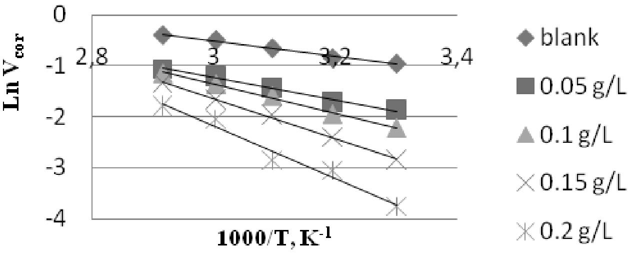


Figure 3. Arrhenius plot for St3 steel in the absence and presence of different concentrations of MA/Tween-DEA

Thermodynamic parameters such as enthalpy and entropy of corrosion process were calculated using the alternative Arrhenius equation [9].

$$W = \frac{RT}{Nh}\exp\left(\frac{\Delta S_a^0}{R}\right)\exp\left(-\frac{\Delta H_a^0}{R}\right),$$

where h — is the Planck's constant 6.6261×10^{-34} Js; N — is the Avogadro's number 6.0225×10^{23} mol^{-1}.

Figure 4 shows a plot of lnV_{cor}/T versus $1/T$ at different inhibitor's concentration, where extrapolation to the y-axis yields $\Delta S_a/R$, and extrapolation to the abscissa axis ($-\Delta H_a/R$) [12, 13].

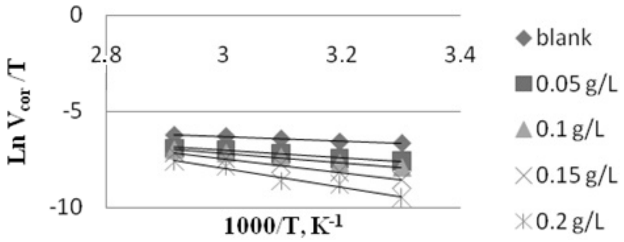


Figure 4. Transition state plot for St3 steel in 0.5M HCl solution in the absence and presence of different concentrations of MA/Tween-DEA

Using the data of the effect of temperature on the corrosion rate, the activation energy was calculated in the presence and absence of an inhibitor. From the obtained values of the activation energy, we can assume the mechanism of action of corrosion inhibition. Calculated values of the activation energy and enthalpy from Figures 3 and 4 are shown in Table 3. As can be seen from Table 3, for the corrosion process at a reactant concentration of 50 ppm E_a is 12.66 kJ / mol and it increases with an increase in the amount of added inhibitor to 42.97 kJ / mol. An increase in the enthalpy with an increase in the amount of inhibitor introduced is explained by the fact that the decrease in the corrosion rate of steel is mainly controlled by kinetic activation parameters [14].

Table 3

The values of the parameters E_a, ΔH_a, ΔS_a in the absence and presence of corrosion inhibitor

Concentration, g/l	E_a, kJ/mol	ΔH_a, kJ/mol^{-1}	ΔS_a (J·mol^{-1}·K^{-1})
Blank	12.66	9.98	–22.59
0.05	18.20	15.52	–11.96
0.1	23.74	21.06	3.55
0.15	32.59	29.92	27.82
0.2	42.97	40.29	54.47

Positive values of the enthalpy of ΔH_a indicate the endothermic nature of the corrosion process. The effectiveness of organic substances as corrosion inhibitors can be attributed to the adsorption of molecules of reagents with the help of polar groups on a metallic surface [15]. Based on the data of thermodynamic calculations, it was shown that, by the mechanism of action, the inhibitor is prone to physical adsorption on the metal surface. The choice of the adsorption isotherm equation depends on the convergence of the obtained data with the trend line. In this paper, we used the equation of the Langmuir adsorption isotherm:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh},$$

where K_{ads} — is adsorption constant; θ — is the fraction of steel surface covered by the adsorbed molecules.

The diagram of the dependence of C_{inh}/θ on C_{inh} is shown in Figure 5, where the value of K_{ads} was obtained by extrapolation to the axis ordinate.

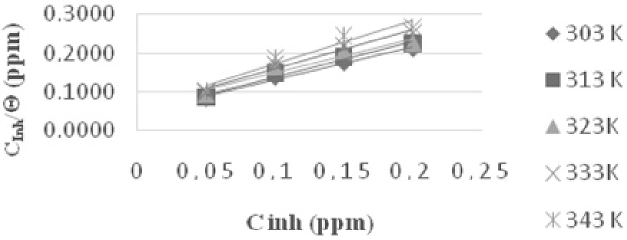


Figure 5. Langmuir adsorption isotherm plots for carbon steel
in 0.5M HCl with different concentrations of MA/Tween-DEA

Calculated values of K_{ads} are given in Table 4. Values of the K_{ads} indicate that at temperatures of 303–313 K the system practically stays in equilibrium (K_{ads}≈1.0). A further increase in temperature from 323 to 343 K leads to an increase of desorption process and decrease in the effectiveness of inhibitory protection. Standard free energy of adsorption ΔG_{ads} was calculated by equation:

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

where ΔG_{ads} — is free energy of adsorption, 55.5 — is the water concentration of the solution mL/L.

