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# Gravimetric and temperature effect studies of a novel imidazolium--based ionic liquid as a corrosion inhibitor for carbon steel in molar hydrochloric acid

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## ABSTRACT

*A novel imidazolium–based ionic liquid, 3-(6-ethoxy-6-oxohexyl)-1-propyl-1H-imidazol-3-ium bromide (BK15), is presented as corrosion inhibitor for carbon steel in molar HCl. The gravimetric investigations revealed the high inhibition efficiency (IE%) of (BK15) with ca. 87.5% in the presence of ca.* $3\times10^{-3}$ *M of the inhibitor. Temperature effect study showed that the (IE%) decreased with increasing temperature and that was attributed to a physical–type adsorption of the (BK15) protective layer onto the carbon steel surface. Thermodynamic parameters were calculated as follows:* $A = 3.641 \times 10^{15}$ *mg.cm*$^{-2}$*.h*$^{-1}$ *;* $E_a = 95.594$ *kJ.mol*$^{-1}$ *;* $\Delta H_a = 92.951$ *kJ.mol*$^{-1}$ *and* $\Delta S_a = 44.098$ *kJ.mol*$^{-1}$ *showing the high effectiveness of (BK15) as corrosion inhibitor, the surface–reaction process of the occurring processes, the endothermic type of the metal corrosion and the induced disorder upon formation of the activation complex. The adsorption process best–fitted the Langmuir adsorption isotherm* ($R^2 = 0.9999$) *and the calculated adsorption free energy* ($\Delta G_{ads} = -36.860$ *kJ.mol*$^{-1}$) *confirmed a mixed–type adsorption, predominantly physisorption of (BK15) in the present work conditions.*

**Keywords:** Corrosion, Hydrochloric acid, Imidazolium, Absorption, Ionic Liquids.

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## INTRODUCTION

Carbon steel corrosion occurs in various industrial processes where the use of mineral acids is inevitable like oil well acidizing, cleaning, and descaling [1]. The use of organic inhibitors is regarded as one of the best methods of protection against the corrosion of metals [1-6] especially those containing heteroatoms (i.e. S, O, N, P), and more specifically nitrogen atom(s) [1-5, 7-11].

In fact, It is well documented that nitrogen-containing compounds are strongly adsorbed onto metals surfaces leading to the formation of protective ad-layer working as a corrosion inhibitor having an efficiency proportional to the compound's concentration and that was shown to be very highly efficient for several compounds [12, 13].

In recent years, ionic liquids (ILs) started to receive some interest as new eco-friendly corrosion inhibitors, but still very little work have been reported so far [14-19].

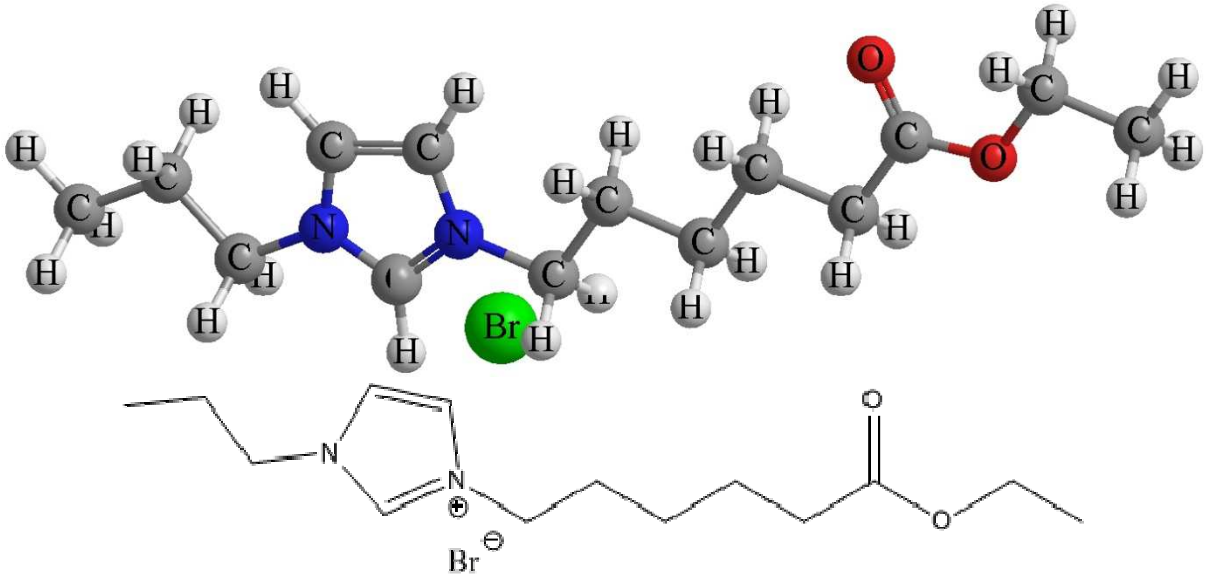
On the other hand, there are several reports showing that the inhibition efficiency of heteroatom–containing compounds increase in the order O < N < S < P [2, 4, 9]. In the current work, we report the gravimetric and temperature effect studies of carbon steel corrosion inhibition by a new imidazoliium-based ionic liquid (IL), namely the 3-(6-ethoxy-6-oxohexyl)-1-propyl-1H-imidazol-3-ium bromide. This compound contains, beside the $\pi$-electrons, both oxygen and nitrogen atoms and is therefore expected to show inhibitive properties for the corrosion of carbon steel.

