ANTI-CORROSIVE ACTIVITIES OF SOME NOVEL SURFACTANTS BASED ON VEGETABLE OILS

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Corrosion inhibition by surfactant molecules are related to the surfactant's ability to aggregate at interfaces and in solution. In this article, the adsorption and corrosion inhibition of series of commercial fatty acid surfactants synthesized based on vegetable oils (sunflower, cottonseed, corn and palm oil) onto mild steel is investigated at 50 ºC in CO_2-saturated brine. The inhibition efficiencies of the tested compounds showed good inhibition and protection of the carbon steel even at low concentrations. The corrosion inhibition tendency correlated to the chemical structure of the compounds.

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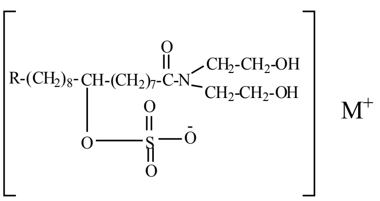
Introduction

The study of CO_2 corrosion started a few decades ago and cannot be considered well resolved yet. Carbon steel is widely used as tubing or as pipeline in the oil and gas industry, and is usually eroded heavily, especially when the corrosion electrolyte contains CO_2.[1] In the oil extraction and processing industries, inhibitors have always been considered to be the first line of defense against corrosion. Most of the inhibitors currently used in producing wells are organic nitrogenous compounds. In that sense, use of surfactants as inhibitors is one of the best-known methods of corrosion protection.[2-4] Corrosion inhibition by surfactant molecules is related to the surfactant's ability to aggregate at interfaces and in solution.

In the present work, we have synthesized novel surfactants isolated from vegetable oils (sunflower (**A**), cottonseed (**B**), corn (**C**) and palm (**D**) oils) and studied their anti-corrosive properties in carbon dioxide environments at 50 °C. The surfactants were prepared in different compositions **(Scheme1)** based on vegetable oils and diethanolamine as in Ref.[5] The structures of synthesized surfactants were confirmed by physical-chemical spectroscopic methods.



Scheme 1. Molecular structure of the synthesized anionic surfactants, where M=Na^+ (Inhibitor I), K^+ (Inhibitor II), NH_4^+ (Inhibitor III), -NH-CH_2CH_2OH (Inhibitor IV),-N-$(CH_2CH_2OH)_2$ (Inhibitor V).

Experiments

Linear polarization resistance corrosion rate (LPR) (bubble-test method) involves evaluating the corrosion of a given metal in simulated brine saturated with CO_2 at a temperature equivalent to that in the field. During the test, CO_2 gas is sparged continuously into the test solution. The rate of corrosion is determined instantaneously with the LPR technique, in which a small direct-current voltage is applied to a pair of identical electrodes and the resultant current is measured. A limitation of the bubble-test method is that it does not provide information on the effect of shear stress on the performance of a given corrosion inhibitor.

Results and Discussion

Figure 1 shows that, the change in corrosion rate (CR) with time for low carbon steel in 1%NaCl solution saturated with CO_2 containing different concentrations form inhibitor **I** at 50 °C synthesized based on all four oils. The inhibitor was added after 1 hour of exposure because at this time the corrosion potential got stable, allowing the measurement of the corrosion rate (CR) prior the injection of the inhibitor. The initial CR, without inhibitor, was measured to be between 3.45 and 5.03 mm/year. It can be observed from Figure **1** that the CR, in the absence of inhibitor, tends to increase with time. The increase in CR has been attributed to the galvanic effect between the ferrite phase and cementite (Fe_3C) which is a part of the original steel in the non-oxidized state and accumulates on the surface after the preferential dissolution of ferrite (α-Fe) into Fe^{2+} **[6].** Fe_3C is known to be less active than the ferrite phase. Therefore, there is a preferential dissolution of ferrite over cementite, working the former as the anode and latter as the cathode, favoring the hydrogen evolved reaction (HER) during the corrosion process.[6,7]

Corrosion parameters were calculated on the basis of LPR test. The inhibition efficiency (*IE*) and degree of surface coverage were calculated according to the following equations:[5]

$$IE,\% = 100\,\frac{CR_0 - CR_i}{CR_0} \qquad (1)$$

$$\theta = 1 - \frac{CR_i}{CR_0} \qquad (2)$$

where

θ = Surface coverage,

CR_o is the corrosion rate without inhibitor and

CR_i the corrosion rate when inhibitor is present.

It can be seen that the presence of inhibitors results a high decrease in the rate of corrosion. In the case of these surfactants, the corrosion rate decreases as the inhibitor concentration increases, getting maximum inhibition efficiency ranged between 91.9 and 99.90 % at 100 ppm after 20 hour of exposure.

