

Corrosion Control by Benzyl Triethylammonium Chloride: Effects of Temperature and Its Concentration

Mohd Nazri Idris, Abdul Razak Daud, Norinsan Kamil Othman, Azman Jalar

Abstract-- The effectiveness of quaternary ammonium compound of benzyl triethylammonium chloride (BTC) as an inhibitor for corrosion of carbon steel in 1.0 M HCl solution has been investigated by weight loss method. Surface morphology of the carbon steel samples was examined using a scanning electron microscope. The solution temperature and inhibitor concentration were varied. Inhibitor efficiency was found to increase with inhibitor concentration. The results revealed that the corrosion rate increases in the presence and absence of BTC as the temperature increased. The adsorption of inhibitor onto sample surface was found to follow Dubinin-Radushkevich adsorption isotherm. Thermodynamic parameters for the corrosion process such as activation energy E_a , activation enthalpy ΔH , and activation entropy ΔS were calculated. The E_a , ΔH , and ΔS obtained indicated that adsorption of the inhibitor was merely physisorption.

Index Term-- Adsorption isotherm, Benzyl triethyl ammonium chloride, Carbon steel, Corrosion inhibitor,

I. INTRODUCTION

Corrosion inhibitors play an important role in corrosion prevention in many industries including petroleum industries. Most commercial inhibitors used are organic compounds containing elements such as sulphur, oxygen, phosphorus and nitrogen [1, 2]. Organic inhibitors are capable to adsorb onto metal surface to form a thin film, which acts as a barrier to protect metal surface from corrosive species in medium and consequently decrease corrosion attack. Quaternary ammonium compounds are considered the most potential for corrosion control especially on the carbon steel materials. Several studies of n-alkyl quaternary ammonium compounds such as benzyl trimethylammonium iodide [3], cethyl benzyl dimethylammonium chloride [4], $C_{10}H_{21}N(C_2H_5)_3Br$ [5] and $C_{16}H_{33}N(C_4H_9)_3Br$ [6] revealed that adsorption process take place through the electrostatic attraction.

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This attraction occurs between the induced negative charges on the metal surface and the polar head group of N^+ ion. Foss et al. [7] proved that by addition of cetyl

trimethylammonium bromide was significantly reduced the corrosion rate through the blocking effect on the iron surface by chemisorption process.

The adsorption process of quaternary ammonium compounds and others organic inhibitors have been investigated as function of the nature and surface charge of metallic materials, adsorption mechanism steps, chemical structures and electrolyte solution types [4, 8, 9]. On top of that, temperature and inhibitor concentration have also a dominant influence on the adsorption of inhibitor molecules as well as the dissolution of metallic materials [10], which involve both thermodynamic and kinetic aspects of the interaction.

In this present study, we introduce BTC, which is one of n-alkyl quaternary ammonium compounds as a new inhibitor to prevent the corrosion of carbon steel in HCl. Molecular structure of BTC is shown in Fig. 1. BTC has strong positively charge N^+ ion and π electron from aromatic benzyl group for adsorption to take place on the carbon steel surface. The aim of this work is to study the effectiveness of BTC as a corrosion inhibitor for carbon steel corrosion in 1.0 M HCl solution with respect to temperature and the inhibitor concentration.

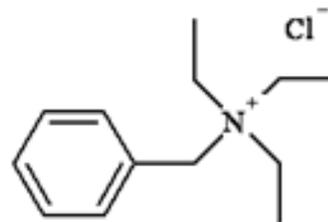


Fig. 1. Chemical structure of BTC

II. MATERIALS AND METHOD

The chemical composition (wt%) of carbon steel used in this study was 0.258 C, 0.466 Mn, 0.008 S, 0.013 P, 0.044 Cr, 0.427 Si, 0.015 Ni, 0.019 Cu, 0.002 Mo, 0.132 Al and balance Fe. BTC was purchased from Sigma Aldrich Co. Ltd. Hydrochloric acid (1.0 M HCl) solution was prepared from analytical grade 36% HCl.

Weight loss experiments were carried out in 200 mL of 1.0 M HCl with absence and presence of BTC. The BTC concentration range employed was 0.05 to 2.0 mM and the experiments were performed at a temperature range of 25 to 60°C. Carbon steel coupons were immersed for 6 hours in a temperature-controlled bath. After immersion, the coupons

were withdrawn from the test solution, cleaned according to ASTM G1-03, and dried by blowing cold air. The weight loss was determined using an analytical balance.