Firstly, the effect of IL concentration on the corrosion inhibition efficiency (IE%) will be examined. Then the effect of temperature on (IE%) will be investigated and based on that the inhibition process kinetics and thermodynamics will be fully described. In addition, the mode of inhibition will be determined based on the assigned adsorption isotherm.

## MATERIALS AND METHODS

### *2-1. Chemicals and materials:*

The investigated (IL), namely the 3-(6-ethoxy-6-oxohexyl)-1-propyl-1H-imidazol-3-ium bromide (BK15) was synthesized using a microwave-assisted procedure as similarly reported for other (ILs) [14-17, 20, 21]. The structure of the currently investigated IL and its chemical formula are shown in scheme 1. The designation (BK15) will be used in the following text.



**$C_{14}H_{25}BrN_2O_2$**

**Scheme 1. Structure and chemical formula of 3-(6-ethoxy-6-oxohexyl)-1-propyl-1H-imidazol-3-ium bromide (BK15)**

The corrosion media,1 M HCl solution, was prepared by diluting the necessary volume of a stock concentrated hydrochloric acid solution (Fisher Scientific Ltd.). Suitable amount of the investigated (BK15) was then added to prepare concentrations in the range $10^{-6}$–$3\times10^{-3}$ mol. $L^{-1}$. Ethanol (99.8%, Sigma-Aldrich) and Acetone (99.5%, Panreac) were employed for the cleaning of carbon steel specimen. Carbon steel (purchased from Sami Belal Est., Al-Madinah Al-Munawarah) having 0.5 mm diameter was precisely cut into (2.5 cm × 3.0 cm) specimens and served for the weight loss experiments.

The working temperature was maintained constant by means of a GFL-1031 water bath (Gesellschaft Labortechnik, Germany). And a digital analytical semi-micro balance (GR-202, A&D Co. Ltd., Japan) was utilized for the precise determination of specimens' masses.

### *2-2. Weight loss measurements:*

Electrochemically-cleaned carbon steel specimens were degreased and polished to a mirror-like finish. The cut sheets had an exposed surface are of ca. 15 $cm^2$ and were thoroughly cleaned with distilled water, dried with ethanol and stored in desiccators for the weight loss experiments. A constant volume of the corrosion solution (ca. 50 mL) was used for all experiments. The immersion time was fixed at 5 hours and all experiments were carried out at room temperature (i.e. ca. 298 K ± 1 K) except for temperature effect experiments. After each experiment, the carbon steel specimen was successively washed with a copious amount of distilled water and acetone to remove all corrosion products then cleaned and dried with ethanol and weighed carefully, afterwards.

Duplicated experiments were carried out and the mean values were considered.

### *2-3. Effect of temperature:*

For this investigation, the effect of temperature was studied in the range 298-343 K. The details will be discussed in subsequent sections.

## RESULTS AND DISCUSSION

*3-1.Gravimetric study:*
Several corrosion parameters can be determined via weight loss investigations [4, 9] and for this many useful mathematical equations were established. First of all, the corrosion rate (CR) of carbon steel was calculated by the following equation:

$$CR = \frac{\Delta m}{At} \tag{1}$$

Δm is the weight loss ($m_i-m_f$) in mg, $m_i$ and $m_f$ are the masses of the corroded specimen, before and after corrosion tests, respectively. A ($cm^2$) is the exposed surface area of the specimen and t (h) is its immersion time in the investigated solution.

The inhibition efficiency (IE%) is, consequently, defined by the following equation:

$$IE\% = \left[1-\frac{CR^0-CR^i}{CR^0}\right] \times 100 \tag{2}$$

where $CR^0$ and $CR^i$ are the corrosion rates in the absence and presence of inhibitor, respectively

And the fractional surface coverage (θ) is then calculated using the equation:

$$\theta = \frac{IE\%}{100} \tag{3}$$

These data at 298 K are tabulated in table 1 in the concentration range 0 – $3\times10^{-3}$ M of (BK15). And the results show a very clear concentration dependence of the corrosion rate (CR), the inhibition efficiency (IE%) and the fractional surface coverage (θ) .

