

## **The Effect of Temperature and Critical Micelle Concentrations (CMC) on the Inhibition Performance of a Quaternary Ammonium-Type Corrosion Inhibitor**

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### **ABSTRACT**

Corrosion inhibition is a highly effective strategy for mitigating metal degradation. However, the effect of high temperature on inhibitor effectiveness is not well documented in the literature. More specifically, the concept of critical micelle concentration (CMC), often used to select optimal inhibitor dosage, is typically based on room temperature experiments and needs to be validated over a wider range of conditions. In the research reported herein, electrochemical measurements were conducted to evaluate the performance of an alkylbenzyltrimethylammonium chloride inhibitor against CO<sub>2</sub> corrosion of mild steel at various temperatures (25°C to 80°C) in a 1 wt.% NaCl electrolyte. CMC values were also evaluated at the same temperatures using a tensiometer to investigate the connection between inhibitor concentration, micellization, and inhibition efficiency. The results showed that the performance of this quaternary ammonium-type inhibitor was extremely sensitive to temperature. The amount of inhibitor required to achieve sufficient efficiency increased considerably from 25°C to 50°C, and no sign of inhibition was observed at 80°C, even at very high inhibitor dosage. CMC values can only partially predict the minimum inhibitor concentration required to provide sufficient protection at 25°C and 50°C, but this concept failed at 80°C. It was further postulated that the structure of the adsorbed inhibitor layer significantly changed with temperature.

**Key words:** CO<sub>2</sub> corrosion, corrosion inhibitor, effect of temperature, CMC, quaternary ammonium type inhibitor.

## INTRODUCTION

In the oil and gas industry, organic inhibitors have been used to control corrosion issues in the production and transportation pipelines for many decades. Their affordability and efficiency made them an extensively applied corrosion mitigation strategy in the field. To better predict inhibitor performance, many research efforts have been made to understand their capabilities and associated mechanistic characteristics<sup>1-6</sup>. Some published research works have focused on the investigation of the behavior of inhibitor molecules<sup>1-3</sup>, some on the development of methodologies for inhibitor performance evaluation<sup>4</sup> and some on standards for inhibitor selection<sup>5, 6</sup>. Most of these experimental works were done in low pressure, low temperature glass cell systems. However, some unexpected behavior has been observed when inhibitors are introduced into more severe working environments. More specifically, limited effectiveness of quaternary ammonium type-inhibitors has been reported at elevated temperatures. Li *et.al*,<sup>7</sup> investigated the inhibition performance of a quaternary ammonium type inhibitor at different temperatures and found that the inhibitor failed to provide protection against CO<sub>2</sub> corrosion at 70°C. Some other researchers also noticed that the performance of inhibitors was lost, or could not be easily distinguished from the effect of corrosion products at high temperature<sup>8,9</sup>. Although examples of limited performance have been identified by many researchers, the reasons for the failure of inhibition of quaternary ammonium-type inhibitors at higher temperature remain unclear.

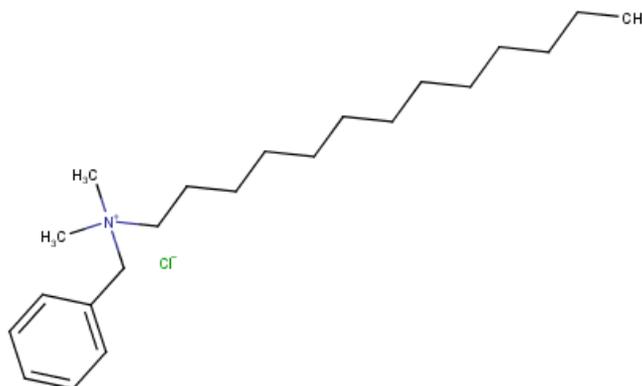
The weak protection at high temperature has been reported to be likely associated with the adsorption/desorption equilibrium of quaternary ammonium inhibitors<sup>10</sup>. It is well-known that performance of quaternary ammonium type inhibitor generally decreases with increasing temperature because desorption of inhibitor is favored at elevated temperatures. However, this may not be the main reason for the failure of the inhibitors since, if the desorption is favored and leads to a lower efficiency, the efficiency should still increase with higher dosage of that inhibitor. However, this was not observed experimentally<sup>7</sup>. Another possible reason for the inhibition failure could be related to the potential degradation of the inhibitor at higher temperatures. This also may not be the case because recent research has shown that the structure of the quaternary ammonium type inhibitor was not altered at elevated temperature using UV-Vis spectroscopy<sup>11</sup>. Another proposed explanation for the inhibitor failure can be related to the role of critical micelles concentration (CMC). To investigate this aspect, Li *et.al*<sup>7</sup> determine the CMC of the quaternary ammonium type inhibitor at 70°C and used this concentration to test the inhibitor efficiency at that same temperature. However, the inhibitor did not provide any protection against CO<sub>2</sub> corrosion in these conditions. This indicates that an inhibitor which exhibits micellar behavior does not necessarily provide protection against corrosion. One last scenario could be hypothesized: the loss of inhibitor efficiency could be due to changes in the inhibitor layer structure at high temperature. However, minimal research efforts have been made in this respect.

