EVALUATION OF GENERIC INHIBITORS BEHAVIOR FOR MULTIPHASE SYSTEMS (STEEL-BRINE-CO$_2$/H$_2$S) BY USING ELECTROCHEMICAL TECHNIQUES

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One of the main ways to inhibit the corrosion is the adsorption of organic compounds on the surface of a metal. This study reports the behavior of six different organic inhibitors in a system carbon steel AISI-SAE1020/brine 3%w of NaCl/ gas mixture of 6% volume of CO$_2$/10 ppm of H$_2$S/ hydrocarbon. Two primary amines with sixteen and eighteen atoms of carbon were used, a secondary amine with twenty atoms and three carboxylic acids of sixteen, eighteen and twenty carbon atoms.

Linear polarization resistance measurements were used, along with Tafel extrapolation and electrochemical impedances to assess the influence of temperature, velocity of fluid, inhibitor concentration and concentration of oleic phase on the inhibition efficiency in the Electrode of Rotational Cylinder, ECR.

Activation and adsorption energies were calculated for the processes of corrosion in the system; according to the values derived, it was possible to define the system brine/CO$_2$/H$_2$S/ inhibitor, as a process with mixed control, where the phenomenon of mass transfer and that of charge transfer are in competition and the values obtained for the energy of adsorption of Gibbs, allowed checking that these compounds showed a chemical adsorption on the metallic surface. Under critical testing conditions (4 m/s, 59°C or 332,15K) the amines present a better efficiency than carboxylic acids, thus complying with the electro-negativity theory applied to inhibitors. It was then possible to establish by the results obtained for the with hydrocarbon cuts tests, that this parameter adversely affects the percentage efficiency of the inhibitor.

Keywords: *corrosion inhibitor, multiphase system, electrochemical test, amines, carbon dioxide, sulfide acid.*

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Uno de los principales caminos para la inhibición de la corrosión lo constituye la adsorción de compuestos orgánicos sobre la superficie de un metal. En este estudio se reporta el comportamiento de seis diferentes inhibidores orgánicos en un sistema acero al carbono AISI-SAE 1020/Salmuera al 3%w de NaCl/ mezcla gaseosa de 6% volumen de CO_2/10 ppm de H_2S/Hidrocarburo. Se utilizaron dos aminas primarias de dieciséis y dieciocho átomos de carbono, una amina secundaria con veinte átomos y tres ácidos carboxílicos de dieciséis, dieciocho y veinte átomos de carbono.

Se emplearon medidas de resistencia a la polarización lineal, extrapolación Tafel e impedancias electroquímicas para evaluar la influencia de la temperatura, velocidad del fluido, concentración de inhibidor y concentración de la fase oleica en la eficiencia de inhibición en el Electrodo de Cilindro Rotatorio (ECR).

Se calcularon las energías de activación y adsorción para los procesos de corrosión en el sistema. Por los valores obtenidos, se logró ubicar el sistema Salmuera /CO_2/H_2S/ inhibidor, como un proceso con control mixto, donde compiten el fenómeno de transferencia de masa con el de transferencia de carga, y los valores obtenidos para las energías de adsorción de Gibbs, permitieron comprobar que estos compuestos presentan una quimiadsorción sobre la superficie metálica. En condiciones de ensayo críticas (4 m/s, 59°C ó 332,15K) las aminas presentan una mejor eficiencia que los ácidos carboxílicos, cumpliendo la teoría de electronegatividad aplicada a los inhibidores. Se pudo establecer con los resultados obtenidos para las pruebas con corte de hidrocarburo, que este parámetro afecta negativamente el porcentaje de eficiencia del inhibidor.

Palabras clave: *inhibidores de corrosión, sistemas multifásicos, pruebas electroquímicas, aminas, dioxido de carbono, acido sulfúrico.*

INTRODUCTION

One of the most commonly methods used for controlling internal corrosion in pipeline is the continuous use of inhibitors, which are known for their low cost and easy application in comparison to other methods. Corrosion inhibitors are a formulation of chemical compounds that when added in small concentrations to an aggressive environment, are able to diminish the corrosion rate of materials. Inhibitors play a key role in the control of corrosion associated with the production and transport of crude oil and gas. The successful selection of inhibitors depends upon a clear understanding of operating conditions, properties of fluids, chemistry and pH of the solution, conditions of flow, in addition to an appropriate knowledge of their action on the kinetics of the electrode process.

In this paper the behavior of some generic inhibitors in multiphase systems of steel-brine-CO_2-H_2S, was evaluated using electrochemical methods. This required the design and adaptation of an axis to the rotating Cylinder Electrode Tree (ECR). Such axis was equipped with a shaker that provided a dispersion of the mixture comprised of 70% mineral oil and 30% brine, with the purpose of characterizing the corrosion rate in the whole pipe, taking into some considerations the hydrodynamic and thermodynamic conditions of fluids (i.e. rate of flow, patterns of flow, pressure, temperature, etc.); and by means of Potentiodynamic tests it was possible to determine the rate of corrosion, activation energies and adsorption energies, the isotherm of adsorption and the inhibition efficiency for six generic inhibitors.

THEORICAL FRAMEWORK

Inhibition in H_2S and CO_2 systems

The nature of interaction of H_2S and CO_2 in aqueous solutions with carbon steel is a complex process. Research work carried out by different authors (Kvarekval, 1997) found that the layers of corrosion product on formed on steel can be either protectors or they can lead to a quick failure, depending on operating conditions. This is mainly due to the development of an iron sulfur film (FeS), if H_2S is predominant, while the formation of iron carbonate ($FeCO_3$) appears if CO_2 is predominant within the gas.