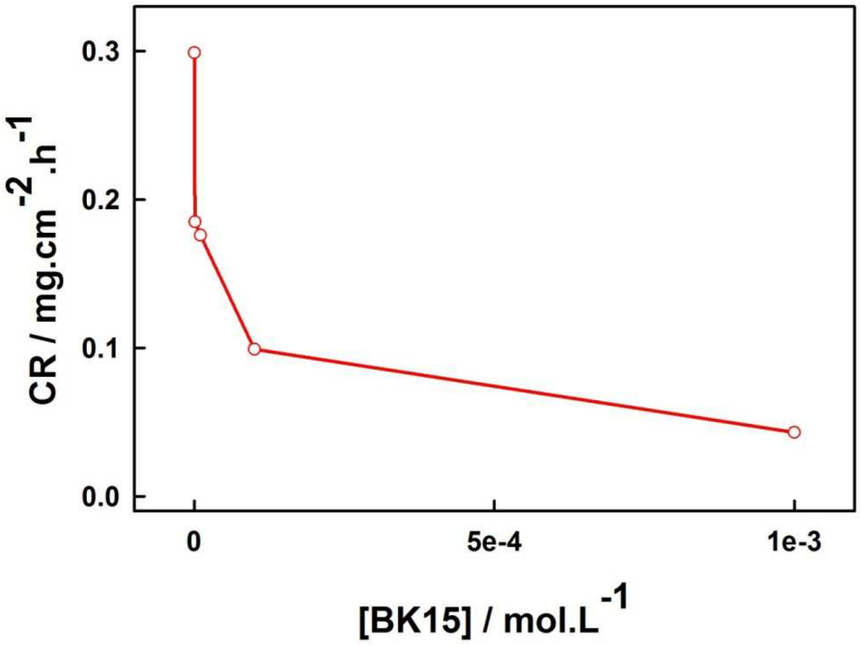


**Figure 1. Variation of the corrosion rate (CR) of carbon steel with the concentration of (BK15) at 298 K**

**Table 1. Gravimetric results for the corrosion parameters of carbon steel corrosion in 1 M HCl with various concentrations of (BK15) obtained at 298 K**

| [BK15] (mol.L$^{-1}$) | CR (mg.cm$^{-2}$.h$^{-1}$) | IE % | Θ |
|---|---|---|---|
| Blank | 0.299 | --------- | ---------- |
| $10^{-6}$ | 0.185 | 38.0 | 0.380 |
| $10^{-5}$ | 0.176 | 41.1 | 0.411 |
| $10^{-4}$ | 0.099 | 67.0 | 0.670 |
| $10^{-3}$ | 0.043 | 85.5 | 0.855 |
| $3\times10^{-3}$ | 0.037 | 87.5 | 0.875 |

The highest efficiency in the present work condition (i.e. ca. 87.5 %) was obtained with ca. 3× $10^{-3}$ M (BK15) which corresponds to the lowest corrosion rate of ca. 0.037 mg.cm$^{-2}$.h$^{-1}$. The plot of the corrosion rate (CR) against (BK15) concentration displayed in figure 1 shows that the former decreased drastically in the presence of a rather low concentration of (BK15) and reaching its minimum value when the concentration of the latter equals 3× $10^{-3}$ M.

On the other hand, the inhibition efficiency variation with (BK15) concentration is plotted in figure 2 showing an opposite trend compared to the corrosion rate. In fact, a significant increase of (IE%) is obtained upon addition of quite low concentrations of (BK15) and reaches the highest value of ca.87.5 % at a (BK15) concentration of ca. $3\times10^{-3}$ M.

This observed behavior would be best explained by the fact that the increasing inhibitor's concentration leads to increasing number of adsorbed molecules onto the carbon steel surface which reduces its exposed surface area to the corrosion media and therefore blocked the direct acid attack on the metal surface [5, 19].

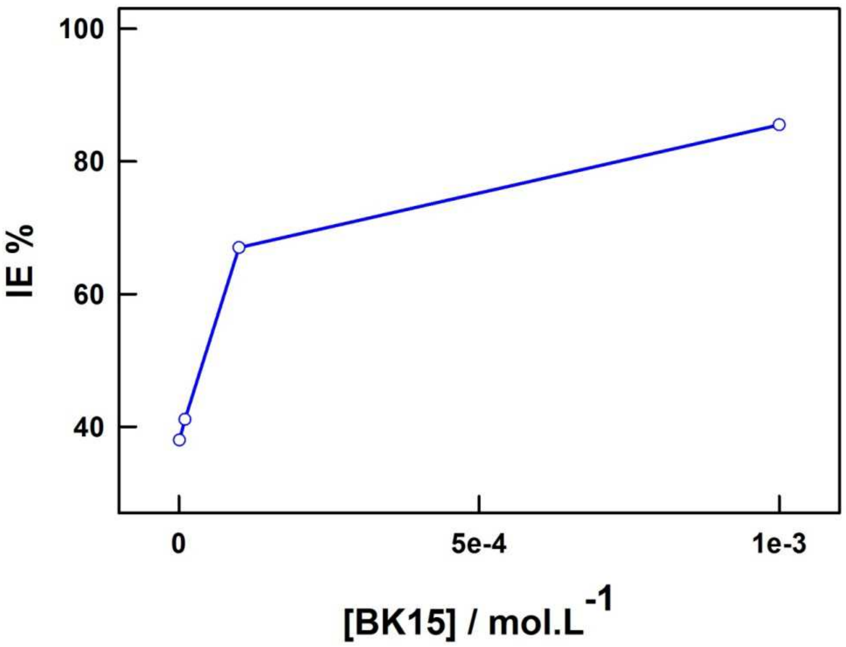


**Figure 2. Variation of the inhibition efficiency (IE%) of carbon steel corrosion with the concentration of (BK15) at 298 K**

The relationship between the corrosion rate (CR) and the concentration of the inhibitor [BK15] would obey the general kinetics equation [22]:

$$CR = k.[BK15]^{a} \qquad (4)$$

with k being the rate constant (mg. cm$^{-2}$. h$^{-1}$) and a is the reaction order which measures the inhibitor efficiency in this case.