All results were reproduced in triplicate and the average values were considered. Surface morphology of tested samples was obtained using a scanning electron microscope, Hitachi TM-1300 SEM.

III. RESULTS AND DISCUSSION

A. Weight Loss Measurement

Fig. 2 and Fig. 3 show the weight loss analysis of carbon steel samples in 1.0 M HCl in the absence and presence of BTC at various concentrations. The corrosion rates C_R from weight loss experiments were calculated using (1);

$$C_R = \frac{\Delta W}{At} \quad (1)$$

where ΔW is the average weight loss (mg) of carbon steel coupons, A is the total exposed surface area of coupon (cm^2) and t is the immersion time (h). Surface coverage θ and inhibition efficiency $IE\%$ were calculated based on (2) and (3), respectively:

$$\theta = 1 - \frac{C'_R}{C_R} \quad (2)$$

$$IE \% = 100 \left(1 - \frac{C'_R}{C_R} \right) \quad (3)$$

where C'_R and C_R are the corrosion rates for the presence and absence of BTC, respectively.

The results in the Fig. 2 show that the corrosion rate of carbon steel in 1.0 M HCl with and without BTC increased when temperature was increased. As can be seen, the corrosion rate increases rapidly with temperature in the absence of BTC compound. The graphs in Fig. 2 show that the adsorption of BTC molecules on the steel surface were unfavourable with increasing of temperatures but the corrosion rate were continuously reduced with increase of BTC concentration.

As the concentrations of BTC increased, the inhibition efficiency for carbon steel is also seen to be increases (Fig. 3). The results were probably due to a higher surface coverage of BTC molecules on the steel surface [11]. This is confirmed that BTC acts as an efficient inhibitor in the range of temperature studies. This behaviour was clearly related to the fact that the adsorption and coverage of BTC molecules on the steel surface increase with the inhibitor concentration. The decreasing of corrosion rate with the increase of inhibitor concentration seems to be similar with other quaternary ammonium compound such as benzyl trimethylammonium iodide [3] and cetyltrimethyl ammonium bromide [7].

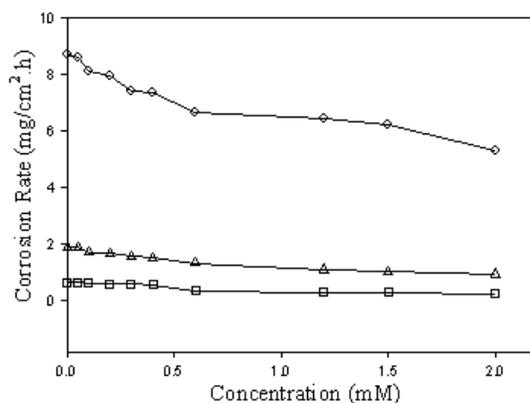


Fig. 2. The plot of corrosion rate against concentration of BTC at (□) 25, (Δ) 40 and (○) 60 °C

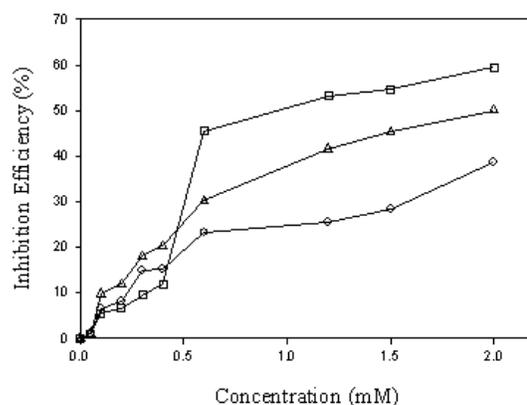


Fig. 3. The plot of Inhibition efficiency against concentration of BTC at (□) 25, (Δ) 40 and (○) 60 °C

The adsorption of the BTC molecules can be represented as a substitution process between BTC in the aqueous solution, $\text{BTC}_{(\text{sol})}$ and the water molecules on the carbon steel surface, $\text{H}_2\text{O}_{(\text{ads})}$ as (4),



where $\text{BTC}_{(\text{sol})}$ and $\text{BTC}_{(\text{ads})}$ are the BTC molecules in the aqueous solution and adsorbed on the carbon steel surface, respectively. $\text{H}_2\text{O}_{(\text{ads})}$ is the water molecules on the carbon steel surface, x is the size ratio representing the number of water molecules replaced by molecules of BTC.