In systems where CO_2 prevails, the presence of small quantities of H_2S (PCO_2/PH_2S >200 ratio) can lead to the development of layers of iron sulfur known as Mackinawite, at temperatures below 120°C (393,15K). This thin layer is produced on the surface of the metal as a function of the reaction between Fe^{++} and S^-, which could be able to onset the corrosion; on the contrary, in systems where H_2S prevails, a meta-stable sulfur layer is formed which displaces the carbonate layer, that would otherwise be formed. This layer can protect the metal within a range from 60°C to 240°C (333,15K to 513,15K) (Srinivasan & Rusell, 1996).

Inhibition

Some studies (Cabarcas & Gelvez, 1996) suggest that inhibition of corrosion is due to the adsorption of positively-loaded inhibitor ions in cathodic areas of the metal. By measuring potentials and polarization of steel in aqueous solution with sulfuric acid and amines, it was determined that anodic and cathodic areas were affected by the amine type inhibitor. Inhibition in the anodic area was attributed to the reduced trend showed by ferrous ions to be dissolved, as result of the migration of the metal electrons towards the positively charged adsorbed inhibitor, rather than the cathodic areas within the metal.

When a strongly adsorbed substance is introduced into a corrosive solution it will compete with other ions or molecules with regard to its accommodation on the surface, thus diminishing the quantity of corrosive substance present by area unit as well as the replacement rate. Therefore, adsorption can occur in different proportions on the parts of the metal covered with oxide (cathode) and the bare parts (anode). This means that many adsorption inhibitors will act with special success, either in anodic region or in the cathode region, so that there is no clear distinction between adsorption inhibitors on the one hand and the cathodic or anodic inhibitors on the other hand.

Some authors (Godinez & Meas, 2003) accept that inhibition depends on the chemical -adsorption of inhibitors that can be produced by the same compound (metal - inhibitor) under the following circumstances:

Interface inhibition: Inhibitor is adsorbed on the metal surface to form a bi-dimensional structure. Its action mechanism can be as follows:

• Blocking of the metal surface due to the formation of a dense molecular single layer, which is chemically and mechanically stable.

• Selective blocking of active sites on the metal where semi-reactions occur of oxidation and/or reduction.

• The coating features reactive properties and its physical adsorption on the metal surface is followed by chemical or electrochemical reactions.

Interphase inhibition: This effect corresponds to the blocking of semi-reactions of corrosion through deposits or multi-molecular films having several amstrongs of thickness. Inhibition in the interface is not selective, since the action mechanism does not imply to selectively blocking the active sites wherein the semi-reactions of oxidation and reduction occur. This mechanism forms a film that, when avoiding the flow of ionic species, will electrically isolate the metal, stopping or decreasing the corrosive process.

Influence of inhibitor concentration on the inhibition efficiency

It is known that inhibitor coverage on metallic surface (θ) is the parameter more used to study the behaviour of inhibitor adsorption (Cao, 1996). If the adsorption is ruled by a reversible chemical reaction (Zhang, X., Wang, F., Yufang, & Yuantang, D., 2001): RY + M RY ….M, where RY is an organic compound with reaction centre Y with a substitute or radical R. M, the metal and RY …. M, the chemiadsorption of the compound. If this compound acts by means of blocking the active sites on the surface, which causes a change in the average of the barriers of activation energy of the anodic and cathodic reactions of corrosion process, and therefore, a change in potential. Then, the current densities will be proportional to the fraction of surface covered θ, according to (Damborenea, 1987): $i_{inh} = i_o$ $(1 - \theta)$, where i_{inh} and i_o are the current density with and without inhibitor respectively. If the compound acts by geometric block, in which the inhibition effect begins for the area reduction of reaction on the corroding metal surface, and hence, the potential change must

be null. The coverage of inhibitor can be calculated thus (Cao, 1996):

$$\theta = \left[\frac{C_d^o - C_d}{C_d^o - C_d^s} \right]$$

Where Cd is the interface capacitance in the inhibited system ($\mu F \ast cm^2$)

C_d^o is the interface capacitance of system without inhibition ($\mu F \ast cm^2$)

C_d^s is the capacitance for the system with complete coverage of inhibitor.

When $C_d^s << C_d^o$ the equation can be simplified at:

$$\theta = 1 - \left[\frac{C_d}{C_d^o} \right]$$

In general it is possible to consider that an increase in the inhibitor concentration will result in the drop of corrosion rate. The inhibition mechanism by means of organic products is due to the adsorption on the metallic surface. The dependence on adsorption of these organic substances with concentration is observed better by using the isotherms of adsorption.

EXPERIMENTAL

Electrodes

Test specimens were machined from AISI SAE 1020 steel and its characterization was carried out by the optical emissions spectroscope technique -EEO, according to ASTM E-415 1999 standard (Peña, D., Vásquez, C., Laverde, D., Villareal, J., & Quiroga, H., 2003); average results and the normal values for a mild steel are shown in Table 1. The initial work solution was a 3% NaCl in weight brine with deionized water, without de-aerating, free of any chemicals or any other gases.