Table 4 shows the values of the equilibrium constant of adsorption-desorption K_{ads} and free Gibbs energy ΔG_{ads}.

Table 4

Values of the adsorption-desorption equilibrium constant K_{ads} and the summary Gibbs energy ΔG_{ads}

Temperature, K	$K_{ads}\times10^3$, mol^{-1}	ΔG_{ads}, kJ/ mol
303	1.1022	–10.4
313	1.0207	–10.5
323	0.9123	–10.7
333	0.8758	–10.9
343	0.8518	–11.3

Negative values of ΔG_{ads} prove [16] the stability of the adsorbed film on the surface of the steel plate. A decrease in ΔG_{ads} (more negative values) with increasing temperature indicates the presence of an endothermic process, which also confirms the mechanism of physical adsorption of the reagent.

Conclusions

MA/Tween-DEA is a good inhibitor for carbon steel in 0.5M HCl solution. The adsorption of reagent on St.3 steel follows the Langmuir adsorption isotherm. Inhibition efficiency increases with increasing inhibition concentration but decreases with increase of temperature. Gibb's free energy, enthalpy and entropy of adsorption indicate that adsorption process is endothermic and inhibitor adsorbed on surface of carbon steel samples through physical adsorption.

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Қышқыл ортада жаңа құрамында азоты бар беттік-белсенді заттардың коррозия ингибиторларының қорғауға температураның әсері

Мақалада жаңа бейорганикалық беттік-белсенді заттың тұз қышқылының 0,5М ерітіндісіндегі коррозия ингибиторы ретінде қолдану нәтижелері келтірілген. Коррозия ингибиторы малеинді ангидриді мен полиоксиэтиленсорбитанның каталитикалық этерификациясы және одан әрі диэтаноламин эфирімен амидтеу арқылы синтезделді. Ингибиторлардың құрылымы мен құрамы ИҚ және ^{1}H ЯМР-спектроскопия әдістерімен сипатталды. Нәтижелер MA/Tween-DEA реагенті гидрохлорлы ерітіндідегі көміртекті болаттың коррозиясын 303 K температурада салмақ жоғалту сынағынан 94 % (100 ppm) оңтайлы тежеу тиімділігін көрсетті. 303-тен 343 K-ге дейін бес температура аралығында ингибрлеу үрдісінің температуралық зерттеудің тәжірибелік деректері нәтижесінде энтальпия (ΔH_a), энтропия (ΔS_a) және Гиббстің бос энергиясы (ΔG_{ads}) сияқты термодинамикалық параметрлері алынды. Коррозияның термодинамикалық параметрлері ингибитор қатысында және ингибиторсыз есептеліп, талқыланды. Әзірленген ингибитормен болат пластинаның ингибиторлы қорғау әрекетінің механизмі зерттелді. 0,5М HCl-дегі MA/Tween-DEA көміртегілік бетіндегі адсорбциясы Ленгмюр изотермиялық моделіне сәйкес келеді.

Кілт сөздер: ионды емес ББЗ, ингибитор, коррозиядан қорғау, ингибиторлы қорғау тиімділігі, температура, адсорбция, термодинамика, көміртегілік болат.

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Исследование ингибиторной активности нового азотсодержащего ПАВ в кислой среде

В статье приведены результаты испытаний нового неиногенного поверхностно-активного вещества в качестве ингибитора коррозии в 0,5М растворе соляной кислоты. Ингибитор коррозии синтезировали каталитической этерификацией малеинового ангидрида с полиоксиэтиленсорбитаном и дальнейшим амидированием эфира диэтаноламином. Структура и состав разработанного ингибитора были охарактеризованы методами ИК- и ^{1}Н ЯМР-спектроскопии. Результаты показали, что реагент MA/Tween-DEA эффективно ингибирует коррозию углеродистой стали в растворе соляной кислоты с оптимальной степенью ингибиторной защиты 94 % (100 ppm) при 303 К гравиметрическим методом. Термодинамические параметры, такие как энтальпия (ΔH_a), энтропия (ΔS_a) и свободная энергия Гиббса (ΔG_{ads}), были получены из экспериментальных данных температурных исследований процесса ингибирования при пяти температурах в диапазоне от 303 до 343 К. Термодинамические параметры коррозии рассчитывали в отсутствие и присутствии ингибитора и обсуждали. Изучен механизм действия ингибиторной защиты стальной пластины синтезированным ингибитором. Адсорбция MA/Tween-DEA ингибитора на углеродной поверхности в 0,5М HCl соответствует модели изотермы Ленгмюра.

Ключевые слова: неионогенный ПАВ, ингибитор, защита от коррозии, эффективность ингибиторной защиты, температура, адсорбция, термодинамика, углеродистая сталь.