The aim of the current study is to test the above hypothesis. The CMC of a quaternary ammonium type inhibitor was investigated from 25°C to 80°C and the performance of the inhibitor against CO<sub>2</sub> corrosion of carbon steel was also examined using electrochemical methods (linear polarization resistance (LPR)), at the same temperatures. The inhibitor layer packing behavior was predicted using Gibbs Isotherm<sup>12</sup>. It was determined by measuring the surface tension and by calculating the surface area occupied per each molecule.

## EXPERIMENTAL PROCEDURE AND TEST MATRIX

### Tested inhibitor

The tested quat-type inhibitor was an alkylbenzyltrimethylammonium chloride. Its molecular structure is given in Figure 1. The inhibitor was added as a package which composition is given in Table 1. The composition of this inhibitor is relatively simple since the quat-type inhibitor is a polar organic salt, which is already relatively soluble in water. Therefore, no additional solvent was required in the package.



**Figure 1: General Structure of the Alkylbenzyltrimethylammonium Chloride Inhibitor**

**Table 1  
Package Information of Quat-Type Inhibitor**

	Alkylbenzyltrimethylammonium chloride	water
<b>Percentage by volume</b>	24%	76%

## Surface tension measurement

The surface tension was measured with the KRÜSS<sup>1</sup> K20 tensiometer in a 1 wt.% NaCl aqueous solution. The temperature of the solution was controlled using a heating jacket. The tested temperatures were 25°C, 50°C and 80°C. Solutions with different concentrations of inhibitor were prepared and then the surface tension was measured directly in the solutions. The measurements of surface tension of each concentration were repeated at least twice.

## Corrosion measurement

Corrosion experiments were carried out in a typical three electrode glass cell. The tested specimens were made from X65 carbon steel. The setup and the procedures as well as the composition of X65 steel can be found in the author's earlier work<sup>13</sup>. Each experiment was repeated at least twice.

## Corrosion test matrix

The corrosion test matrix can be found in Table 2. The tested temperatures were the same as for the surface tension measurements. The range of inhibitor concentrations tested was different at different temperatures because the concentration of the quat-type inhibitor required for delivering adequate performance was much higher at higher temperatures. In this document, the inhibitor concentrations are labelled as ppm by volume

**Table 2**  
**Test Matrix for Corrosion Measurements of the Quat-Type Inhibitor**

Description	Parameters
Temperature/°C	25                      50                      80
Electrolyte	1 wt.% NaCl solution saturated with CO <sub>2</sub>
Inhibitor	Quat-type inhibitor
Inhibitor concentration/ppm	Concentration varies at different temperature
Material	API 5L X65
pH	4.0
Stirring bar speed/rpm	200
Techniques applied	Linear polarization resistance (LPR), open circuit potential (OCP)