Solubility and dispersion tests

These tests were carried out to evaluate the solutions in brine and oil and partitioning tests of oil/water, the test used was the partitioning equilibrium, in which an amount known of corrosion inhibitor was distrib-

Table 1. Chemical composition for the AISI 1020

Element	Sample	AISI - SAE 1020
C	0,224 ± 0,0014	0,18 - 0,23
Mn	0,521 ± 0,0071	0,30 - 0,59
P	0,001 ± 0,0012	0,040 max.
S	0,009 ± 0,0041	0,050 max.
Si	0,157 ± 0,0031	
Cu	0,322 ± 0,0366	
Ni	0,135 ± 0,0053	
Cr	0,189 ± 0,0017	
Mo	0,023 ± 0,0005	
As	0,007 ± 0,0008	
Nb	0,013 ± 0,0008	
Co	0,028 ± 0,0023	
Sn	Balance	
Fe		

uted between the oil phase and brine for a time over 24 hours and with a cut of oleic phase-brine of 30/70. During each test, the fluids were inspected by visual test to assure that corrosion inhibitors do not cause the formation of a stable emulsion or excess of foam. After 16 hours, the brine phase was separated from oleic phase and its corrosivity was measured. These tests were carried out in a concentrations range between 1 and 30 ppm of inhibitor, and the results from the evaluation of behaviour partitioning which allow to determine the level of inhibitor dosing required into two phases mixtures to obtain a good inhibition in the aqueous phase.

Preparation of generic inhibiting substances

Six organic compounds: Hexadecylamine, Octadecylamine, Didecylamine, Hexadecanoic acid, Octadecanoic acid, and Eicosanoic acid (analytical reagents) were used. In the first stage of solubility and dispersibility of inhibitors it was decided that the dissolution of each of these compounds would be implemented using the benzene - ethanol mixture obtaining patterns of concentration of 100 ppm and 500 ppm for each inhibitor, which were used to prepare solutions of 1, 3, 10 and 30 ppm of inhibitor with brine respectively. The work solution with inhibiting substances consisted of

the initial brine adding the dosage of the corresponding inhibitor. After performing a de-aeration during two hours with high purity nitrogen, grade 5,0 the corresponding gas mixture of CO_2/H_2S was bubbled for two additional hours. Their characterization was performed by the application of colorimetric/spectrophotometric techniques (HACH Company). The test pressure was 1 atm for all experiments.

Electrochemical tests

Tests were carried out in a rotating cylinder electrode, RCE, (EG&G 636) together with a Gamry potentiostat. The working electrodes had a dimension showed in the Figure 1 and with exposition area of 3,02cm². The electrodes were polished until emery paper 600 and then washed them with ethylic alcohol. The auxiliary electrode was an electrolytic graphite and as reference electrode Ag/AgCl. For the ECR, an axis provided with a shaker was designed and adapted to the ECR tree, which provided a mixture dispersion made of 70% water and 30% of mineral oil, without altering the vortex formed around the working electrode; therefore the shear stress would not be affected. Table 2 shows the experimental programming for the hydrodynamic evaluation of multiphase system. Figure 2 shows the experimental setup. A factorial design of experiments 24 with repetitions in center was used. Table 2 shows the range of the variables of the factorial design for each inhibitor evaluated in the multiphase hydrodynamic system. The experimental conditions were determined according to the field data provided by a oil company and the response variable was corrosion rate.
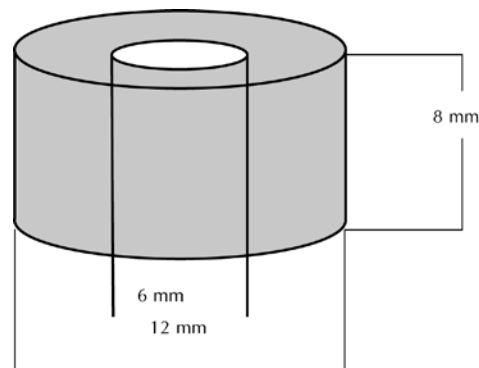

8 mm

6 mm

12 mm

Figure 1. Dimensions de of working electrode for the ECR

The electrochemical techniques used in this work were lineal polarization resistance, Tafel Extrapolation and Electrochemical Impedance Spectroscopy (EIS); the tests with EIS were carried out in a range between 100 000 and 0,01 Hz and voltage amplitude of 10 mv. The corrosion rate was calculated by using Slopes Tafel and the inhibitor efficiency was determined from corrosion rates with and without inhibitor.
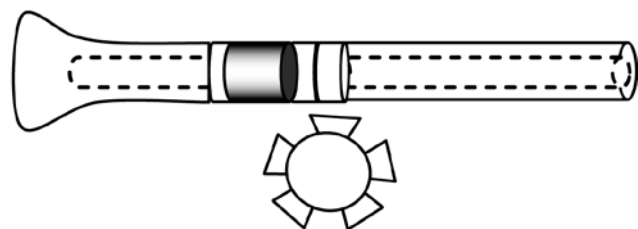
(a)
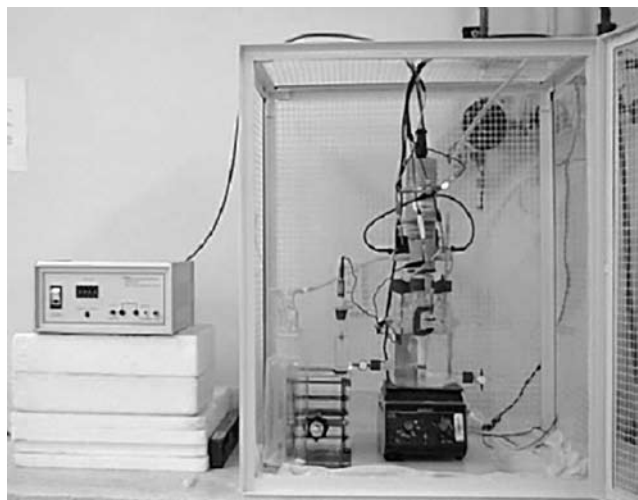
(b)

Figure 2. (a) Experimental setup, (b) Axis designed for the tests in RCE

RESULTS

Determination of Corrosion Rates and Inhibition Efficiencies in ECR

Tests were run on the six previously described organic products, within the range of temperatures and rates of flow specified as variables, with concentrations from 4 to 10 ppm of H_2S and different concentrations (in ppm) of inhibitor, with the purpose of observing the influence of the temperature and velocity of the fluid on the inhibitor efficiency. Table 3 shows the data obtained for Didecylamine (1 ppm).