In order to measure the activation parameter for dissolution process, the Arrhenius equation was used as (5);

$$C_R = \lambda \exp \left(-\frac{E_a}{RT} \right) \quad (5)$$

where C_R is corrosion rate, λ is Arrhenius pre-exponential factor and E_a (kJ/mol) is the activation energy for dissolution process. R is the gas constant and T is the absolute temperature. The activation energy is calculated by linear regression of $\ln C_R$ against $1/T$.

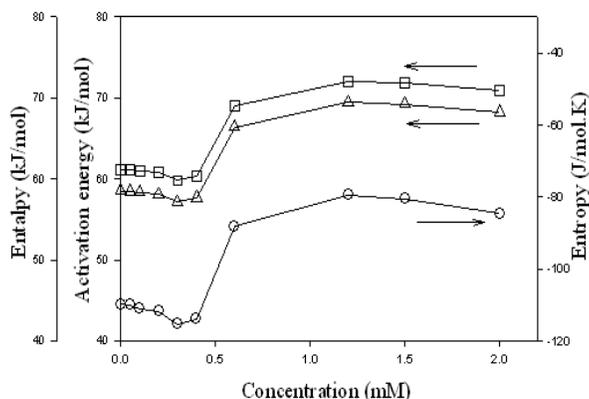


Fig. 4. The plots of activation energy, E_a (\square), enthalpy, ΔH (Δ) and entropy, ΔS (\circ) for dissolution reaction

The values of E_a in the absence and the presence of BTC are shown in Fig. 4. The results reveal that values of E_a obtained in the presence of BTC are slightly lower at low BTC concentration compared to BTC-free solution. At higher BTC concentrations, E_a values show a significant increment. This is owing to higher thickness of thin layer formed at higher BTC concentrations compared to lower BTC concentrations. The decrease in $IE\%$ with the increase of temperature at higher inhibitor concentration (Fig. 3) and the higher values of E_a at higher inhibitor concentrations (Fig. 4) indicated that the adsorption mechanism in this case was physisorption.

The enthalpy, ΔH (kJ/mol) and entropy, ΔS (J/mol.K) of activation were obtained from a transition state equation as (6);

$$C_R = \left(\frac{RT}{Nh}\right) \exp\left(\frac{\Delta S}{R}\right) \exp\left(\frac{-\Delta H}{RT}\right) \quad (6)$$

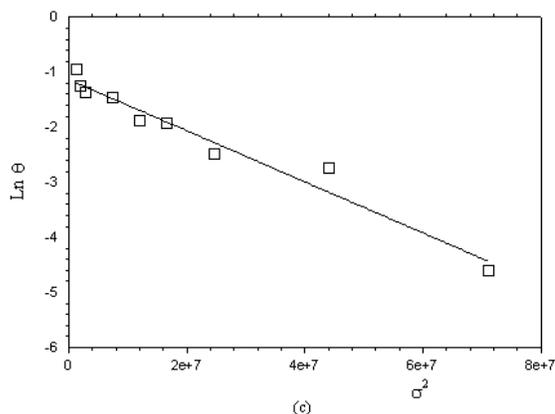
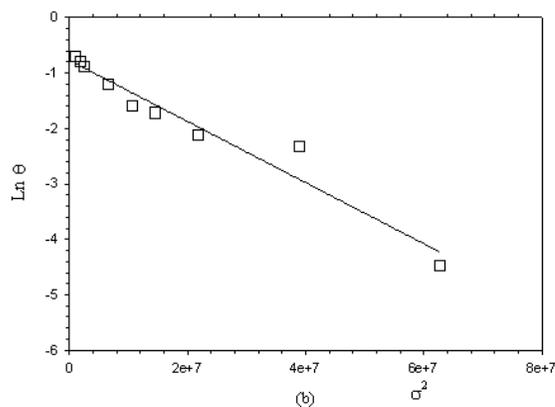
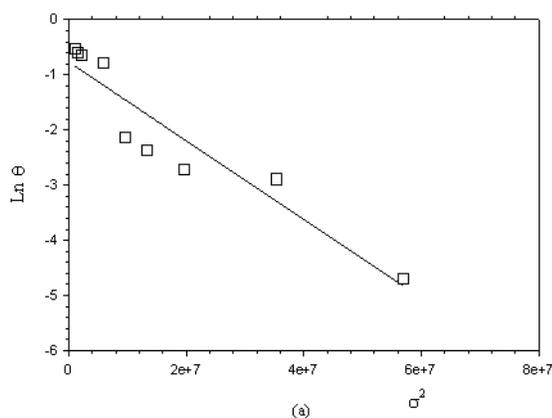