<sup>1</sup> Trade Name

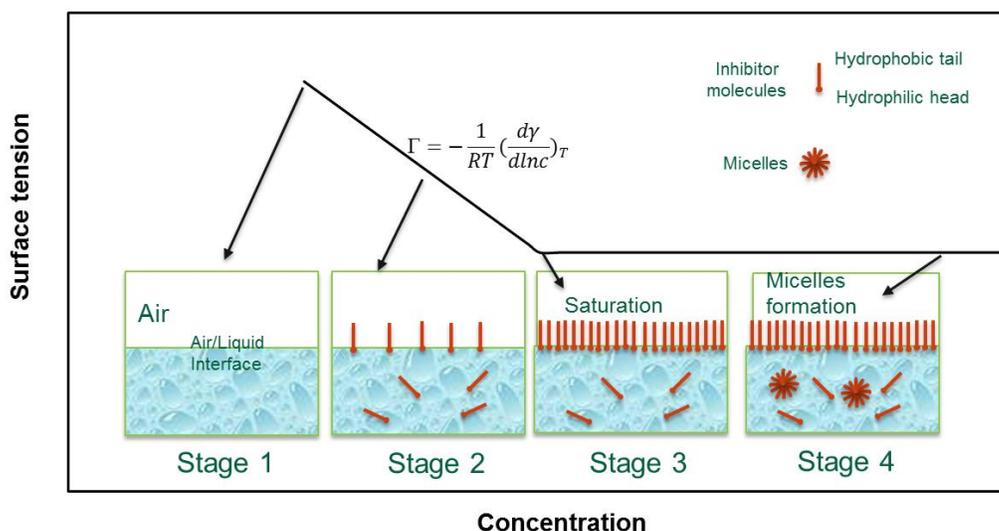
## RESULTS AND DISCUSSION

### The effect of temperature on the CMC of the quat-type inhibitor

The determination of CMC is usually done by measuring the surface tension using solutions at different inhibitor concentrations<sup>14</sup>. Since the inhibitor molecules are comprised of a hydrophilic head group and a hydrophobic tail, they are attracted to the interfaces (water/gas, water/solid, or water/oil) where the hydrophobic tail orients to minimize its interaction with water. This process is schematically described in Figure 2, considering a water/gas interface. As the concentration of an inhibitor increases, more inhibitor molecules accumulate at the interface and therefore lead to a gradual decrease in surface tension at the interface (stage 2). The CMC represents the inhibitor concentration corresponding to a situation where the interface is fully occupied by inhibitor molecules. When the inhibitor concentration is higher than the CMC, these molecules do not go to the interfaces anymore but accumulate in the solution (stage 3) by forming micelles to minimize contact between the water and tail group. At this point, the surface tension does not increase anymore, and the excess inhibitor molecules start to aggregate into micelles in the aqueous phase (stage 4). By finding the cross point of stage 2 and stage 4, the CMC can be easily obtained. The decrease in surface tension is usually a linear relationship with the logarithm of inhibitor concentration. This is because the surface tension is also linearly related to the logarithm of the adsorbed inhibitor concentration as shown in Equation (1)<sup>12</sup>.

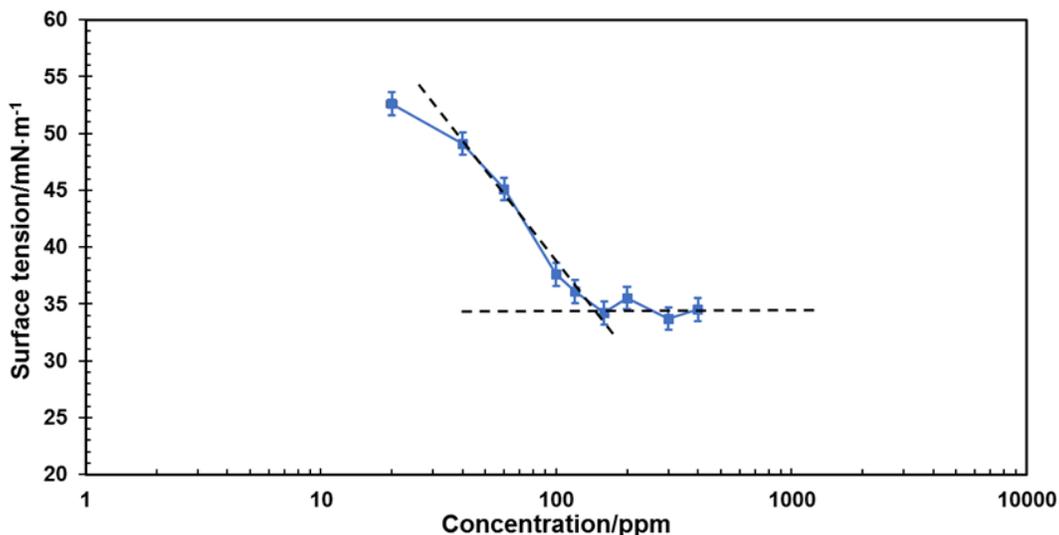
$$\Gamma = -\frac{1}{RT} \left[ \frac{d\gamma}{d(\ln c)} \right]_T \quad (1)$$

Where,  $\Gamma$  is the surface excess concentration ( $\text{mol}\cdot\text{m}^{-2}$ ),  $\gamma$  is the surface tension ( $\text{N}\cdot\text{m}^{-1}$ ),  $c$  is the inhibitor concentration ( $\text{mol}\cdot\text{m}^{-3}$ ),  $R$  is the gas constant ( $8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) and  $T$  is temperature (K). This linear relationship is only valid during stage 2.