From the table, the Didecylamine (1 ppm) data do not show any definite tendency in terms of the inhibitor behavior with the variation of velocity of fluid and temperature, and in the case of Hexadecilamine (T = 59ºC or 332,15K and 10 ppm), by increasing the rotation speed the corrosion rate is also increased, diminishing the inhibition efficiency (Figure 3), while for Octadecylamine no remarkable variation was seen. Similar to what occurs with organic substances of amine base, the fatty acids base compounds do not show any definite trend of inhibition with regard to the variation in the rotation speed and temperature (Figure 4).

Effect of fluid Velocity on the inhibition efficiency

Figure 5 shows the influence of velocity of fluid on the efficiency of inhibition in each organic compound having an amine base, for one of the tests carried out (1 ppm). When the inhibition efficiency is reduced by increase of the fluid velocity, behaviors seen for Hexadecylamine and Octadecylamine, it

Table 2. Variables for the hydrodynamic evaluation of multiphase system

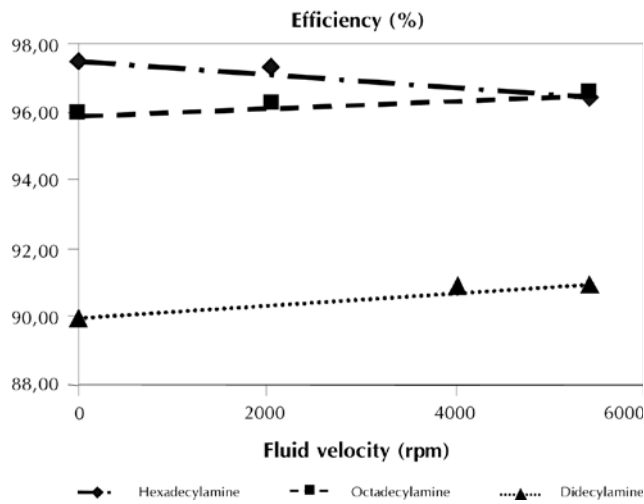| Techniques	Velocity (m/s)	Gas Relation	T °C	% OIL	Inhibitor Type	Inhibitor (ppm)
R.P Tafel Slope Impedance (EIS)	0 1 4	6%VCO2 / 4ppmH2S 6%VCO2v/ 10ppmH2S	30 45 59	0 30	**Amines** Hexadecilamine Octadecylamine Didecylamine	0 1 3 10
					Acids Hexadecanoic Octadecylamine Aracidic	0 1 3 10 30

Figure 3. Influence of rotation speed on the inhibition efficiency in the steel - brine system with amines at 59°C (332,15K) and 10 ppm concentration

could be said that the phenomenon of corrosion is under mixed control in that interval, which decrease the chemical adsorption process of inhibitor on the metallic surface. Additionally, some efficiencies were negative because the inhibiting film is very unstable and it is not persistent, due to the small concentration of amines (1 ppm) and the velocity of fluid; which could also be due to the fact that while increasing shear stresses on the walls, while increasing the speed of rotation, the adsorption bonds are not sufficiently strong making them to break, leading to a detachment of the inhibitor molecules of the wall, which in turn
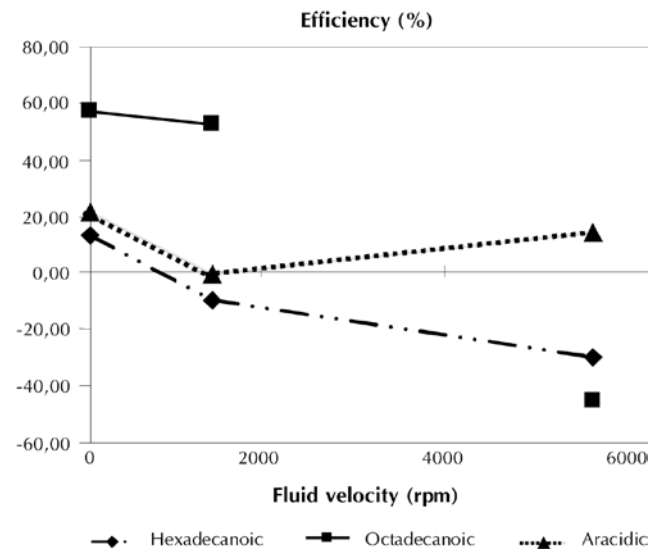

Figure 4. Influence of rotation speed on the inhibition efficiency in the steel - brine system- mixture of 6% CO2 -10 ppm H_2S with acids at 59°C (332,15K) and 1 ppm concentration

is reflected on a decrease in percentage of efficiency of some inhibitors.

The opposite behavior, that is, that the inhibition efficiency increases, when increasing the velocity of fluid, as was observed for Didecylamine, explained by the increase of the transfer of mass towards the metallic surface. This lead to that a larger amount of inhibitor atoms are chemically adsorbed on the surface or that they are available to form links, therefore the corrosion rate decreased with the increase of revolutions per minute (Table 3).