Fig. 5. Dubinin-Radushkevich adsorption isotherm for BTC in 1.0 M HCl at 25°C (a), 40°C (b) and 60°C (c)

where C_R is the corrosion rate, R is the gas constant, T is the absolute temperature, N is the Avogadro's number and h is the Planck's constant. The plot of $\ln(C_R/T)$ versus $1/T$ provides a linear regression with slope of $(-\Delta H/R)$ and an intercept of $(\ln(R/Nh) + \Delta S/R)$, from which the values of ΔH and ΔS were computed respectively. These results are shown in Fig. 4. The values of ΔS are large and negative in all concentrations with and without BTC. The negative ΔS values imply that the dissolved molecules at activated complex condition are more ordered than the reactant or at initial stage. The greater value indicated that the dissolution reaction would be slower due to adsorption process of BTC molecules on the carbon steel surface [12].

The positive values of ΔH indicate that the dissolution process of carbon steel is endothermic in nature. The increase in ΔH values with the increase of BTC concentrations indicated that BTC molecules have provided a better coverage for samples surface from dissolution.

B. Adsorption Isotherm Model

Adsorption isotherm such as Langmuir, Temkin, Freundlich and Dubinin-Radushkevich models were applied to evaluate adsorption process of BTC molecules and carbon steel surface. The obtained results were best fitted by Dubinin-Radushkevich adsorption isotherm and this model can be expressed as [13];

$$\ln \theta = \ln \theta_{max} - a\sigma^2 \quad (7)$$

$$\sigma = RT \ln \left(1 + \frac{1}{C_{BTC}} \right) \quad (8)$$

where θ and θ_{max} are the degree of surface coverage and maximum surface coverage, respectively. σ is known as Polanyi potential and can be expressed as (8);

