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**UNIVERSIDAD NACIONAL AUTÓNOMA DE MÉXICO**

**FACULTAD DE QUÍMICA**

5-Methylmellein as a Corrosion Inhibitor for API 5L X65 in a Saline  
Medium

**ACTIVIDAD DE INVESTIGACIÓN**

QUE PARA OBTENER EL TÍTULO DE:

**INGENIERO QUÍMICO METALÚRGICO**

**PRESENTA:**

**ÁNGEL MAURICIO PEÑA VILLANUEVA**

CIUDAD UNIVERSITARIA, CDMX, AÑO 2021





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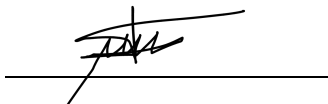
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## **SITIO DONDE SE DESARROLLÓ EL TEMA:**

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# 1. INTRODUCCIÓN

## INTRODUCCIÓN

LA CORROSIÓN MARÍTIMA ES UNO DE LOS TIPOS DE CORROSIÓN MÁS CONOCIDOS Y EL QUE AFECTA A LA INDUSTRIA PETROLERA PRINCIPALMENTE. DEBIDO A DIVERSOS FACTORES MÁS ALLÁ DEL MEDIO SALINO, PESE A ESTE ÚLTIMO SER EL FUNDAMENTAL, COMO LO SON LA ATMÓSFERA DEL SITIO, O LOS MATERIALES EMPLEADOS PARA DICHA INDUSTRIA Y LA SUSCEPTIBILIDAD DE ESTOS CON LA QUE SON ATACADOS.

EL ACERO API 5L X65 HA SIDO EMPLEADO DURANTE MUCHOS AÑOS PARA ESTA INDUSTRIA EN EL TRANSPORTE DE HIDROCARBUROS AL CONTAMINARSE CON EL MEDIO SALINO Y LODOS DE EXTRACCIÓN. POR OTRO LADO, LOS IONES CLORURO ABUNDAN EN LAS ATMÓSFERAS MARINAS POR LAS PARTÍCULAS DE AGUA SALADA PRESENTES. EL DEPÓSITO DE ESTAS PARTÍCULAS SOBRE LA SUPERFICIE DEL ACERO INTENSIFICA EL PROCESO DE CORROSIÓN POR VARIADOS MECANISMOS: AUMENTO DE LA CONDUCTIVIDAD DEL ELECTRÓLITO, FORMACIÓN DE PRODUCTOS DE CORROSIÓN SOLUBLES, ENTRE OTROS [1].

PARA PROTEGER ESTE MATERIAL DE LA CORROSIÓN EN ESTE MEDIO, SE HAN EMPLEADO INHIBIDORES ORGÁNICOS AMIGABLES CON EL MEDIO AMBIENTE, CONSIDERADOS EN SU MAYORÍA COMO “INHIBIDORES VERDES”. LA PROTECCIÓN INTERIOR DE DUCTOS CON INHIBIDORES REQUIERE DE PRUEBAS DE LABORATORIO, QUE DEBEN CUMPLIR LOS INHIBIDORES DE CORROSIÓN BAJO LAS NORMAS NACIONALES O INTERNACIONALES. PARA LA EVALUACIÓN DE INHIBIDORES EN INDUSTRIA PETROLERA SE REQUIERE EL USO DE ELECTRODO DE CILINDRO ROTATORIO PARA SIMULAR LAS DIFERENTES VELOCIDADES DE FLUJO Y EL USO DE UNA SALMUERA DE CLORURO DE SODIO, POR MEDIO DE LA UTILIZACIÓN DE UNA TÉCNICA ELECTROQUÍMICA DE CARACTERIZACIÓN COMO LO ES LA ESPECTROSCOPIA DE IMPEDANCIA ELECTROQUÍMICA (EIS POR SUS SIGLAS EN INGLÉS) [2].

ESTA TÉCNICA, CARACTERIZADA POR SUS SIMILITUDES CON LA LEY DE OHM Y SUS BASES TEÓRICAS FUNDAMENTADAS EN EL CAMPO COMPLEJO, DETERMINADAS A CORRIENTE ALTERNA (CA) BAJO DIFERENTES FRECUENCIAS NOS PERMITE OBTENER PARÁMETROS ELECTROQUÍMICOS PARA EL CONTROL Y LA REDUCCIÓN DE LA VELOCIDAD

DE CORROSIÓN EN PROBLEMAS COMO EL MENCIONADO AL COMENZAR [3].