Table 3. Values of polarization resistance, current of corrosion, corrosion rate and inhibitor efficiency (1 ppm of Didecylamine), 6% volume of CO_2 and 1 ppm de H_2S

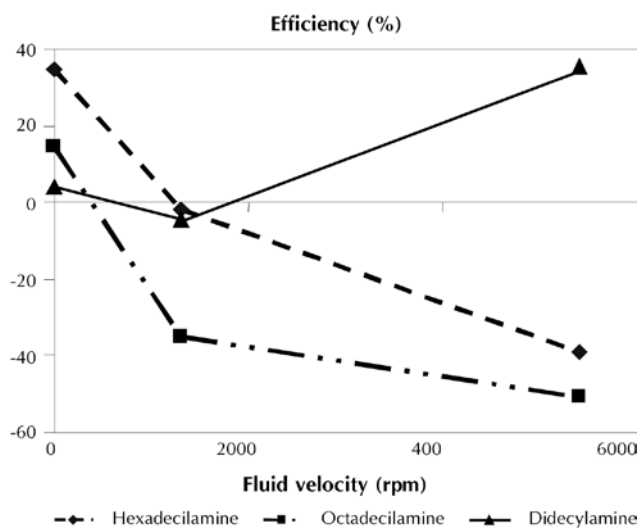| Temperature (°C)	Fluid Velocity (rpm)	Rp (Ω*cm2)	I_{corr} (A/cm2)	V_{corr} (mpy)	Efficiency (%)
30	0	3616	5,11E-06	2,36	69,07
30	1301	1229	1,38E-05	6,35	8,50
30	5421	918,3	1,92E-05	8,84	10,80
45	0	2185	9,10E-06	4,2	58,94
45	1301	890	2,15E-05	9,9	13,91
45	5421	738,1	2,29E-05	10,57	20,35
59	0	695,8	3,27E-05	15,1	4,01
59	1301	465,5	3,79E-05	17,5	-4,73
59	5421	881,1	2,15E-05	9,89	35,61

Figure 5. Influence of rotation speed on amine inhibition efficiency. 59°C (332,15K) and 1 ppm

Since the behavior of both amines and acids was not steady at 1 ppm of concentration; some tests were carried out at 3 ppm of concentration, however data were not reported, as no favorable results were obtained. By increasing to 10 ppm the inhibitor concentration, there was a considerable increase of efficiency, obtaining efficiencies of up to 97% under the most critical conditions, as seen in Figure 3.

Influence of temperature on the inhibition efficiency

Figure 6 shows the behavior of efficiency while varying the temperature for tests performed using the 16 carbon atoms base amine substance.
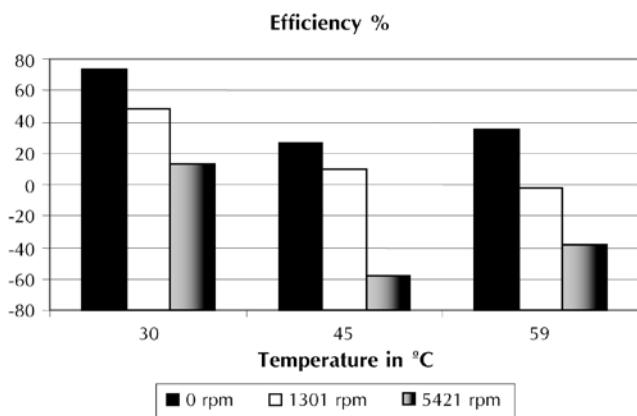

Figure 6. Influence of temperature on the inhibition efficiency for 1 ppm of Hexadecylamine

As seen in the graph, there is a tendency for inhibition efficiency to drop with the increase in temperature. This event could be attributed to a process of partial desorption of the inhibitor on the metallic surface, when the corrosion phenomenon in the system is being ruled by the charge transfer.

Didecylamine was the substance showing the best behavior and better conditions of efficiency in almost all tests performed, due to the fact that the alkyl group having the amine causes the nitrogen atom to be more negative, and the pair of electrons to be more available (Figure 5). Therefore, there is more electronic availability of atom of nitrogen of the amine. For this reason, this compound is more stable than the other two amines in the tests (Sykes, 1985).

The lack of tendency is more notorious in acids than in amines. Remember this when observing that oxygen electro-negativity which is sufficiently high as not to leave a pair of electrons available, which possibly could act in the coordinated covalent bond according to the Acid - Base Lewis theory. Through the equation of Arrhenius ($k = Ae^{-Ea/RT}$), the values of activation energy corresponding to the process of inhibition of tested solutions were calculated. Table 4 shows the data obtained.

This table shows that the smallest values of activation energy were obtained for the Octadecanoic acid and Didecylamine, which confirms their best inhibitory performance, by presenting better persistence and permanency on the metallic surface to tested temperatures, as a smaller energy range is needed for the bond to occur.