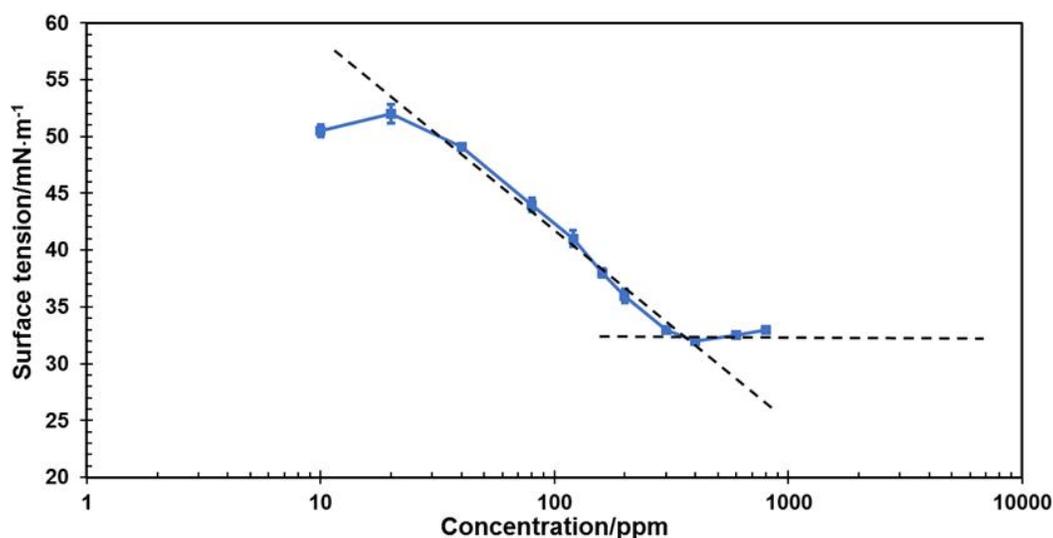
**Figure 2: The Schematic of the Formation of Micelles**

The change in surface tension with inhibitor concentrations is shown in Figure 3 for 25°C. The surface tension of 1 wt.% NaCl solution was around 72 mN·m<sup>-1</sup>. With the introduction of corrosion inhibitor, the surface tension first decreased almost linearly from 52 to 33 mN·m<sup>-1</sup> and then remained constant even as more inhibitor was added (up to 400 ppm). According to the definition of CMC (Figure 2), the CMC value of the quat-type inhibitor at 25°C can be determined at 130±5 ppm.