SI SE DESEA QUE HAYA UN SUMINISTRO DE SUSTANCIA ACTIVA A BAJO COSTO Y EN CANTIDADES GRANDES, LA RESPUESTA PODRÍA HALLARSE NO EN LAS PLANTAS SINO EN LOS HONGOS.

A PARTIR DE ESTA PREMISA, EN EL SIGUIENTE PROTOCOLO SE COMENTA CÓMO DECIDIMOS EVALUAR EL COMPUESTO ORGÁNICO EXTRAÍDO DEL HONGO, PUNTUALMENTE, A LA 5-METILMELEINA.

## 1.1 **OBJETIVOS**

- DETERMINAR LA FUNCIÓN DE LA 5-METILMELEINA COMO INHIBIDOR DE CORROSIÓN CON CADA UNA DE LAS CONDICIONES HIDRODINÁMICAS.
- DETERMINAR LA MAYOR EFICIENCIA DE INHIBICIÓN DE LA 5-METILMELEINA EN FUNCIÓN DE LA CONCENTRACIÓN DE INHIBIDOR Y DE LAS CONDICIONES HIDRODINÁMICAS.

## 2. MATERIALES Y EQUIPO



A CONTINUACIÓN, SE ENLISTA LOS MATERIALES Y EQUIPOS EMPLEADOS EN EL DESARROLLO DE ESTE PROYECTO:

- DISOLUCIÓN DE CLORURO DE SODIO (NaCl) AL 3 % p/v
- PROBETAS PEQUEÑAS DE ACERO API 5L X65 ADAPTADAS CON BARRENO Y CUERDA PARA CILINDRO ROTATORIO (ELECTRODOS DE TRABAJO)
- POTENCIOSTATO
- VASO DE PRECIPITADOS GRADUADO DE 200 ml
- ELECTRODO DE CARBONO DE ½ cm DE DIÁMETRO (CONTRAELECTRODO)
- ELECTRODO DE REFERENCIA DE PLATA/CLORURO DE PLATA (Ag/AgCl saturado)
- EQUIPO DE DISCO ROTATORIO ACOPLADO AL POTENCIOSTATO
- CILINDRO ROTATORIO CON LA CUERDA O TORNILLO NECESARIO PARA LAS MUESTRAS
- PARES DE CABLES CAIMÁN CON UN CAIMÁN A CADA EXTREMO
- CABLES EXTENSORES CON UN EXTREMO DE CAIMÁN

## 2.1 DISEÑO EXPERIMENTAL

A) PREPARAR DISOLUCIÓN DE NaCl 3% p/v, Y PREPARACIÓN METALOGRAFICA DE PROBETAS DEL ACERO API 5L X60 A BASE DE LIJADO Y PULIDO.

B) REALIZAR LA SECUENCIA DE PRUEBAS EN CONDICIONES ESTÁTICAS DE LA FORMA SIGUIENTE: MEDICIÓN DE POTENCIAL A CIRCUITO ABIERTO (OCP), IMPEDANCIA ELECTROQUÍMICA (EIS) Y CURVAS DE POLARIZACIÓN (CP).

LA MEDICIÓN DE OCP SE REALIZARÁ CONTRA ELECTRODO DE PLATA/CLORURO DE PLATA EN UN EQUIPO GILL AC DURANTE 30 MINUTOS.

EIS. LA AMPLITUD DE LA SEÑAL SERÁ DE  $\pm 10$  MV Y EL INTERVALO DE FRECUENCIAS SERÁ DE 10 KHZ A 10 MHZ, EMPLEANDO POTENCIOSTATO GILL AC, ELECTRODO DE REFERENCIA DE PLATA/CLORURO DE PLATA Y CONTRAELECTRODO DE GRAFITO. CÁLCULO DE LA DENSIDAD DE CORRIENTE DE CORROSIÓN ASUMIENDO CONTROL

ACTIVACIONAL A PARTIR DE LA RESISTENCIA A LA TRANSFERENCIA DE CARGA MEDIANTE LA ECUACIÓN DE STERN-GEARY.

LAS CP SE REALIZARÁN CON SOBREPOTENCIALES DESDE -500 mV HASTA +500 mV CON EL MISMO ARREGLO EXPERIMENTAL YA DESCRITO EN (D). VELOCIDAD DE BARRIDO 1 mV/s.