The validity of such relationship was checked by simply plotting log CR against log [BK15] using the data given in table 2. The resulting figure 3 shows a very good linearity ($R^2 = 0.9299$). The slope of this line gives the value of (a) and the rate constant (k) was calculated from its intercept as given in table 2.

The inverse proportionality of the corrosion rate (CR) to the inhibitor concentration [BK15] is shown here as a negative sign of (a) and the good inhibitory properties of (BK15) can be concluded from its relatively high value [22].

**Table 2. Kinetic parameters of carbon steel corrosion in 1 M HCl with various concentrations of (BK15) obtained at 298 K**

| [BK15] (mol.L$^{-1}$) | 0 | $10^{-6}$ | $10^{-5}$ | $10^{-4}$ | $10^{-3}$ | $3\times10^{-3}$ |
|---|---|---|---|---|---|---|
| log [BK15] | -------- | −6.00 | −5.00 | −4.00 | −3.00 | −2.52 |
| CR (mg.cm$^{-2}$.h$^{-1}$) | 0.299 | 0.185 | 0.176 | 0.099 | 0.043 | 0.037 |
| Log CR | −0.524 | −0.733 | −0.755 | −1.004 | −1.367 | −1.432 |
| a | −0.223 | | | | | |
| k (mg.cm$^{-2}$.h$^{-1}$) | $10.617\times10^{-3}$ | | | | | |

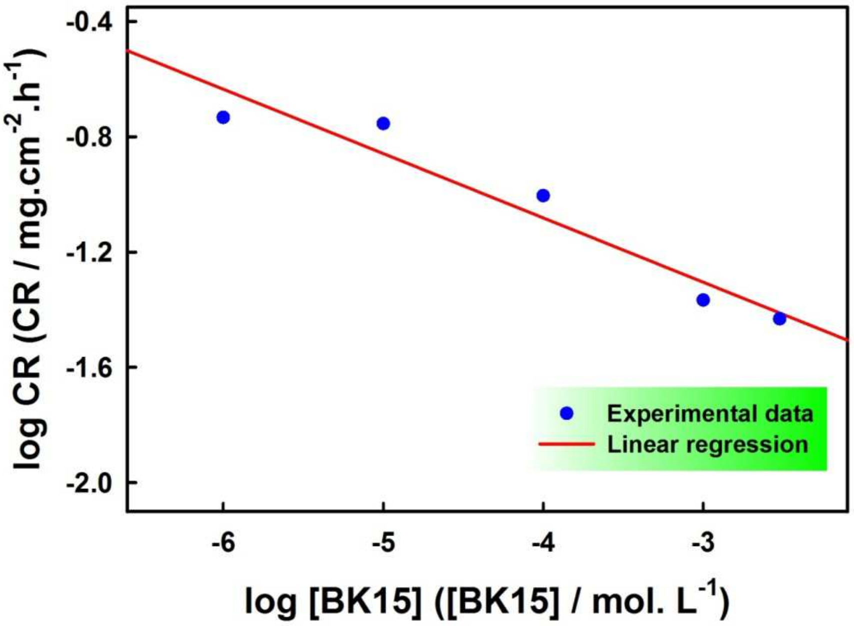


**Figure 3. Variation of log CR with log [BK15] for carbon steel corrosion in 1 M HCl at 298 K**

*3-1.Effect of temperature:*

Among the factors affecting metals corrosion, temperature has a special importance. However, its effect on the acid-metal inhibition reaction is well reported to be sometimes very complex because of the various changes taking place on the metal surfaces. For example, the rapid etching, inhibitor desorption and/or possible degradation [22, 23]. Moreover, it is well known that hydrogen reduction reaction (HRR) occurs simultaneously with metal corrosion in acid media and the evolved gas is directly proportional in amount to the temperature which increases the metal corrosion rate at higher temperature. This adds to the fact that the energy required for the formation of the activated complex that dissociates to yield the corrosion products increases with increasing temperature [8, 24].

The investigation of the effect of temperature on the corrosion rate in the absence and presence of $10^{-3}$ M (BK15) was carried on in the temperature range (298 K–343 K) and results are reported in table 3. Obviously, in all experiments, the corrosion rate increases with rising temperature, as expected, and this is easily seen in the corresponding figure 4.