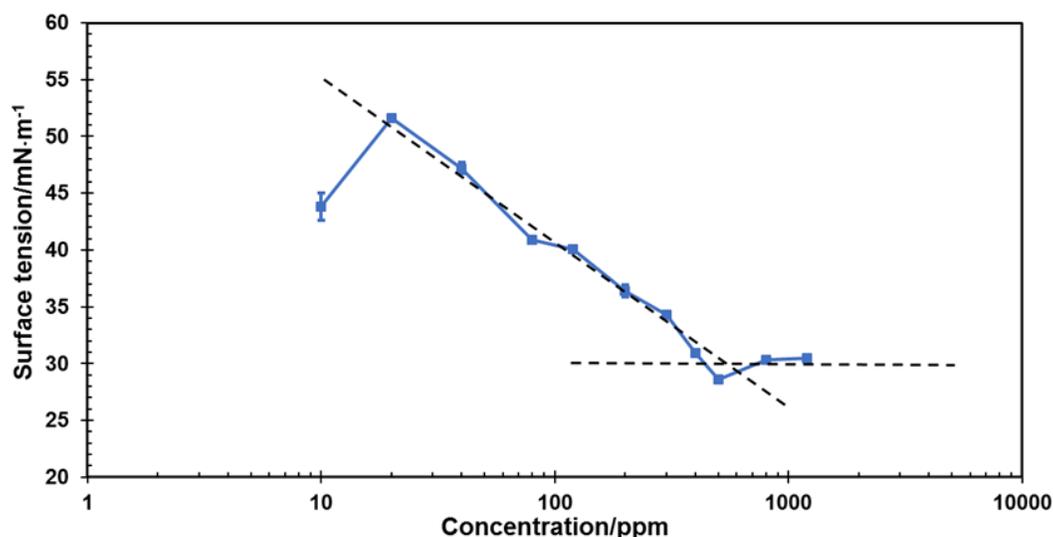


**Figure 3: Surface Tension Vs. The Quat-Type Inhibitor Concentration at 25°C in 1 Wt. % NaCl Solution**

The changes of surface tension with inhibitor concentration at 50°C and 80°C are shown in Figure 4 and Figure 5, respectively. Results show that the CMC values of the quat-type inhibitor at 50°C and 80°C are 375±5 and 495±5 ppm, respectively. Clearly, there was a significant change of CMC with the tested temperatures, as observed by other researchers <sup>7</sup>.