C) PARA LAS CONDICIONES HIDRODINÁMICAS (500 RPM Y 1000 RPM), CONDICIONES DE TURBULENCIA DE ACUERDO A LA NORMA NRF-007 PEMEX-2009, SOLAMENTE SE REALIZARÁ EIS DE ACUERDO CON LAS CONDICIONES INDICADAS A PARTIR DEL INCISO

(D).

D) LAS CONCENTRACIONES DE INHIBIDORES A EMPLEAR SON 0, 10, 20 Y 50 ppm.

E) TODOS LOS ENSAYOS SE REALIZARÁN POR TRIPLICADO.

### 3. ARTÍCULO PUBLICADO

## 5-Methylmellein as a Corrosion Inhibitor for API 5L X65 in a Saline Medium

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The polyketide 5-methylmellein was isolated from *Biscogniauxia* sp. (Xylariaceae), an endophytic fungal strain obtained from an epiphytic bromeliad species collected in the Ecological Reserve at the Universidad Nacional Autónoma de México. This compound was investigated as a corrosion inhibitor for metallic materials, such as API 5L X65, in a corrosive 3% NaCl solution using electrochemical technique (electrochemical impedance spectroscopy). The results showed that 50 ppm of 5-methylmellein protected the metallic surface. Measurements at different rotation rates (500 and 1000 rpm) indicate that this compound decreases the charge transfer resistance ( $R_{ct}$ ) as a result of the desorption of organic molecules.

### Introduction

Corrosion of metallic materials is an undesirable process for many applications (1), ranging from structural damage of buildings to catastrophic failures in different industries. In the oil and petrochemical industries, particularly for the hydrocarbons transport pipes (2), corrosion inhibition is crucial.

Corrosion inhibitors are commonly used to obtain strong and durable metallic objects. These are compounds that, when added to the metallic object, enable the control of corrosion by decreasing its rate. API 5L X-65 steel is a special steel made for the pipes construction industry. This carbon steel has high resistance, which is necessary for the transport of raw materials and final products in the oil industry (3).

Among the vast number of corrosion inhibitors (alkanes, alkenes, alkynes or aromatic compounds group), there are hydrocarbons with big ramifications, either compounds inside of the principal of the. Inhibitors can be from natural or synthetic origin. An example of the former is 5-methylmellein (Figure 1) (4). Thus, the aim of this work was to evaluate the corrosion inhibitory properties of 5-methylmellein in carbon steel.

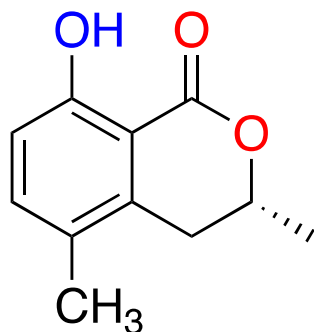


Figure 1. 5-methylmellein [(R)-8-hydroxy-3,5-dimethyl isochroman-1-one].

## Experimental

### Isolation and identification of 5-methylmellein

The endophyte fungal strain *Biscogniauxia* sp. (Xylariaceae), was isolated from an epiphytic bromeliad collected in the Ecological Reserve at the Universidad Nacional Autónoma de México, Mexico City (4). The fungal strain was deposited at the personal collection from Dr. Figueroa's research group at the Faculty of Chemistry, UNAM, and identified based on the morphological characteristics and ITS molecular sequence analysis

Seed cultures of the fungal strain (15 mL) were grown for five days on YESD media and then used to inoculate five Erlenmeyer flasks with rice media (15 g/30 mL of H<sub>2</sub>O). The fungus was grown for 21 days and extracted with 60 mL of 1:1 MeOH-CHCl<sub>3</sub>. Then, the extract was defatted with hexane as previously described (4). Separation and purification were done by chromatographic means yield a yellow anamorphous powder characterized as 5-methylmellein by comparing its NMR and HRESIMS data with those reported (4).

### API 5L X65 steel

The following is the average commercial composition of the steel (5):

**Table I.** Chemical composition of API 5LX65

<i>Grade</i>	<b>C</b>	<b>Mn</b>	<b>P</b>	<b>S</b>
X65	0.24 Max	1.60	0.30 Max	0.30 Max

### Electrochemical evaluation

The potential was stabilized for 1800 seconds to ensure that it was in steady state using the Gill- Ac potentiostat. The inhibitor 5-methylmelleine was added at different concentrations (0 to 50 ppm). By electrochemical impedance spectroscopy (EIS), using

the amplitude  $\pm 10$  mV, frequency interval 100 KHz to 0.1 Hz). Working electrode: API 5L X65 ( $A = 3.8 \text{ cm}^2$ ). Reference electrode: saturated Ag /AgCl. Counter electrode: graphite.