**Table 3. Gravimetric results for the corrosion parameters of carbon steel corrosion in 1 M HCl in the absence and presence of $10^{-3}$ M (BK15) obtained at different working temperatures**

| T (K) | CR$_0$ (mg.cm$^{-2}$.h$^{-1}$) | CR$_i$ (mg.cm$^{-2}$.h$^{-1}$) | IE % | θ |
|---|---|---|---|---|
| 298 | 0.299 | 0.043 | 85.5 | 0.855 |
| 313 | 1.447 | 0.696 | 51.9 | 0.519 |
| 323 | 2.221 | 1.457 | 34.3 | 0.343 |
| 333 | 4.651 | 3.461 | 25.6 | 0.256 |
| 343 | 9.416 | 7.939 | 15.7 | 0.157 |

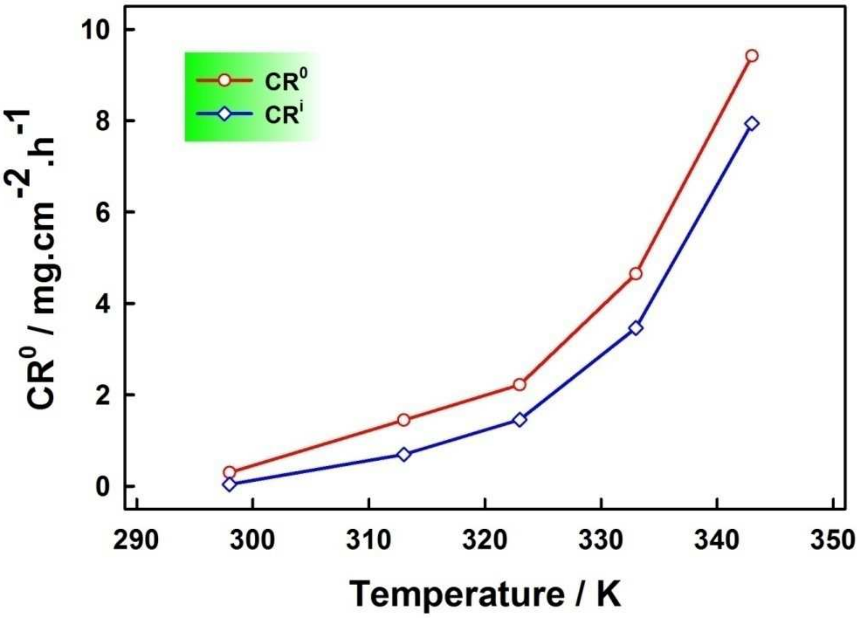


**Figure 4. Effect of temperature on the corrosion rate of carbon steel in 1 M HCl in the absence ($CR^0$) and the presence ($CR^i$) of $10^{-3}$ M (BK15)**

With increasing temperature both corrosion rates (whether in the presence of the absence of BK15) and the inhibition efficiency (IE%) increase in a very clear fashion. Such a behavior, as displayed in figure 5, is very common among organic corrosion inhibitors [1, 3-5, 8-11, 22, 25, 26].

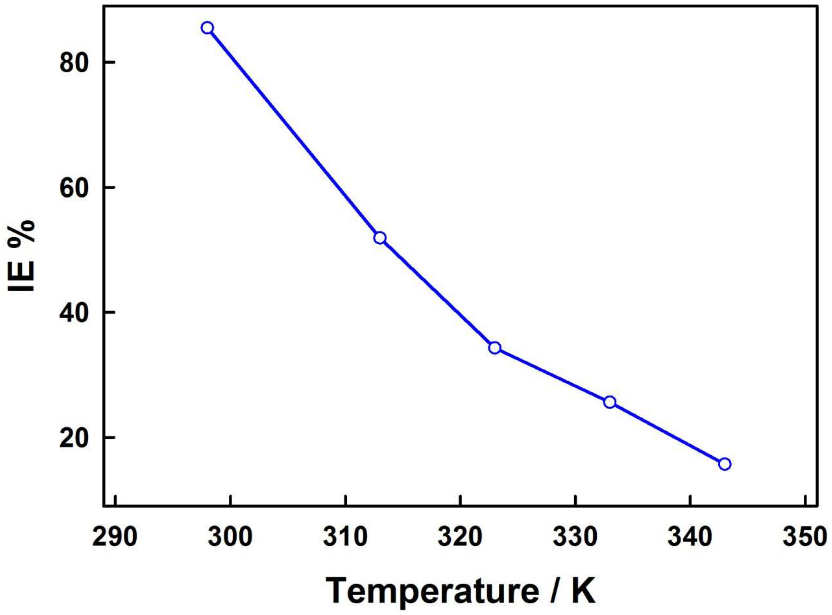


**Figure 5. Effect of temperature (298 K–343 K) on the inhibition efficiency (IE%) of carbon steel corrosion in a ($10^{-3}$ M BK15 + 1 M HCl) solution**

The decreasing (IE%) with increasing temperature proves that the inhibitor action is essentially based on adsorption onto the carbon steel surface which blocks the active sites and forms a sort of protection shield against the corrosive media [11, 25]. Moreover, the observed (IE%) decrease would be explained by the weakening of the inhibitor's adsorption at higher temperature [5] and probably its partial desorption. This explanation puts forward the speculation of physical adsorption (physisorption) of (BK15) molecules onto the carbon steel surface [1, 3].

