

Corrosion Inhibition and Adsorption Properties of Methocarbamol on Mild Steel in Acidic Medium

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Abstract

The corrosion inhibition of mild steel in H₂SO₄ in the presence of methocarbamol was studied using thermometric and gasometric (hydrogen evolution) methods. The study revealed that the corrosion rate increases with temperature, time and concentration of H₂SO₄. Addition of methocarbamol to the corrodent solution lowered the corrosion rate of mild steel. Inhibition efficiency (%I) of methocarbamol was found to increase with concentration and decreased with temperature. Adsorption of methocarbamol molecule on mild steel surface was found to obey the Langmuir adsorption isotherm. The phenomenon of physical adsorption is proposed from the obtained thermodynamic parameters.

Keywords: corrosion inhibition, mild steel, adsorption, methocarbamol.

Introduction

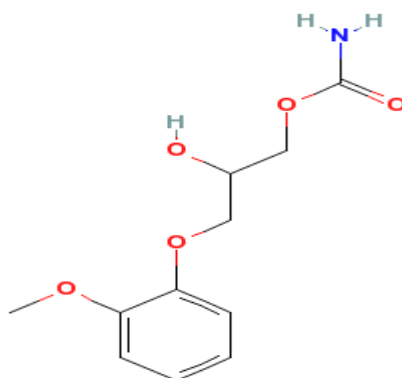
A number of organic compounds are known to be applied as corrosion inhibitors for steel in acidic environments [1-11]. Such compounds typically contain nitrogen, oxygen or sulphur in a conjugated system and function via adsorption of the molecules on the metal surface, creating a barrier to corrodent attack. The adsorption bond strength is dependent on the composition of the metal and corrodent, inhibitor structure and concentration as well as temperature. Despite the broad spectrum of organic compounds, the choice of the appropriate inhibitor for a particular application is restricted by several factors. Several research groups have concluded that the adsorption on the metal surface depends mainly

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on the physico-chemical properties of the inhibitor group, such as the functional group, electron density at the donor atom, π – orbital character [12 - 24].

A few investigations have been reported on the use of antibacterial drugs as corrosion inhibitors. Rhodanine azosulpha drugs have been reported as corrosion inhibitors for the corrosion of 304 stainless steel in HCl solutions using weight loss and potentiostatic polarization techniques by Abdallah [25]. They inhibited the corrosion by parallel adsorption on the surface of steel due to the presence of more than one active centre in the inhibitor. Abdallah [26] also studied some antibacterial drugs viz. ampicillin, cloxacillin, flucloxacillin and amoxicillin as corrosion inhibitors for aluminium in HCl solutions using hydrogen evolution, weight loss and potentiostat polarization techniques. The inhibitive effect of four sulpha drug compounds viz. sulfaguanidine, sulfamethazine, sulfamethoxazole and sulfadiazine on mild steel corrosion in HCl solutions was reported using both weight loss and galvanostatic polarization [27]. The sulfa drugs have a large number of functional adsorption centres (e.g. $-\text{NH}_2$ group, $-\text{SO}_2\text{-NH-}$ group, O and/or N heteroatoms and aromatic rings). They are strongly basic and are readily soluble in the acid medium. Rhodanine has also been reported as corrosion inhibitor for mild steel in HCl by Solmaz et. al. [28] using potentiodynamic polarization, electrochemical impedance spectroscopy, etc. Most of the drugs used play important roles in biological reactions because of their anticonvulsant, antibacterial, antidiabetic, inhibitive to mycobacterium tuberculosis and other properties [29, 30]. The choice of some of the drugs used as corrosion inhibitors is based on the following facts: (a) the molecules have oxygen, nitrogen and sulphur as active centres, (b) they are healthy and reportedly very important in biological reactions (i.e. not hazardous and environmentally friendly) and (c) they can be easily produced and purified. In view of the above, the objective of the present work is to study the corrosion inhibitive action of methocarbamol (another drug) on mild steel in acidic medium using thermometric and gasometric (hydrogen evolution) method.

The chemical structure of methocarbamol [2 – hydroxyl-3-(2-methoxyphenoxy)-propylaminoformate] is shown below. The molecular weight of the compound is 241.241 g/mol and its melting point is 366 K.



Experimental details

Materials preparation

Materials used for the study were mild steel sheet of composition (wt %) Mn (0.6), P(0.36), C(0.15) and Si(0.03). The sheet was mechanically pressed cut to form different coupons, each of dimension, 5 x 4 x 0.11 cm. Each coupon was degreased by washing with ethanol, rinsed in acetone, allowed to dry and preserved in a desiccator. All reagents used for the study were analar grade and double distilled water was used for their preparation. Concentrations of H₂SO₄ used for the study were 1, 1.5, 2, and 2.5 M while those of methocarbamol (the inhibitor used) were 4 x 10⁻⁴, 8 x 10⁻⁴, 1.2 x 10⁻³, 1.6 x 10⁻³ and 2.0 x 10⁻³ M.

The methocarbamol [2-hydroxyl-3-(2-methoxyphenoxy)-propylaminoformate] used as inhibitor was obtained commercially and used without further purification.