## Results and discussion

In the Nyquist diagram (Figure 2) for API 5L X65 steel without inhibitor, a time constant is observed for the static state, which is attributed to charge transfer resistance ( $R_{tc}$ ) (6). For 500 and 1000 rpm, the semicircle is depressed, and two-time constants are proposed: one related to charge transfer resistance and the other to a corrosion process (7).

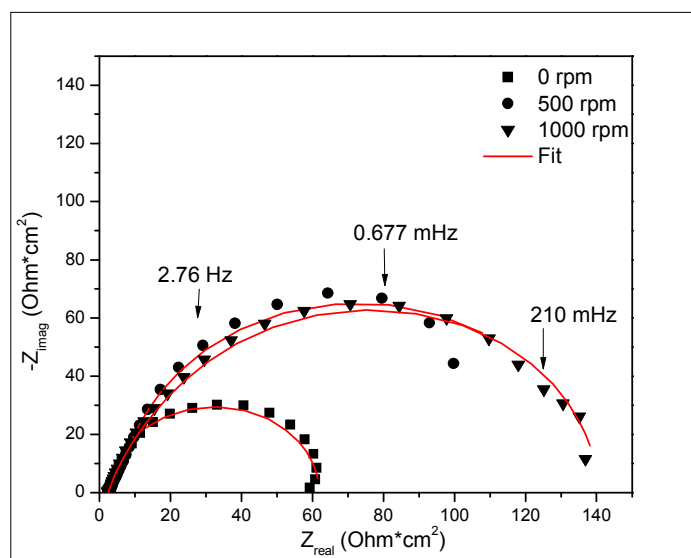


Figure 2. Nyquist diagram of API 5L X65 without inhibitor at different rotation rates

Nyquist diagrams for API 5L X65 steel immersed in 3% NaCl in the presence of different concentrations of 5-methylmellein under static conditions and at different rotational rates are shown in Figure 3. In presence of the inhibitor, the semicircle remarkably increases compared to the one with no inhibitor; the semicircle shape is depressed, therefore, two time constants are proposed: one attributed to the resistance of adsorbed organic molecules and the second to the charge transfer resistance (8). In addition, as the concentration increases, the semicircle diameter increases and thus the corrosion process decreases (Figure 3b).

For hydrodynamic conditions (500 and 1000 rpm) were observed two-time constants and the Nyquist diagrams indicate that one time constant at high frequencies is attributed to the formation of a film, composed of the corrosion products and the attached inhibitor molecules, while the second time constant, a semicircle at low frequencies, is attributed to the charge transfer resistance in the pores or defects of the film formed by the corrosion products.

At 500 rpm, Figure 3b the  $Z_{\text{real}}$  value constantly increases as the concentration of the inhibitor increases, reaching a maximum value of  $303 \Omega \text{ cm}^2$  for 50 ppm (9).

Comparing 0 rpm (Figure 3a) and 500 rpm (Figure 3b), there is a considerable decrease in the semicircle diameter because the rotation dynamics leads to an increase of the adsorption-desorption process of organic molecules (10).

At 1000 rpm (Figure 3c) the semicircle diameter reached a maximum at 10 ppm, then the diameter decreases when the concentration of 5-methylmellein further increases (20 or 50 ppm). Comparing 500 and 1000 rpm, at low 5-methylmellein concentrations, the inhibitor has a faster desorption process at 500 rpm because the  $Z_{\text{real}}$  value is lower.