From the temperature effect investigation, several thermodynamic parameters can be calculated [27, 28] using the following Arrhenius and transition–state equations:

$$CR = A \exp\left[-\frac{E_a}{RT}\right] \tag{5}$$

$$CR = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a}{R}\right) \exp\left(-\frac{\Delta H_a}{RT}\right) \tag{6}$$

where A ($mg.cm^{-2}.h^{-1}$) is the Arrhenius pre-exponential factor, R is the universal gas constants (8.3144621 $J.K^{-1}.mol^{-1}$), N is Avogadro's number ($6.02252 \times 10^{-23}$ $mol^{-1}$) and h is Plank's constant ($6.626176 \times 10^{-34}$ J.s).

Accordingly, Ln(CR) against (1/T) and Ln(CR/T) against (1/T) were plotted, as displayed in figure 6 and figure 7, respectively. All graphs show, both in the absence and presence of $10^{-3}$ M (BK15), excellent linearity as expected from equations (5) and (6), respectively.

The intercepts of the lines in figure 6 permit the calculation of the values of the pre-exponetial factor (A) and the slopes which equal ($-E_a/RT$) allowed the determination of the activation energy ($E_a$) both in the absence and presence of the inhibitor, respectively.

On the other hand, the obtained straight lines in figure 7 have a slope of ($-\Delta H_a/R$) and an intercept of (Ln[R/Nh] + $\Delta S_a/R$), each. Consequently, the values of $\Delta H_a$ and $\Delta S_a$ were calculated, respectively. All of these results are tabulated in table 4.

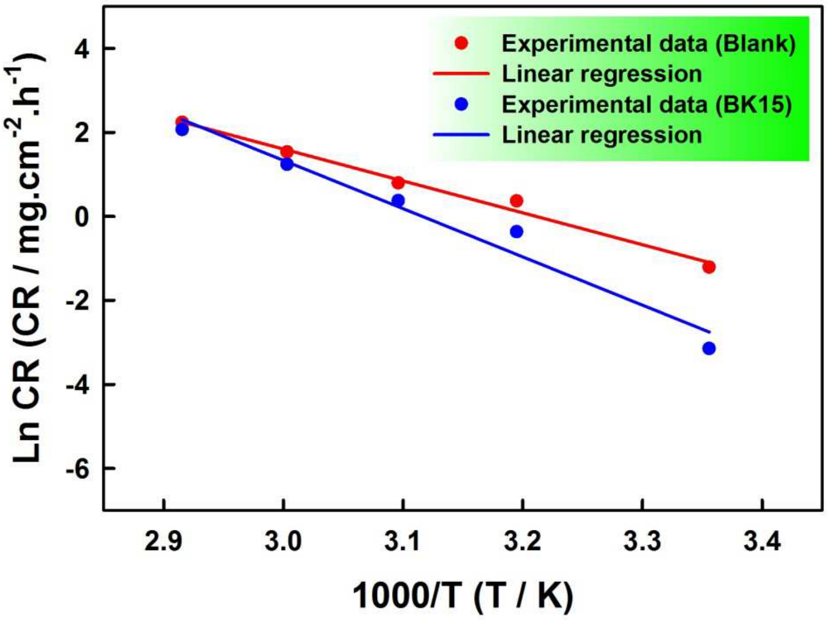


**Figure 6. Arrhenius plots for carbon steel corrosion rates (CR) in 1 M HCl in the presence and absence of $10^{-3}$ M (BK15)**

**Table 4. Corrosion thermodynamic parameters for carbon steel in 1 M HCl with and without $10^{-3}$ M (BK15)**

| Solution | Fig.6 Slope | Fig6. intercept | Fig.7 slope | Fig7. intercept | A ($mg.cm^{-2}.h^{-1}$) | $E_a$ $kJ.mol^{-1}$ | $\Delta H_a$ $kJ.mol^{-1}$ | ΔSa $kJ.mol^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| Blank | −7.592 | 24.381 | −7.273 | 17.614 | $3.877 \times 10^{10}$ | 63.120 | 60.470 | −51.098 |
| BK15 | −11.50 | 35.831 | −11.180 | 29.064 | $3.641 \times 10^{15}$ | 95.594 | 92.951 | 44.098 |

As can be depicted from table 4, the activation energy in both solutions is greater than a value of 20 $kJ.mol^{-1}$ owing to a surface-reaction process either in the absence or presence of (BK15) [3, 29]. Additionally, there is a clearly significant increase of ca. 50% in the apparent activation energy ($E_a$) in the presence of inhibitor which is suggestive of a physical adsorption (physisorption) or a relatively weak chemical bonding between (BK15) molecules and carbon steel surface associated with the higher energy barrier for the corrosion of carbon steel in the presence of (BK15) in the present work conditions [22, 30, 31]. Likewise, the similar variation of to the Arrhenius pre-exponential factor (A) shows the high inhibitive properties of the investigated (BK15), as well documented in literature [22, 31-33].