**Figure 4: Surface Tension Vs. the Quat-Type Inhibitor Concentration at 50°C in 1 Wt. % NaCl Solution**

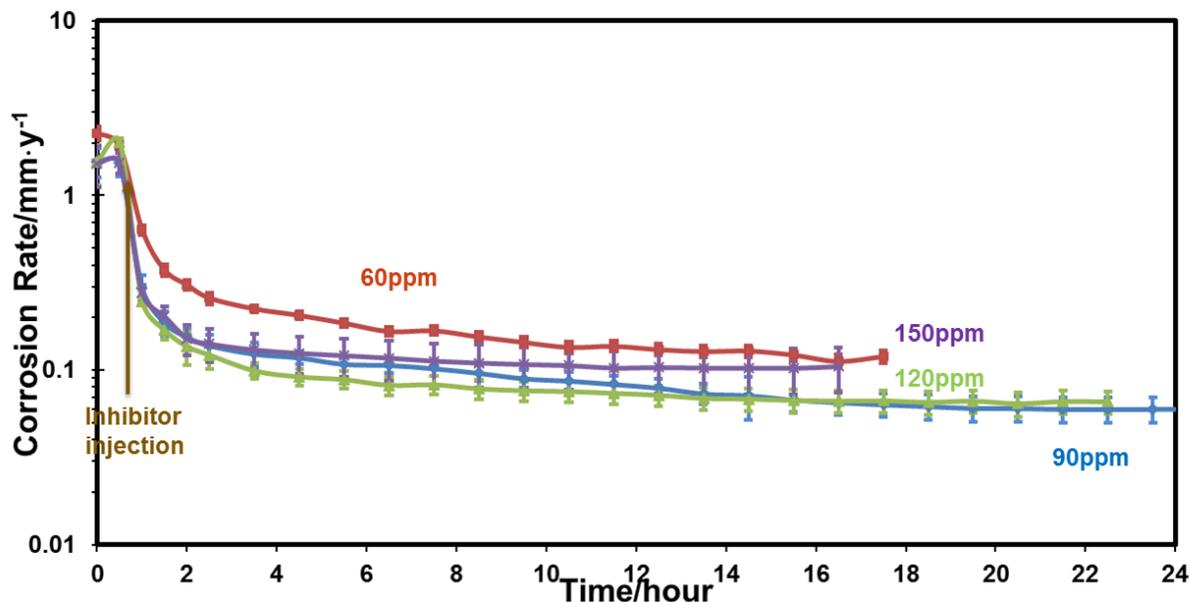


**Figure 5: Surface Tension Vs. the Quat-Type Inhibitor Concentration at 80°C in 1 Wt. % NaCl Solution**

### The effect of temperature on the performance of quat-type inhibitors

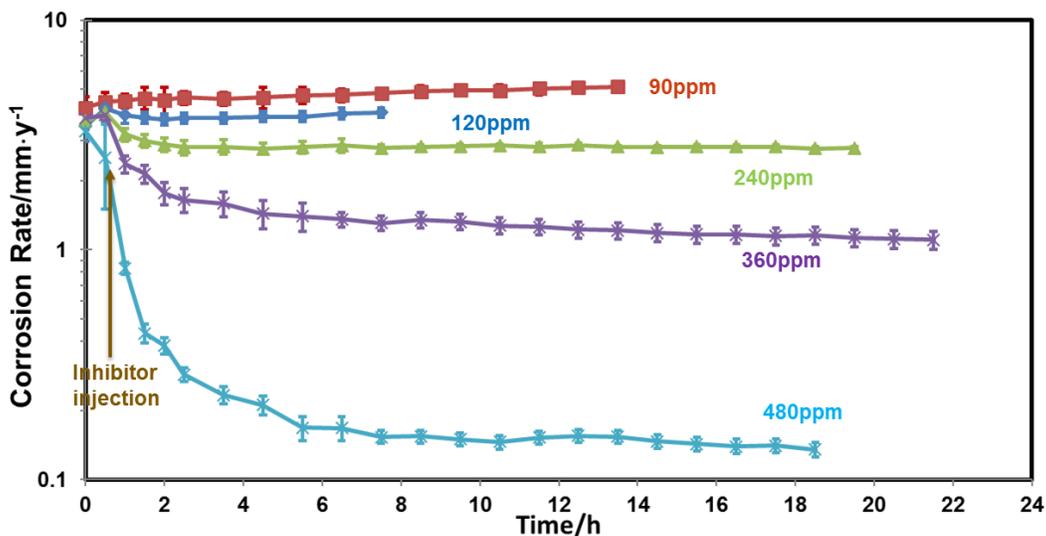
In this section, the inhibition performance of the quat-type inhibitor was evaluated at 25°C, 50°C and 80°C, and the results are shown in Figure 6, Figure 7 and Figure 8, respectively. The quat-type inhibitor exhibited excellent inhibition performance at 25°C. With the injection of 60 ppm quat-type inhibitor, corrosion rates quickly decreased to 0.4mm·y<sup>-1</sup> over the first two hours of exposure and stabilized around 0.15mm·y<sup>-1</sup> after 10

hours. Similarly, with the injection of 90 ppm, 120 ppm and 150 ppm inhibitor, the corrosion rates decreased to 0.06, 0.06 and 0.09 mm·y<sup>-1</sup>, respectively. For comparison, the CMC of the inhibitor at 25°C was determined to be 130±5 ppm.



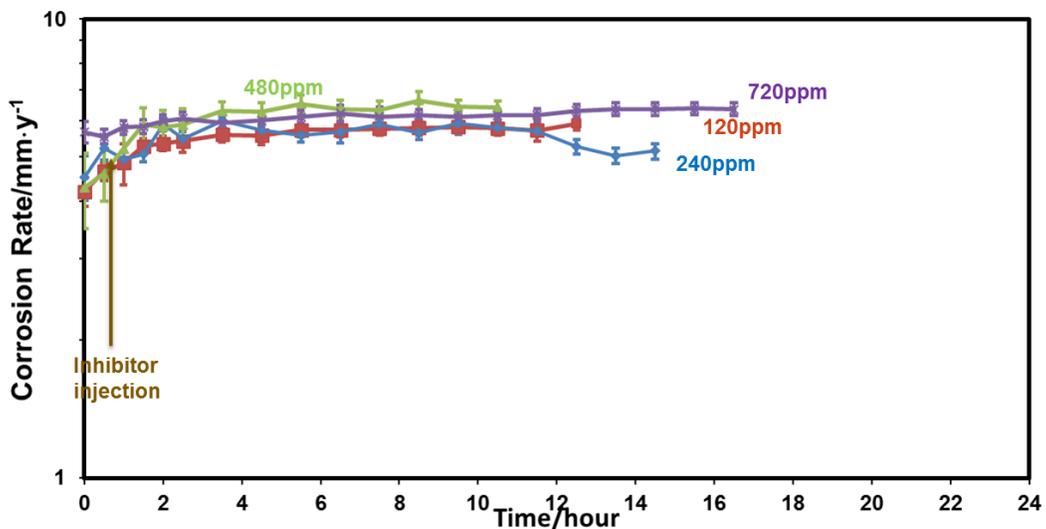
**Figure 6: Corrosion Rates with the Injection of Different Concentrations of Quat-Type Inhibitor at 25°C. (1 Wt.% NaCl, pH=4.0, X65 Mild Steel; B=23 mV/Decade)**