The results showed that all synthesized inhibitors were good inhibitors and their inhibition efficiencies were significantly increased with increasing the concentration of surfactant. The increase of inhibitor efficiency with increasing the concentration can be interpreted on the basis the adsorption amount and the coverage of surfactants molecules, increases with increasing concentration. The inhibition efficiency of the investigated inhibitors which synthesized based on vegetable oils was increased in the following order (after 20 hours):

$\mathbf{A_{II}} > \mathbf{A_{I}} > \mathbf{A_{III}} > \mathbf{A_{IV}} > \mathbf{A_{V}}$ based on sunflower oil

$\mathbf{B_{II}} > \mathbf{B_{I}} > \mathbf{B_{V}} > \mathbf{B_{IV}} > \mathbf{B_{III}}$ based on cottonseed oil

$\mathbf{C_{II}} > \mathbf{C_{IV}} > \mathbf{C_{V}} > \mathbf{C_{I}} > \mathbf{C_{III}}$ based on corn oil

$\mathbf{D_{V}} > \mathbf{D_{IV}} > \mathbf{D_{II}} > \mathbf{D_{III}} > \mathbf{D_{I}}$ based on palm oil

There was an increase in the efficiency of corrosion inhibition with increasing concentration, Due to their containment of C=O, oxygen, nitrogen and sulfur groups these molecules contribute towards inhibition, and effectively protecting the surface. Adsorption of these surface active molecules forms thin inhibitor films on the metal surface which in order relatively isolate the metal surface from the corrosive environment causing much reduced corrosion rates. Inhibition efficiency of these films depends on various factors including but not limited to corrosivity of the environment, concentration of the active inhibitor molecules, any synergetic effects with other molecules present in the environment and/or flow/shear effects.

The surface coverage rates (θ) are found to depend on the concentrations of the inhibitors. The surface coverage rates are increased with the increase of the surfactant concentrations. This indicates that the inhibitory action of the investigated inhibitors against carbon steel corrosion can be attributed to the adsorption of these molecules on the metal surface, limits the dissolution of carbon steel, and the adsorption amounts of surfactants on carbon steel increase with concentrations in the corrosive solutions.

The results also showed that, the inhibition efficiencies in the case of surfactants obtained on the basis of palm oil are higher compared with those of inhibitors obtained on the basis of cottonseed, corn and sunflower oils at the same conditions. This behavior may be due to the difference in fatty acids compositions of oils. The fatty acid composition of oils from vegetable sources varies depending on plant origin and sort (Table **1**).[8]

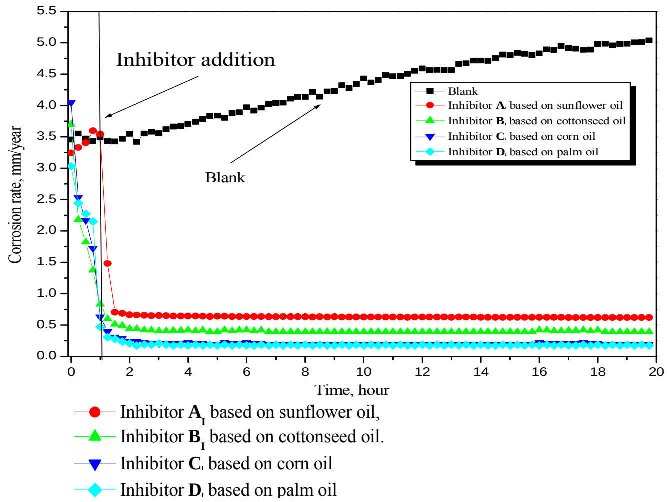


Figure 1. Variation of the corrosion rate with time for carbon steel in 1 % NaCl solution saturated with CO_2 containing different concentrations of inhibitor (I) at 50 °C.

In order to obtain the isotherm, the linear relation between θ values and C_{inh} must be found. Attempts were made to fit the θ values to various isotherms including Langmuir, Temkin, Frumkin and Flory–Huggins. By far the best fit is obtained with the Langmuir isotherm. This model has also been used for other inhibitor systems **[9, 10].** According to this isotherm, θ is related to C_{inh} by **[11]:**

$$\frac{C_{inh}}{\theta} = C_{inh} + \frac{1}{K_{ads}} \qquad (3)$$

Where

K_{ads} is the equilibrium constant of the inhibitor adsorption process and

C_{inh} is the inhibitor concentration.

Plots of C_{inh}/θ versus C_{inh} yielded a straight line as shown in Fig. 2, which suggested that the adsorption of inhibitors on metal surface obeyed Langmuir adsorption isotherm model. This isotherm assumed that the adsorbed molecules occupied only one site and there was no interaction with other molecules adsorbed. The linear regression coefficients (R^2) and the slopes parameter variations were calculated. All correlation coefficient (R^2>0.9597) indicated that the inhibition of carbon steel by these inhibitors was attributed to the adsorption of surfactant molecule on the metal surface. However, the slopes of the C_{inh}/θ versus C_{inh} plots were close to 1 and showed a little deviation from unity which meant non-ideal simulating[12] and unexpected from Langmuir adsorption isotherm. They might be the results of the interactions between the adsorbed species on the metal surface.[13, 14].