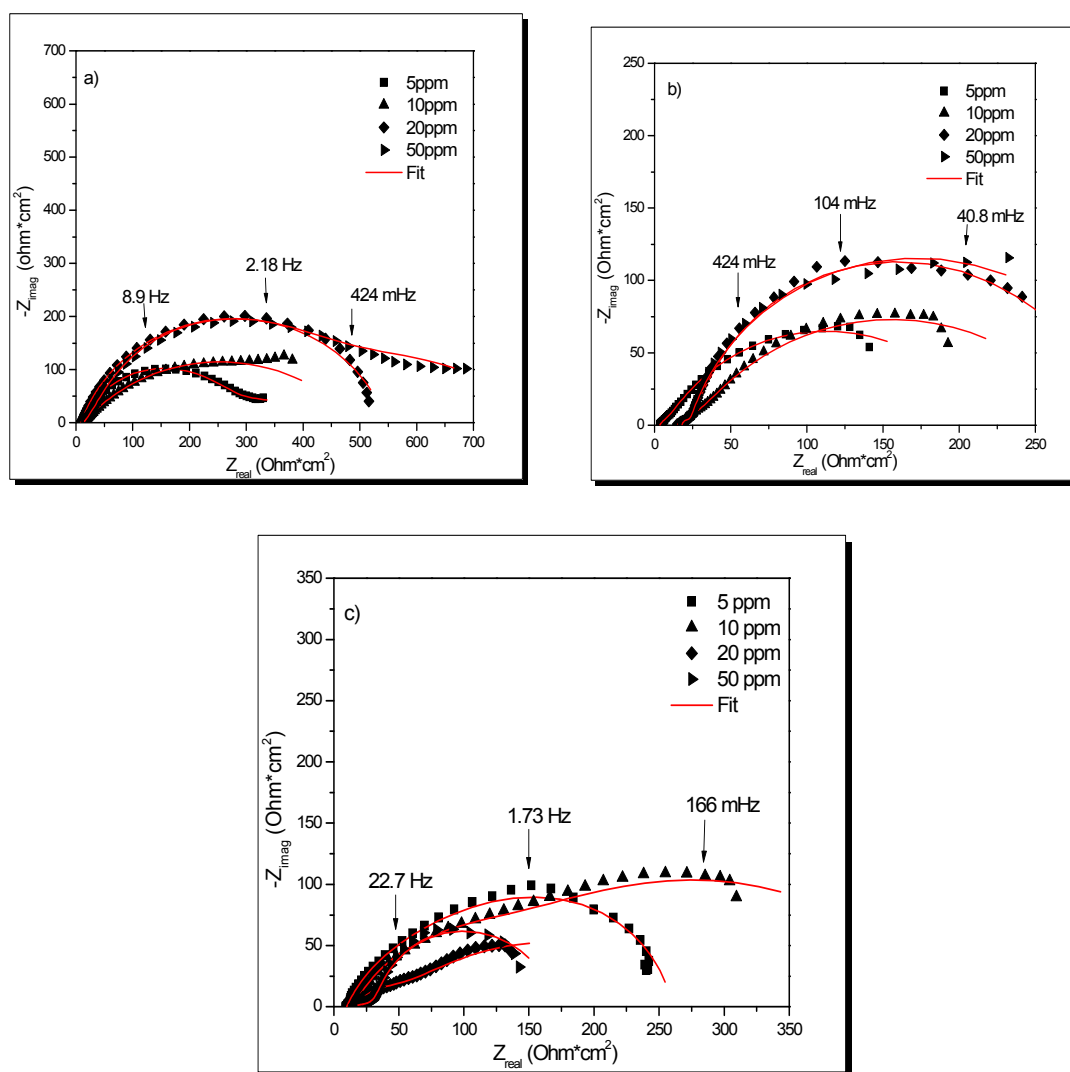


Figure 3. Nyquist diagrams for API 5L X65 with 5-methylmellein as inhibitor a) under static conditions (0 rpm), at b) 500 and c) 1000 rpm.

The inhibition efficiency ( $IE$ ) (11) is given by Equation 1:

$$IE (\%) = \frac{\left(\frac{1}{R_p}\right)_{blank} - \left(\frac{1}{R_p}\right)_{inhibitor}}{\left(\frac{1}{R_p}\right)_{blank}} \times 100 \quad [1]$$

Where  $R_p$  blank and  $R_p$  inhibitor are the polarization resistance without and with the inhibitor, respectively.

The polarization resistance ( $R_p$ ) is given by equation 2:

$$R_p = R_{ct} + R_F \quad [2]$$

The double-layer capacitance ( $C_{dl}$ ) was calculated from the constant phase element (CPE) using Brug's equation (3) (12):

$$C_{dl} = Y_0^{1/n} \cdot [(1/R_s) + (1/R_{ct})]^{(n-1)/n} \quad [3]$$

where  $Y_0$  is the CPE constant,  $n$  is the CPE exponent, that can be used as an indicator of the heterogeneity or roughness of the surface.  $R_s$  is the solution resistance and  $R_{ct}$  is the charge transfer resistance.