However, at 50°C, the inhibition ability of the quat-type inhibitor was significantly diminished. The injection of 90 ppm and 120 ppm corrosion inhibitor did not provide any protection at all, as the corrosion rate basically did not change with the addition of the inhibitor. A higher dosage was added to determine whether the inhibitor could have any effect at this temperature. The presence of 240 ppm and 360 ppm inhibitor did decrease the corrosion rates to 2.8 mm·y<sup>-1</sup> and 1.1 mm·y<sup>-1</sup>, respectively. Eventually, 480 ppm of inhibitor (slightly higher than 1CMC at 50°C) was necessary to decrease the corrosion rate to 0.14 mm·y<sup>-1</sup>. As a comparison, only 60 ppm inhibitor was required to achieve the same results at 25°C. Clearly, the inhibition performance of the quat-type inhibitor was significantly diminished at 50°C. Yet, the inhibitor eventually performed well at a dosage similar to the measured CMC at 50°C.



**Figure 7: Corrosion Rates with the Injection of Different Amounts of Quat-Type Inhibitor at 50°C (1 Wt.% NaCl, pH=4.0, X65 Mild Steel; B=23 mV/Decade)**

The performance of the quat-type inhibitor deteriorated even further at 80°C. There was no significant change in corrosion rate even with the addition of 720 ppm of the quat-type inhibitor. Figure 8 shows that the corrosion rates essentially did not change over the tested period, no matter what concentrations of inhibitor (120-720 ppm) were introduced. This lack of protection suggests that the inhibitor was likely completely ineffective at 80°C. For comparison, the CMC of the inhibitor at 80°C was determined to be  $495 \pm 5$  ppm.



**Figure 8. Corrosion Rates with the Injection of Different Amount of Quat-Type Inhibitor at 80°C (1 Wt.% NaCl, pH=4.0, X65 Mild Steel; B=23 mV/Decade)**

The inhibition efficiency of the corrosion inhibitor was calculated based on the following equation:

$$\text{Inhibition efficiency}(\eta) = \left(1 - \frac{CR_{inh}}{CR_{uni}}\right) \times 100\% \quad (2)$$

Where,  $CR_{inh}$  is the steady state inhibited corrosion rate and  $CR_{uni}$  is the initial (baseline) corrosion rate without inhibitor in  $\text{mm}\cdot\text{y}^{-1}$ . The inhibition efficiencies values at different temperatures are given in Table 3. The inhibition efficiency usually increased with higher concentration of inhibitor at the same temperature. The performance of the inhibitor also decreased with temperature. At  $25^\circ\text{C}$ , 120 ppm inhibitor conferred 97% protection against corrosion. However, this concentration of inhibitor provided no protection at  $50^\circ\text{C}$  or at  $80^\circ\text{C}$ . In addition, no inhibition was observed at  $80^\circ\text{C}$  even with 720 ppm quat-type inhibitor. This behavior suggests that the performance of quat-type inhibitors is critically dependent on temperature. These results all agree well with other researchers' observations <sup>7</sup>.

**Table 3**  
**Inhibition Test Results with the Quat-Type Inhibitor from  $25^\circ\text{C}$  to  $80^\circ\text{C}$**

Temperature $^\circ\text{C}$	Inhibitor concentration/ppm	Initial corrosion rate/ $\text{mm}\cdot\text{y}^{-1}$	Final corrosion rate/ $\text{mm}\cdot\text{y}^{-1}$	Localized corrosion	Inhibition efficiency
25	60	2.1	0.12	No	94%
	90	1.55	0.06	No	96%
	120	1.8	0.06	No	97%
	150	1.53	0.10	No	94%
50	90	4.2	5.0	No	-
	120	3.9	3.9	No	-
	240	3.9	2.8	No	28%
	360	3.9	1.1	No	72%
80	480	3.8	0.14	No	96%
	120	4.8	5.9	No	-
	240	4.9	5.2	No	-
	480	4.7	6.4	No	-
	720	4.2	6.4	No	-

\* Here, '-' indicates that the inhibition efficiency was such that there was no inhibited corrosion rate.