Table 1. Fatty acid composition of the oils (percent by weight of total fatty acids).

Oil	Unsatd/ Satd. ratio	Saturated acids					Unsaturated acids		
		Capric C10:0	Lauric C12:0	Myristic C14:0	Palmitic C16:0	Stearic C18:0	Oleic C18:1	Linoleic C18:2	α-Linolenic C18:3
Sunflower(A)	7.3	-	-	-	7	5	19	68	1
Cottonseed (B)	2.8	-	-	1	22	3	19	54	1
Corn (C)	6.7	-	-	-	11	2	28	58	1
Palm (D)	1.0	-	-	1	45	4	40	10	-

The values of K obtained from the Langmuir adsorption isotherm are calculated, together with the values of the Gibbs free energy of adsorption (ΔG^0_{ads}) calculated from

$$K_{ads} = \frac{1}{55.5}\exp\left(-\frac{\Delta G^0_{ads}}{RT}\right) \tag{4}$$

where

R is the universal gas constant,

T the thermodynamic temperature and

the value of 55.5 is the concentration of water in the solution.

The high values of K_{ads} for the studied surfactants indicate stronger adsorption on the metal steel surface in CO_2-saturated brine. Large values of K_{ads} imply more efficient adsorption and hence better inhibition efficiency.[4] The large value of K_{ads} obtained for the studied surfactants agree with the high inhibition efficiency obtained.

The negative ΔG^0_{ads} values are consistent with the spontaneity of the adsorption process and the stability of the adsorbed layer on the carbon steel surface. Generally, values of ΔG^0_{ads} up to -20 kJ mol^{-1}, the types of adsorption was regarded as physisorption, the inhibition acted due to the electrostatic interactions between the charged molecules and the charged metal, while the values around -40 kJ mol^{-1}or smaller were associated with chemisorption as a result of sharing or transfer of electrons from organic molecules to the metal surface to form a coordinate type of bond (chemisorption).[15] The values of ΔG^0_{ads} in our measurements for all inhibitors synthesized based on all oils were found around -40 kJ mol^{-1}, thus the adsorption mechanism of the surfactants on carbon steel in 1% NaCl solution saturated with CO_2 was typical chemisorption.

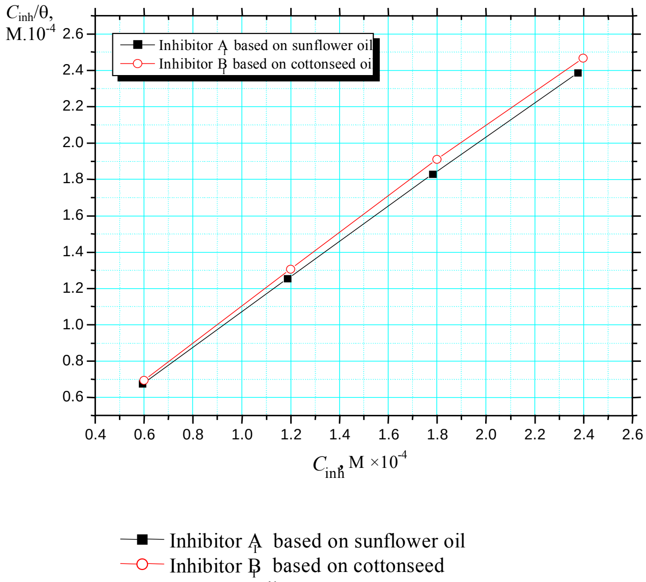


Figure 2. Langmuir adsorption isotherms for carbon steel in 1 % NaCl saturated wirh CO_2 in the presence of different inhibitors at 50 °C.

The corrosion process is inhibited by the adsorption of these surfactants on carbon steel surface. Inhibition efficiency increased with increase in concentration of the surfactants, getting maximum inhibition efficiency ranged between 91.9 and 99.90 % at 100 ppm after 20 hour of exposure.

The inhibition efficiencies in the case of inhibitors obtained based on sunflower oil are higher compared with those of inhibitors obtained based on sunflower, corn and palm oils at the same conditions. This behavior may be due to the difference in fatty acids compositions of two oils.

The adsorption of synthesized surfactants on carbon steel surface obeyed Langmuir adsorption isotherm. The high value of adsorption equilibrium constant and negative value of standard free energy of adsorption suggested that surfactants are strongly adsorbed on carbon steel surface, and are chemically adsorbed on the metal surface.

Conclusions

Linear polarization corrosion rate was employed to study the corrosion inhibition of carbon steel in CO_2-saturated solutions using some novel surfactants as corrosion inhibitors synthesized based on vegetable oils.

All inhibitors were found to be effective inhibitors for carbon steel corrosion in CO_2-saturated solutions.

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