The equivalent electric circuit 'a' was used for the system without inhibitor and 'b' for the system with different concentrations of 5-methylmellein (Figure 4).

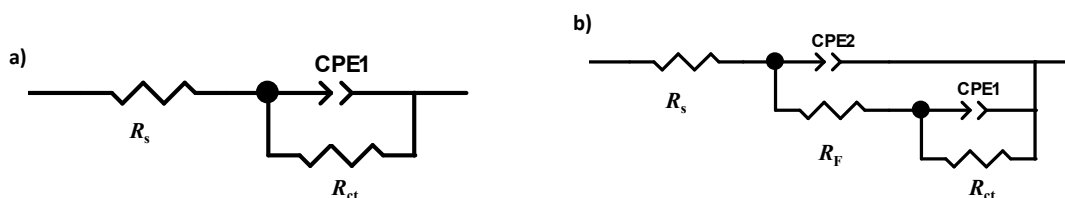


Figure 4. Equivalent electric circuits.

Where the solution resistance ( $R_s$ ), charge transfer resistance ( $R_{ct}$ ), double electrochemical layer capacitance ( $C_{dl}$ ), and organic molecules film resistance ( $R_F$ ).

For the equivalent electric circuits fitting of the Nyquist diagram at different inhibitor concentrations are shown in Table II for both, static and hydrodynamic conditions.

The charge transfer resistance values ( $R_{ct}$ ) increase as the concentration of 5-methylmellein increases, which can be attributed to the enhanced protection of the metal as the concentration increases. At 1000 rpm, the highest  $R_{ct}$  value is at 10 ppm (74.8% inhibition efficiency). Finally, the charge transfer resistance values under turbulent flow conditions decrease compared to static conditions, this can be attributed to the desorption process of organic molecules (13).



On the other hand, the double layer capacitance values ( $C_{dl}$ ) were lower with respect to the target due to a decrease in the local dielectric constant and/or an increase in the thickness of the electric double layer, suggesting that the inhibitor molecules act via adsorption on the interface metal/solution.

**Table II.** Electrochemical parameters obtained from the Nyquist plots analysis for API 5L X65 steel immersed in saline media with and without 5-methylmellein under hydrodynamic conditions.

<i>Rotation Rate</i>	<i>C (ppm)</i>	<i>R<sub>s</sub> (Ωcm<sup>2</sup>)</i>	<i>n</i>	<i>C<sub>dl</sub> (μF/cm<sup>2</sup>)</i>	<i>R<sub>ct</sub> (Ω cm<sup>2</sup>)</i>	<i>R<sub>F</sub> (Ω cm<sup>2</sup>)</i>	<i>R<sub>p</sub> (Ω cm<sup>2</sup>)</i>	<i>IE (%)</i>
0	0	2.9	0.8	421.9	59	-	59	-
	5	12.2	0.8	30.9	246.5	177.4	423.9	86.1
	10	13.4	0.8	15.6	481.7	-	481.7	87.8
	20	8.8	0.8	41.6	539.2	-	539.2	89.1
	50	12.3	0.8	14.3	532.2	291.3	823.5	92.8
500	0	2.5	0.7	33.4	128.6	6.997	135.6	-
	5	3.5	0.7	36.9	208.4	6.598	215.0	40.2
	10	16.5	0.8	70.5	254.6	15.36	270.0	52.4
	20	13.9	0.9	38.8	224.5	30.5	255.0	49.6
	50	18.0	0.9	53.9	298.3	4.741	303.0	57.6
1000	0	2.4	0.8	61.3	113.3	25.04	113.3	-
	5	9.8	0.7	51.8	121.1	12.83	133.9	15.4
	10	15.0	0.8	37.5	341.3	108.8	450.1	74.8
	20	16.0	0.7	74.6	245.7	28.72	274.4	58.7
	50	9.8	1.0	95.2	121	129.7	250.7	76.5

## Conclusions

The corrosion inhibition efficiency of 5-methylmellein for API 5L X65 steel in saline medium, simulating an oil-well environment, was investigated. The best inhibition activity was reached at a concentration of 50 ppm ( $IE \sim 90\%$ ) under static conditions.

The inhibition is better at 1000 rpm than 500 rpm because there is a homogeneous solution, allowing the organic molecules to be more easily adsorbed to the metal surface.

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