Activation energies can also be used to confirm the dominant mechanisms of corrosion in the system, as it has been stated that for the case of energies of less than 6 kcal ($\leq$25 kj mol^{-1}) the controlling phenomenon is the transfer of mass or the diffusion of species. For systems between six and ten kcal a mixed mechanism controls (diffusion and charge transfer) and for systems with energy of activation of over 10 kcal, the ruling mechanism is that of charge transfer (Sherryl, Jeffrey, Zhang, & Ho, 2005). According to this classification it is possible to see that in general terms, the systems with amines the mechanism is governed by charge transfer at 0 rpm. By increasing the fluid velocity, the mechanism

Table 4. Energy of Activation for the different organic compounds used at different fluid rates, obtained with the application of the direct current techniques (CD). 6% volume of CO_2 and 10 ppm de H_2S

Compound	Fluid Velocity (rpm)	Ln (Vcorr)/1/T	Ea (kJ/mol) with CD	Ea (kcal) with CD
Hexadecylamine	0	-5888	48,95	11,70
Hexadecylamine	1301	-5597	46,53	11,12
Hexadecylamine	5421	-3350	27,85	6,66
Octadecylamine	0	-4115	34,21	8,18
Octadecylamine	1301	-5954	49,50	11,83
Octadecylamine	5421	-7219	59,09	14,34
Didecylamine	0	-6522	54,22	12,96
Didecylamine	1301	-3591,1	29,86	7,14
Didecylamine	5421	-433,84	3,59	0,86
Hexadecanoic Acid	0	-8097	67,32	15,99
Hexadecanoic Acid	1301	-9190,8	76,41	18,26
Hexadecanoic Acid	5421	-3598,6	30,00	7,17
Octadecanoic Acid	0	-559,07	4,66	1,11
Octadecanoic Acid	1301	-868,13	7,22	1,72
Octadecanoic Acid	5421	-4840	40,24	9,62
Aracidic Acid	0	-2057	17,10	4,09
Aracidic Acid	1301	-4215,3	35,05	8,38
Aracidic Acid	5421	-2899,7	24,11	5,76

is located in a mixed control. This behavior is because by increasing the fluid rate, the transport of species and reactive agents is improved, thus facilitating the diffusion process. In acids there is no tendency observed with regards to the rate of the fluid, and systems mainly these are controlled by mixed control.

Inhibition Adsorption

In the Figure 7, we can see two clearly differentiated zones. The first area (low concentrations) a significant change is seen on the surface coverage with small increments on the concentration, then an area is seen where the inhibitor concentration increases exert a smaller influence on the inhibition grade. The layout in semi "s" shape observed is already a classic model in the representation of isotherms of adsorption. This tracing is identified as a transition in the inhibition process; passing from the existence of some chemically adsorbed molecules on some points of the surface, up to the formation of a continuous and even film on the entire metallic surface. In Figure 7 we can see the

relationship between the grade of surface covered by the inhibitor and the concentration of the inhibitor, for the tests performed using the Octadecanoic acid (Peña *et al*., 2003).
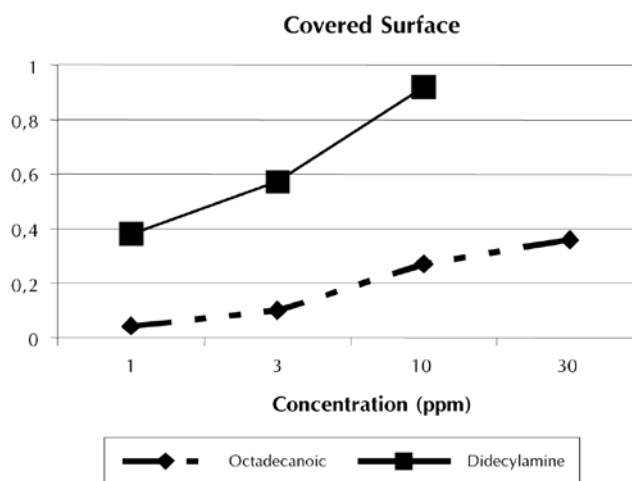

Figure 7. Isotherm of adsorption for the system studied with octadecanoic acid and Didecylamine, by using EIS (CA)

To determine if the process of adsorption is a chemical adsorption, some curves were traced of the relationship ($\theta/1-\theta$) vs. concentration as seen in Figure 8, from it can be deduced that the adsorption energy of octadecilamine and hexadecilamine are higher that the didecylamine one, due to their slopes are higher ($K_{adsorption}$). Energies of adsorption were calculated (as seen in Table 5) by means of the following equation: $\Delta G = -RTLnK_{ads}$.
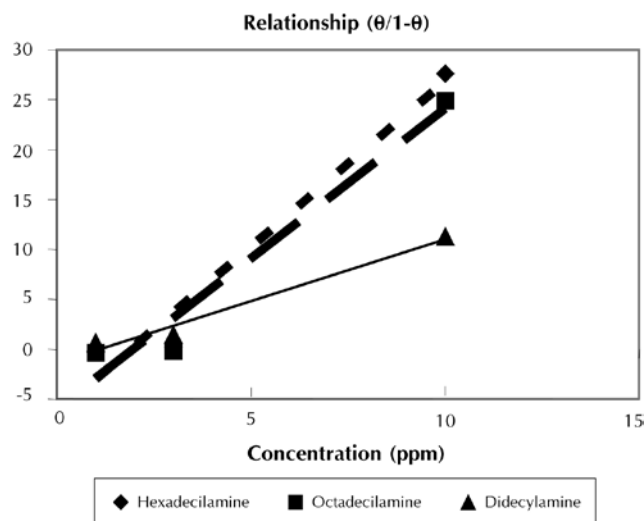

Figure 8. Energy adsorption curves for systems with amines by using EIS (CA). The value of θ corresponds to the coverage of the inhibitor on the surface

The adsorption of amines is explained by theories of thermodynamics and by the isotherm theory of Lagmuir. For acids this behavior is not so marked, however for Octadecanoic acid and Hexadecanoic acid, acceptable approaches were achieved.

With respect to the adsorption energies obtained (Table 5), the compounds used showed some adsorption of chemical type, because all the values obtained for this parameter were above 20 kjmol^{-1}; and in coherence with our previous observations, it is clearly seen that the highest energies of adsorption were presented by the inhibitor compounds having an amine base, confirming their best performance as inhibitors for the system studied. The inhibitor compounds having an acid base showed values approaching the classification threshold for physical adsorption (20 kjmol^{-1}), which could explain their poor performance as inhibitors in these systems.