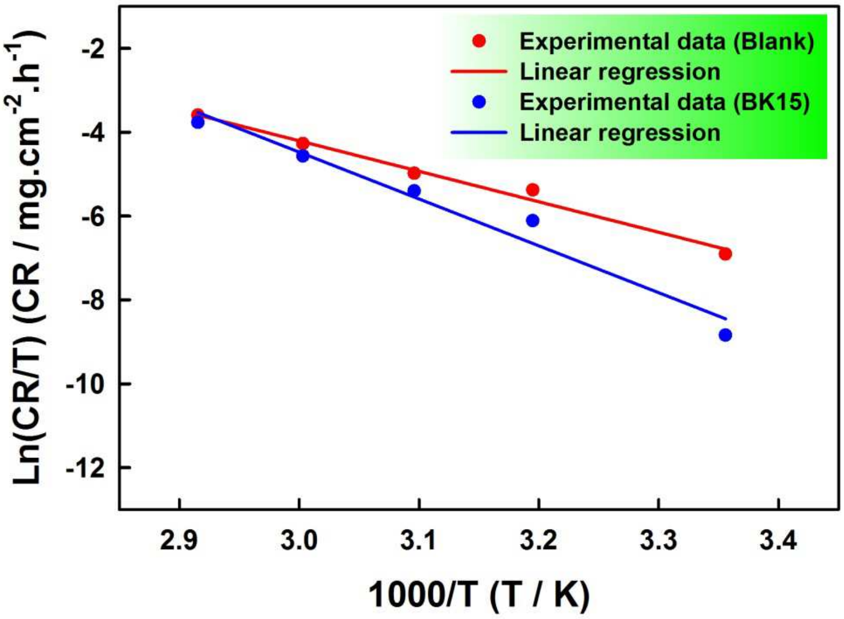


**Figure 7. Transition-state plots for carbon steel corrosion rates (CR) in 1 M HCl in the presence and absence of $10^{-3}$ M (BK15)**

Additionally, in all cases, $\Delta H_a$ have lower values as compared to their corresponding activation energies resulting in a decrease in the total volume of the reaction media as a consequence of the hydrogen evolution reaction. The positive sign of $\Delta H_a$ implies that the carbon steel dissolution is an endothermic process which is in a good agreement with the observed increasing corrosion rate with increasing temperature. Moreover, it is noteworthy that the average value of the difference between the activation energy and the enthalpy change (i.e. ca. 2.65 kJ.mol$^{-1}$) is very close to the average value of the product RT (i.e. ca. 2.69 kJ.mol$^{-1}$) in the investigated temperature range identifying the corrosion process as a unimolecular reaction as per the equation [11, 22, 34]:

$$E_a - \Delta H_a = RT \qquad (7)$$

The entropy of activation ($\Delta S_a$) shows two distinguished characteristics. In uninhibited corrosion process, the negative value of $\Delta S_a$ is typical of an association-based formation of the activated complex in the rate determining step of the reaction mechanism [35]. While the increase and positive sign of $\Delta S_a$ in the presence of (BK15) indicates the formation of an ordered layer onto the metal surface [11] and accounts for the disorder occurring during the formation of the activated complex [8].

### *3-3. Adsorption isotherm:*

Essential information to understand the inhibition mechanism of the studied (BK15) can be provided by the investigation of its adsorption onto the carbon steel surface [36-38] which can be checked through the determination of the corresponding adsorption isotherm. This adsorption depends on several parameters discussed in details in literature, among them one can cite the nature and charge of the corroding metal, the inhibitor's chemical structure, the charge distribution in the inhibitor's molecule and the corrosive media [30, 39-43].

In the present study, the best–fitting isotherm ($R^2$ = ca. 0.9999) is the Langmuir isotherm [10, 22] given by the following equation:

Langmuir isotherm

$$\left\{\frac{\theta}{1-\theta}\right\} = K_{ads}.C_{inh} \qquad (9)$$

Where $C_{inh}$ is the bulk concentration of the investigated inhibitor, $K_{ads}$ is its adsorption equilibrium constant and $\theta$ is the surface coverage.

The corresponding plot of $C_{inh}/\theta$ against $C_{inh}$ is displayed in figure 8.