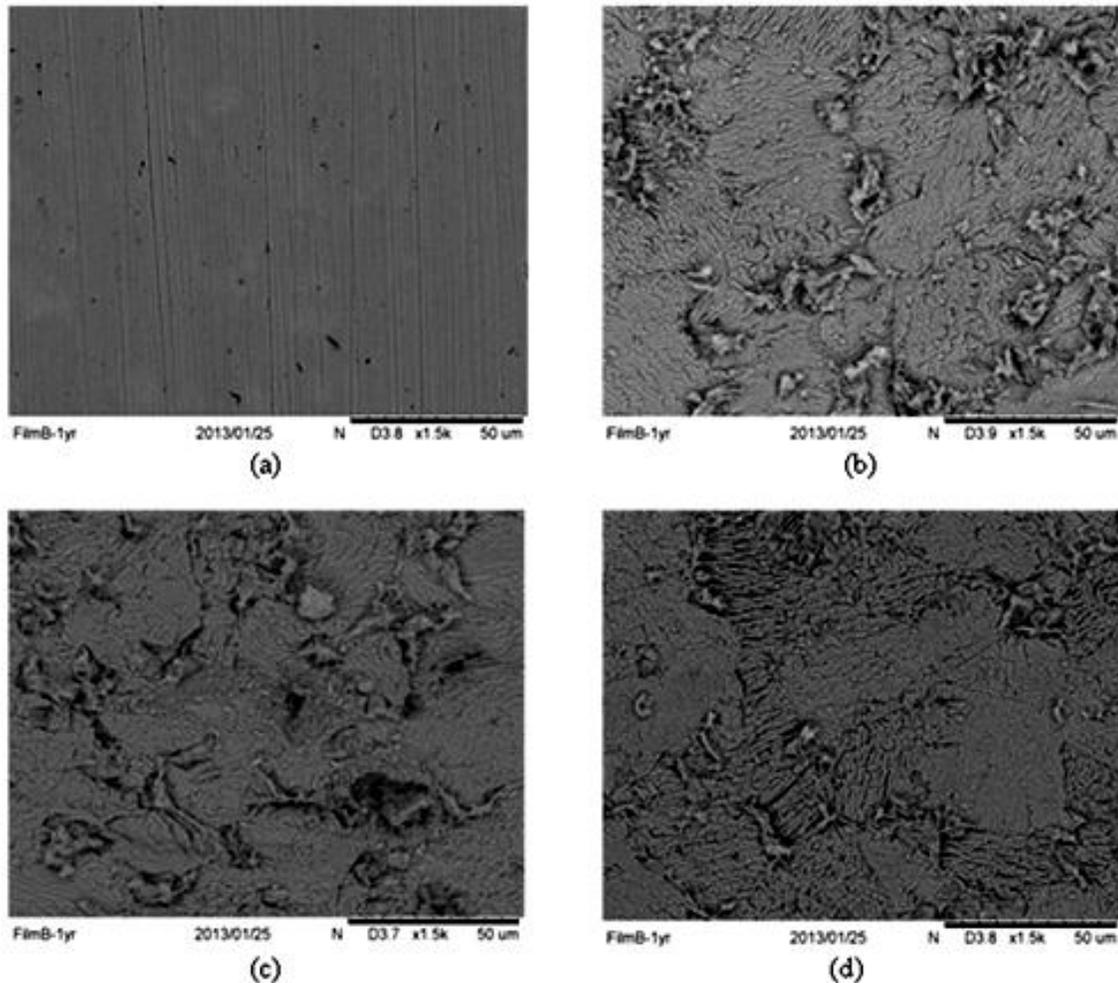


Fig. 6. SEM images of carbon steel surface (a) before immersion, (b) after 6 hours immersion in 1.0 M HCl without BTC, (c) immersion with 0.60 mM BTC and (d) 2.0 mM BTC

where R is the gas constant, T is the absolute temperature and C_{BTC} is inhibitor concentration. a is a constant represents the mean adsorption energy E , which is defined as the amount of energy required for transferring one mole of adsorbate from infinity (bulk solution) to the surface of adsorbent. The adsorption energy, E can be applied in explaining the mechanism of adsorption of corrosion inhibitor onto a metal surface and can be calculated as [14];

$$E = (2a)^{-0.5} \quad (9)$$

If the E value is greater than 8 kJ/moles, the adsorption mechanism is considered in favour of chemisorptions adsorption, whereas if the value of E is less than 8 kJ/moles, then the adsorption mechanism signifies physisorption [2, 14]. However, this model is more general and does not assume a

homogenous surface or constant sorption potential as compared to Langmuir isotherm [2].

Fig. 5 shows the plots of $\ln \theta$ verses σ^2 for adsorption of BTC at 25, 40 and 60 °C. The mean adsorption energy, E calculated for the above temperatures are 2.64, 3.01 and 3.28 kJ/mol, respectively. These results indicated that the adsorption mechanism of BTC molecules onto the steel surface is merely physisorption. Thus, the results are in good agreement with activation energy, E_a data for dissolution processes in the absence and presence of BTC.

The adsorption process of BTC molecules is based on molecular structure consideration. BTC molecules having strong charge of N^+ ion and the benzyl group with delocalized π electrons (aromaticity) which can serve as centre of adsorption [15]. However, as compared to longer alkyl chain [16], the ability of BTC alkyl structure to be oriented and form

a layer above the head group is relatively less. As a result, the adsorption energy, E of BTC molecules on the steel surface were merely favoured to physisorption mechanism.

C. Surface Morphology

Surface morphological study was performed by using SEM to investigate the effect of BTC on inhibition of the carbon steel corrosion. Fig. 6 shows the SEM images of the carbon steel before and after 6 hours immersion in 1.0 M HCl with and without BTC. The micrographs in Fig. 6b-c show that the sample surface was seriously corroded and heavily covered by corrosion product. However, damage of the sample surface was less when the solution contained higher concentration of BTC (Fig. 6d). This is due to the formation of a better protective film on the carbon steel surface by BTC molecules. A good protective film on the steel surface with higher inhibitor concentration provides good protection for various metal [10, 11], which was in good agreement with adsorption thermodynamic measurement reported in the present study.

IV. CONCLUSION

Benzyl triethylammonium chloride is a potential corrosion inhibitor for carbon steel in HCl solution. The inhibition efficiency of BTC increases with BTC concentration, but decreases with temperature. The adsorption process of BTC seems to follow Dubinin-Radushkevich adsorption isotherm model. The activation energy for dissolution and adsorption energy estimated from Dubinin-Radushkevich adsorption model strongly indicate that BTC molecules in HCl solution are adsorbed on carbon steel surface by physisorption mechanism. However, several studies with different concentration of corrosive medium such as HCl and higher concentration of BTC will need to be considered for further investigation.