In the diagrams of Nyquist obtained for two of six substances, the typical spectrum of double dome was not obtained for systems with inhibitors; however, the decrease of the dome by increasing rotation speed was clearly seen (Figure 9). This behavior can be explained assuming the fact that these compounds present a cationic nature that enables them to establish a double bond that is unsaturated and chemically adsorbed on the surface of iron forming a stable but thin film, whose structure consists of a simple layer or monolayer that could have a thickness of Angstroms. Therefore, the method of impedances is not able to detect the dome that would otherwise indicate the formation of the inhibitor layer, indicating that these compounds act by means of the inhibition mechanism in the interface and by changes in the double electrical layer. In these mechanisms the inhibitor is adsorbed in the surface of the metal to form a two-dimensional structure (Chesnut & Emmons, 1989).

Table 5. Energy of adsorption obtained by direct current (DC) and alternate current (AC) in the presence of organic compounds used as generic inhibitors at 59°C (332,15K) 6% volume of CO_2 and 10 ppm de H_2S

Compound	Kads by DC	Kads by AC	Adsorption Energy (kjmol-1) by DC	Adsorption Energy (kjmol-1) by AC
Hexadecylamine	3,2547	3,3195	37,42	37,59
Octadecylamine	3,3741	3,008	37,99	37,67
Didecylamine	1,0911	1,2371	34,88	35,26
Hexadecanoic Acid	0,067	0,0584	26,62	28,49
Octadecanoic Acid	0,0294	0,022	25,01	24,20
Aracidic Acid	0,0149	0,0084	23,39	21,81
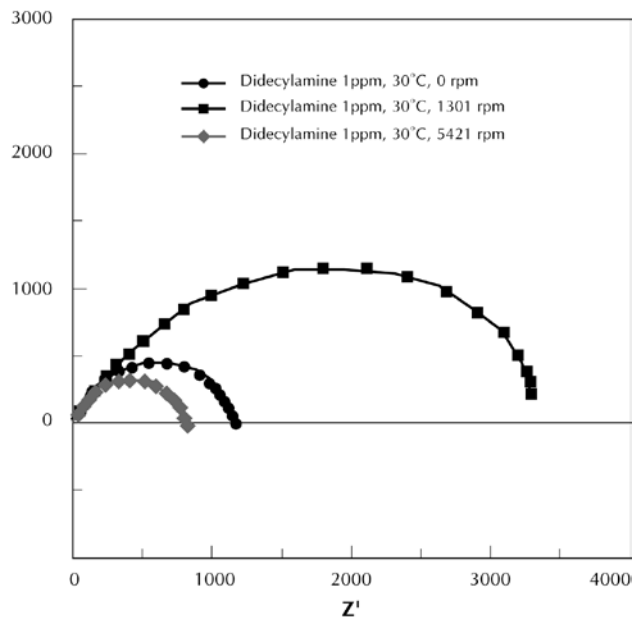
Figure 9. Nyquist diagrams for didecylamine at different rotation speeds and 30°C (303,15K)

Figure 10. Tafel extrapolation for different concentrations of didecylamine and rotation speed of RCE

The adsorption of organic cation in acid solutions causes that the potential shift to more positive values, what difficult the discharge of ions hydrogen on the metal and, therefore, the risk of penetration of hydrogen into metallic substrate. This effect of potential change and the modification of the kinetic of electrochemical reactions can be observed in the figure 10, for the Didecylamine.

The effect of inhibitor is evident both cathodic and anodic curves of Tafel. According to model of Nesic (Nesic, Pots, Postlethwaite, & Thevenot, 1995) and the shape of cathodic curves, it can determine that the cathodic reaction dominant is the reduction of H_2CO_3, which can be seen in the figure when the inhibitor concentration is increased, the formation of this product is delayed, which can be observed in the shift of this curve towards left and the verticality of the zone of formation of H_2CO_3 was getting smaller. As to the anodic curves, show a increase of the iron dissolution as the speed increases, but the dissolution decreases when the inhibitor concentration increases.