The correlation between the CMC values and the concentration required for adequate protection was also dependent on temperature. At  $25^\circ\text{C}$ , the minimum effective concentration is in agreement with corrosion inhibition measurement, which showed that inhibition efficiency did not change past 120 ppm of inhibitor. In general, the inhibition performance is expected to increase with inhibitor concentration for values below the CMC. The inhibition efficiency should remain unchanged for inhibitor concentration above the CMC because it was assumed that the surface is optimally covered with

inhibitor at this point. Moreover, the minimum effective concentration (480 ppm) of the inhibitor at 50°C also agreed with CMC value obtained at 50°C (375±5 ppm). Therefore, a link could be established between the lack of inhibitor performance and increase in the CMC at elevated temperatures, at least up to 50°C. However, this potential correlation between optimum inhibitor concentration and CMC did not seem to hold at 80°C. No protection was observed at 80°C even up to 720 ppm, despite the fact the CMC was determined as 495±5 ppm. Clearly, something else is responsible for the inadequate performance of this quaternary ammonium type inhibitor at elevated temperatures. Consequently, further investigations were performed to find the reason behind the inhibition failure of the quat-type inhibitor at 80°C.

### The effect of temperature on the structures of the adsorbed layer

One possible explanation for the complete loss in inhibition efficiency at 80°C could be related to the change of planar density of the adsorbed molecules. The CMC measurements clearly show that the inhibitor molecules still accumulated at the air/water interface at 80°C as it did at 25°C and 50°C. However, the adsorption of the inhibitor on the steel surface was clearly different, as shown by the corrosion rate results, at 80°C, compared to 25°C or 50°C. It can be hypothesized that the structure of the inhibitor layer changed at elevated temperatures. One of the possible changes is that the layer can become loosely packed.

To investigate this, the surface areas per molecule of the quat-type inhibitor at 25°C, 50°C and 80°C are calculated and shown in Table 4. The area per molecule is calculated through the following equation:

$$a = \frac{10^{20}}{N_{avog} \Gamma} \quad (3)^{12}$$

where  $a$  is the surface area occupied per molecule ( $\text{\AA}^2 \cdot \text{molecule}^{-1}$ ),  $N_{avog}$  is the Avogadro constant ( $6.02 \times 10^{23} \text{ mol}^{-1}$ ), and  $\Gamma$  is the surface excess ( $\text{mol} \cdot \text{m}^{-2}$ ) that can be calculated through Equation (1). To validate the calculated values, the surface area of the quat-type inhibitor is also determined using a molecule footprint method generated using Avogadro software<sup>15</sup>. The estimated surface areas of the quat-type inhibitor using footprint methods is  $54 \text{ \AA}^2$ <sup>16</sup>. These values agree well with the values obtained using Equation (3). Table 4 shows that the 'a' value of the quat-type inhibitor increases from 36 to  $107 \text{ \AA}^2 \cdot \text{molecule}^{-1}$  as the temperature increases from 25°C to 80°C. This means that the surface area per molecule increased three times over the tested range of temperatures. This significant change might explain why inhibition failed at 80°C. A low 'a' value means that the inhibitor molecules are closely packed at interfaces. An increase of the 'a' value of the quat-type inhibitor with temperature suggests that the quat-type inhibitor molecules lose their closely packed structures. As a result, corrosive species can diffuse more easily to the substrate surfaces at higher temperatures, even though the inhibitor concentration is at or above the CMC value.

**Table 4**  
**Measured Surface per Molecule of the Quat-Type Inhibitor at 25°C, 50°C and 80°C**

	Quat-type inhibitor
Surface area per molecule at 25°C/ Å <sup>2</sup> ·molecule <sup>-1</sup>	36
Surface area per molecule at 50°C/ Å <sup>2</sup> ·molecule <sup>-1</sup>	52
Surface area per molecule at 80°C/ Å <sup>2</sup> ·molecule <sup>-1</sup>	107

## CONCLUSIONS

The effect of temperature on the CMC and performance of the quat-type inhibitor against CO<sub>2</sub> corrosion of carbon steel were investigated in this study. The following conclusions can be presented:

- The CMC value of the quaternary ammonium type inhibitor increased with the tested temperatures.
- Temperature also significantly affected the performance of the quat-type inhibitor. The quat-type inhibitor showed excellent corrosion inhibition performance at 25°C. However, the inhibition performance of the quat-type inhibitor was significantly diminished at higher temperature. Higher concentrations of inhibitor were required to achieve acceptable inhibition performance at 50°C. No inhibition was observed at 80°C, even in the presence of 720 ppm of inhibitor.
- The change of CMC value could explain the increased concentration required to achieve sufficient protection at 50°C but cannot explain the failure of inhibition at 80°C.
- The ineffectiveness of the quat-type inhibitor at 80°C could probably be related to the predicted increase in intermolecular spacing on the substrate surface at higher temperatures.

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