REFERENCES

- [1] M. A. Hegazy, "A novel Schiff base-based cationic gemini surfactants: Synthesis and effect on corrosion inhibition of carbon steel in hydrochloric acid solution," *Corros Sci*, vol. 51, pp. 2610-2618, 2009.
- [2] N. Caliskan, and E. Akbas, "The inhibition effect of some pyrimidine derivatives on austenitic stainless steel in acidic media," *Mater Chem Phys*, vol. 126, pp. 983-988, 2011.
- [3] X. Li, S. Deng, and H. Fu, "Benzyl trimethylammonium iodide as a corrosion inhibitor for steel in phosphoric acid produced by dihydrate wet method process," *Corros Sci*, vol. 53, pp. 664-670, 2011.
- [4] T. Vasudevan, S. Muralidharan, S. Alwarappan, and S. V. K. Iyer, "The influence of N-hexadecyl benzyl dimethyl ammonium chloride on the corrosion of mild steel in acids," *Corros Sci*, vol. 37, pp. 1235-1244, 1995.
- [5] A. Frignani, M. Tassinari, L. Meszaros, and G. Trabanelli, "The use of electrochemical impedance spectroscopy to study ARMCO iron corrosion in acid solutions inhibited by quaternary ammonium compounds," *Corros Sci*, vol. 32, pp. 903-911, 1991.
- [6] M. L. Free, "Understanding the effect of surfactant aggregation on corrosion inhibition of mild steel in acidic medium," *Corros Sci*, vol. 44, pp. 2865-2870, 2002.
- [7] M. Foss, S. Diplas, and E. Gulbrandsen, "Mechanistic study of adsorption of cetyltrimethyl ammonium bromide on high purity iron using contact angle, polarization resistance and XPS," *Electrochim Acta*, vol. 55, pp. 4851-4857, 2010.
- [8] A. Popova, M. Christov, and A. Vasilev, "Mono- and dicationic benzothiazolic quaternary ammonium bromides as mild steel corrosion inhibitors. Part II: Electrochemical impedance and polarisation resistance results," *Corros Sci*, vol. 53, pp. 1770-1777, 2011.
- [9] N. A. Negm, N. G. Kandile, E. A. Badr, and M. A. Mohammed, "Gravimetric and electrochemical evaluation of environmentally friendly nonionic corrosion inhibitors for carbon steel in 1.0 M HCl," *Corros Sci*, vol. 65, pp. 94-103, 2012.
- [10] A. M. Badawi, M. A. Hegazy, A. A. El-Sawy, H. M. Ahmed, and W. M. Kamel, "Novel quaternary ammonium hydroxide cationic surfactants as corrosion inhibitors for carbon steel and as biocides for sulfate reducing bacteria (SRB)," *Mater Chem Phys*, vol. 124, pp. 458-465, 2010.
- [11] M. Behpour, S. M. Ghoreishi, A. Gandomi-Niasar, N. Soltani, and M. Salavati-Niasari, "The inhibition of mild steel corrosion in hydrochloric acid media by two Schiff base compounds," *J Mater Sci*, vol. 44, pp. 2444-2453, 2009.
- [12] A. S. Negi, and S.C. Anand, *A textbook of physical chemistry*. New Delhi: New Age International (P) Limited, 1985, pp. 705-712.
- [13] I. B. Obot, and N. O. Obi-Egbedi, "Anti-corrosive properties of xanthone on mild steel corrosion in sulphuric acid: Experimental and theoretical investigations," *Curr Appl Phys*, vol. 11, pp. 382-392, 2011.
- [14] M. M. Solomon, S. A. Umoren, I. I. Udosoro, and A. P. Udoh, "Inhibitive and adsorption behaviour of carboxymethyl cellulose on mild steel corrosion in sulphuric acid solution," *Corros Sci*, vol. 52, pp. 1317-1325, 2010.
- [15] G. Ayyannan, K. Karthikeyan, S. Vivekananthan, M. Gopiraman, and A. Rathinavelu, "Chemical and electrochemical investigations of high carbon steel corrosion inhibition in 10 % HCl medium by quinoline chalcones," *Ionics* pp. 1-14, 2012.
- [16] R. Fuchs-Godec, "The adsorption, CMC determination and corrosion inhibition of some N-alkyl quaternary ammonium salts on carbon steel surface in 2 M H₂SO₄," *Colloids Surf*, vol. 280, pp. 130-139, 2006.