Influence of the cut of hydrocarbon (Mineral Oil) in the inhibition efficiency

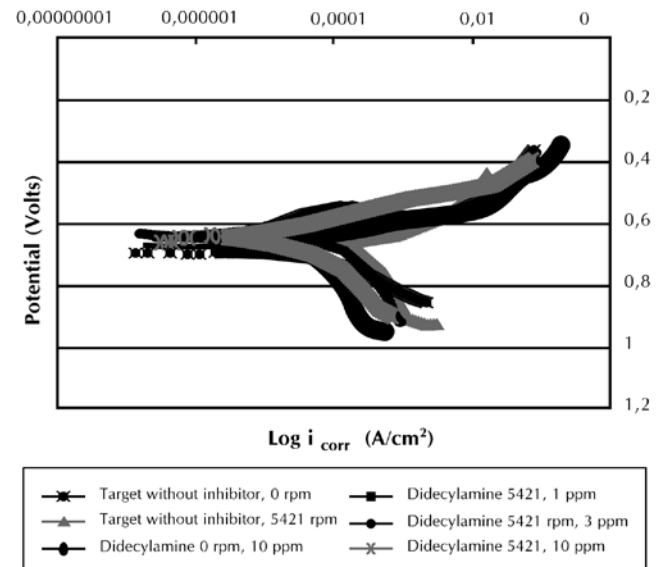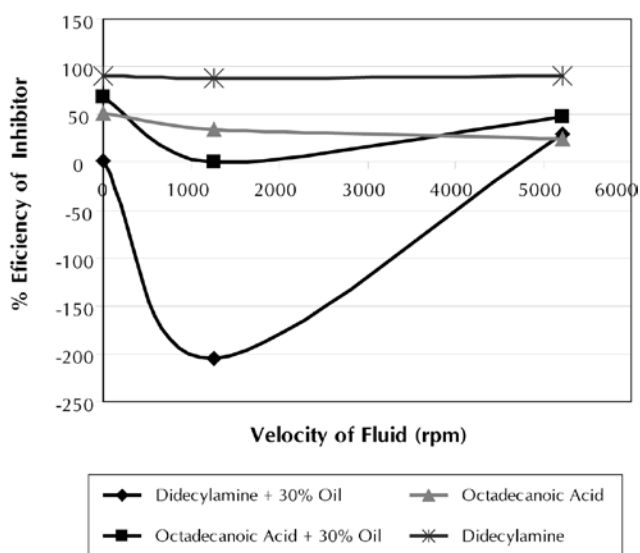During this research work it was not possible to obtain any steady emulsion but a dispersion that was kept by means of mechanical agitation. According to this dispersion, water is a continuous phase and crude is found in small proportions. The disperse drops of hydrocarbon in water start to be coalescent tending to wet the surface of the metal in a non-homogeneous way, increasing the anodic and cathodic sites causing increases and decreases in the corrosion rate, since the factor prevailing in corrosion is not the conductivity in this specific case, but the transport of corrosive agents towards the metallic surface. Table 6 shows the results obtained for tests carried out with a cut of water/hydrocarbons in a 70/30 ratio with different inhibitors efficiencies. The corrosion rates for the brine-30%Oil-6%CO_2-10 ppm H_2S system are shown in Table 7.

Figure 11 shows how inhibition efficiency is negatively affected by the presence of an oil phase. The decrease of inhibition efficiency with the increment of a hydrocarbon cut can be attributed to two causes: the first one due to the effect of non-homogeneous wetting that is produced by the dispersion of oil droplets on the metallic surface modifying its wetting conditions, and the second is the partitioning suffered by the inhibitor concentration. Since they are related to the oil phase, they do not only concentrate on the solid-liquid interface, but rather migrate towards the oil-water interface of dispersion, and hence it could reduce the molecules concentration on the metallic surface (Villareal, 2003). The physical phenomenon

Table 6. Corrosion rate and inhibition efficiencies for steel AISI SAE1020 at 70/30 water cut,
using direct current (DC). 6% volume of CO_2 and 10 ppm de H_2S

Compound	Temperature °C	Fluid Velocity (rpm)	Corrosion Rate (mpy)	Inhibition Efficiency (%)
Didecylamine 10 ppm	30	0	4,84	50,36
		1120	6,97	52,26
		4667	14,74	40,37
	45	0	5,39	63,58
		1183	13,57	54,62
		4930	35,2	-28,94
	59	0	9,58	2,24
		1252	29,79	-205,54
		5215	23,23	30,03
Octadecanoic Acid 10 ppm	30	0	3,99	59,08
		1120	6,95	52,40
		4667	6,72	72,82
	45	0	5,74	61,22
		1183	13,71	54,15
		4930	34,64	-26,89
	59	0	3,04	68,98
		1252	9,72	0,31
		5215	17,32	47,83

Figure 11. Influence of the oil phase and speed of rotation of the cylinder on the inhibition efficiency for 59°C (332,15K), 6% volume of CO_2, 10 ppm de H_2S and 10 ppm de Inhibitor

that occurred when efficiency inhibitor increased, by increasing fluid velocity in the RCE, after a decrease in efficiency, is the homogenization of the brine-oil-gases-inhibitor system and hence, the inhibitor could diminished the corrosion rate.

CONCLUSIONS

- According to the experimental results, the smaller values obtained for the activation energy corresponded to the Octadecanoic acid and the Didecylamine, which allowed to corroborate its better inhibiting behavior due to their better stability and permanence on the metallic surface to the temperatures tests.

- Under critical testing conditions (4 m/s, 59ºC or 332,15K) amines showed a better efficiency than carboxylic acid, fulfilling the electro-negativity theory applied to inhibitors, since the oxygen is

Table 7. Corrosion rate for steel AISI SAE1020 at 70/30 water cut, using direct current (DC). 6% volume of CO_2 and 10 ppm de H_2S

Compound	Temperature °C	Fluid Velocity (rpm)	Corrosion Velocity (mpy)
Salmuera + 30% Oil	30	0	9,75
		1120	14,6
		4667	24,72
	45	0	14,8
		1183	29,9
		4930	27,3
	59	0	9,8
		1252	9,75
		5215	33,2

more electro-negative than nitrogen and it will not easily leave available the pair of electrons to form the coordinated covalent bond according to Lewis acid-base theory.

- According to the behavior of amines and carboxylic acids obtained from polarization curves, it is deduced that these compounds act through the inhibition mechanism in the interface and for changes in the double electric layer, mechanisms in which, the inhibitor is adsorbed on the surface of the metal to form a two-dimensional structure.

- It was possible to establish from the results obtained for tests with 30% of hydrocarbon cut, that this variable affects negatively the percentage of efficiency of the inhibitor, and this implies many consequences that have not been sufficiently discussed in the literature, due to the consideration that hydrocarbons have some inhibitory power, however, it is very related to the dispersion of mixtures.

ACKNOWLEDGEMENTS

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