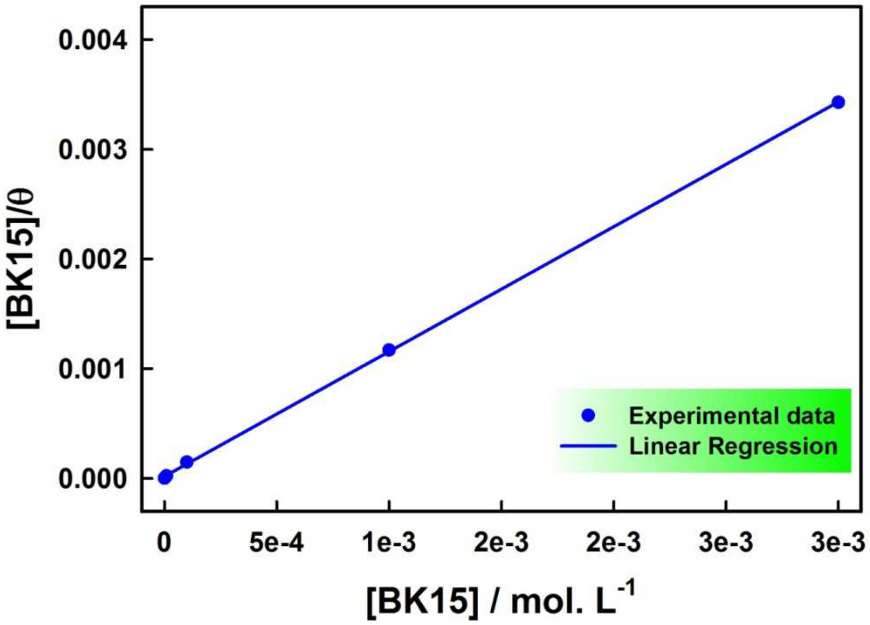


**Figure 8. Langmuir adsorption isotherm of (BK15) on carbon steel surface in 1 M HCl at 298 K**

The slope of the straight line equals almost unity and the value of the adsorption equilibrium constant ($K_{ads}$) calculated from the intercept was ca. $52.056 \times 10^3$ $mol^{-1}.L$ and results are tabulated in table 5.

The value of the Gibbs free energy of adsorption can then be calculated by means of the following equation [8] (55.5 being the value of the molar concentration of water in the solution [44] ):

$$\Delta G_{ads} = -RT\ Ln(55.5.K_{ads}) \qquad (12)$$

**Table 5 Thermodynamic parameters for the adsorption of (BK15) onto the carbon steel surface in 1 M HCl**

| Inhibitor | Slope | $K_{ads}$ ($mol^{-1}.L$) | $R^2$ | $\Delta G_{ads}$ ($kJ.mol^{-1}$) |
|---|---|---|---|---|
| BK15 | 1.138 | $52.056 \times 10^3$ | 0.9999 | −36.860 |

The relatively high value of ($K_{ads}$) shows the high adsorption capacity of (BK15) onto the carbon steel surface [4] and the negative sign of the adsorption free energy ($\Delta G_{ads}$) as shown in table 5 proves the spontaneous, relatively strong and highly stable adsorption of (BK15) molecules onto the metal surface [4, 8, 10, 11, 16, 34, 45, 46].

The nature of the adsorption process of (BK15) onto the carbon steel surface is mainly judged from the value of ($\Delta G_{ads}$) to be either chemisorption or physisorption process [3, 43, 47-55]. The present value being $\Delta G_{ads}$ = ca. −36.860 $kJ.mol^{-1}$ is suggestive of a rather complex mixed–type of interactions [3, 4, 10, 11] with a predominant physisorption as similarly reported for (BT39) [9] through an electrostatic interaction between the charged (BK15) molecules and the charged carbon steel surface. While the contributing chemisorption would be the result of the adsorption of (BK15) molecules onto, most probably, both anodic and cathodic sites of the corroding carbon steel surface [19, 34]. In fact, we have noticed a clear decrease in the amount of exhausted hydrogen in the presence of (BK15), proving the adsorption of the latter on the cathodic sites of carbon steel. As for its adsorption on the anodic sites this can be expected due to the chemical structure of BT15 (cf. scheme 1), for instance the π-electrons of C=N and C=C bonds and the lone electron pairs of nitrogen atoms.

## CONCLUSION

This work presented a novel imdazolium-based ionic liquid as a corrosion inhibitor for carbon steel in molar hydrocholoric acid solution. The investigated (BK15) (IL) showed a highly inhibition efficiency at rather low concentrations (i.e. within the mM range). The data obtained from gravimetric investigation suggested a physical adsorption process of the (BK15) molecules onto the metal surface as the driving force for the corrosion inhibition obtained in the present work conditions. This was further confirmed by temperature effect study showing that the adsorption process followed a Langmuir–type isotherm. Several thermodynamic parameters were calculated as follows:

- A = 3.641 × $10^{15}$ mg.$cm^{-2}$.$h^{-1}$ ; showing the high inhibitive properties of the investigated (BK15)
- $E_a$ = 95.594 kJ.$mol^{-1}$ ; proving that carbon steel corrosion is indeed a surface–reaction process, in the present work conditions.
- $\Delta H_a$ = 92.951 kJ.$mol^{-1}$ ; implying that the corrosion of the metal is an endothermic process and that explains the increasing corrosion rate with increasing temperature.
- $\Delta S_a$ = 44.098 kJ.$mol^{-1}$ ; indicating the formation of an ordered protective layer adsorbed onto the carbon steel surface and that the formation of the activated complex is accompanied by an increase in the disorder of the system.
- $K_{ads}$ = 52.056 × $10^3$ $mol^{-1}$.L ; characterizing a rather strong adsorption of the BK15 inhibitor onto the carbon steel surface.
- $\Delta G_{ads\,=}$ −36.860 kJ.$mol^{-1}$ ; confirming the comprehensive type of adsorption (i.e. both physical and chemical). The former being the predominant one, however.

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