Gasometric measurements

Gasometric methods were carried out at 303 and 333 K as described in literature [31 – 32]. From the volume of hydrogen evolved per minute, inhibition efficiency (%I), and degree of surface coverage (θ) were calculated using equations 1 and 2, respectively.

$$\%I = \left(1 - \frac{V_{Ht}^1}{V_{Ht}^0} \right) \times 100 \quad (1)$$

$$\theta = 1 - \frac{V_{Ht}^1}{V_{Ht}^0} \quad (2)$$

where V_{Ht}^1 is the volume of hydrogen evolved at time t for inhibited solution and V_{Ht}^0 is the volume of hydrogen evolved at time t for uninhibited solution.

Thermometric method

This was also carried out as reported elsewhere [32]. From the rise in temperature of the system per minute, the reaction number (RN) was calculated using equation 3:

$$RN(^{\circ}C / \text{min}) = \frac{T_m - T_i}{t} \quad (3)$$

where T_m is the maximum temperature attained by the system, T_i is the initial temperature and t is the time. From the above, the inhibition efficiency (%I) of the used inhibitor was computed using equation 4:

$$\%I = \frac{RN_{aq} - RN_{wi}}{RN_{aq}} \times 100 \quad (4)$$

where RN_{aq} and RN_{wi} are the reaction numbers for uninhibited and inhibited systems, respectively.

Results and discussion

Table 1 shows values of corrosion rate (CR) and the inhibition efficiency (%I) of methocarbamol on mild steel in 2.5 M H₂SO₄ at 303 and 333 K. The results obtained show that the corrosion rate of mild steel in 2.5 M H₂SO₄ decreases as the concentration of methocarbamol increases, while inhibition efficiency increases with concentration.

Table 1. Values of inhibition efficiency(%I) and corrosion rate (at 303 and 333 K) obtained from gasometric method and inhibition efficiency(%I) at 303 K obtained from thermometric method for the corrosion of mild steel in 2.5 M H₂SO₄ solution containing different concentrations of methocarbamol.

Conc. of methocarbamol (M)	Gasometric				Thermometric
	%I(303 K)	%I(333 K)	CR (cm ³ /min) (303 K)	CR (cm ³ /min) (333 K)	%I (303 K)
Blank(2.5 M H ₂ SO ₄)			0.38	4.22	0.50
4 x 10 ⁻⁴	46.05	13.30	0.21	2.60	46.08
8 x 10 ⁻⁴	47.37	21.95	0.20	2.34	48.12
1.2 x 10 ⁻³	56.58	22.17	0.17	2.34	59.80
1.6 x 10 ⁻³	57.89	23.73	0.16	2.29	52.30
2.0 x 10 ⁻³	67.12	34.59	0.13	1.97	64.54

Fig. 1 shows the plot for the variation of volume of hydrogen gas evolved with time during the corrosion of mild steel in the presence of different concentrations of H₂SO₄. The figure shows that more hydrogen is evolved at the highest concentration (2.5 M) of acid studied. Figs. 2 and 3 show plots of the variation of the volume of hydrogen gas evolved with time during the inhibition of the corrosion of mild steel in 2.5 M H₂SO₄ at various concentrations of methocarbamol at 303 and 333 K, respectively. From the figures, it is seen that the volume of hydrogen gas evolved is found to reduce on addition of different concentrations of methocarbamol. This indicates that methocarbamol inhibits the corrosion of mild steel in 2.5 M H₂SO₄. Comparing Figs. 2 and 3, it is seen that inhibition efficiency of methocarbamol for mild steel corrosion decreases with temperature, suggesting the mechanism of physical adsorption. The results obtained from the thermometric method (Table 1) also confirm that methocarbamol inhibits the corrosion of mild steel. Values of inhibition efficiency of methocarbamol were observed to increase with increase in concentration, but decreases with increase in temperature. Values of inhibition efficiency (%I) obtained at 333 K were lower than values obtained at 303 K

indicating that at higher temperature the inhibitor is gradually desorbed from the surface of mild steel [33].

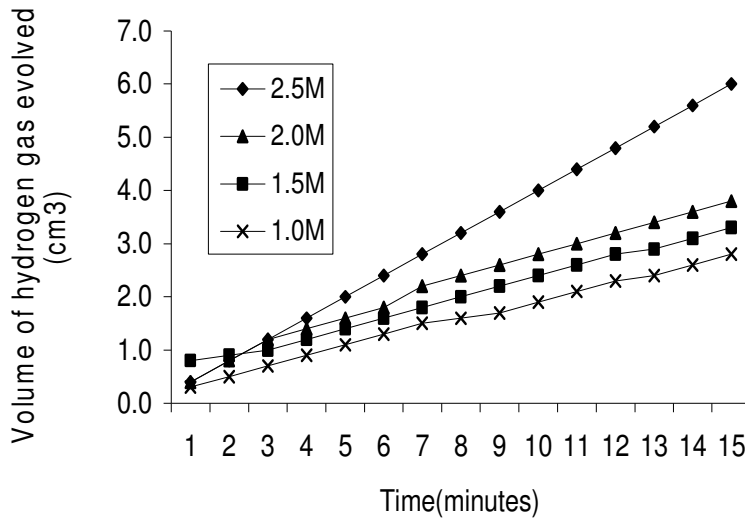


Figure 1. Gasometric plot for the corrosion of mild steel in different concentrations of acid.

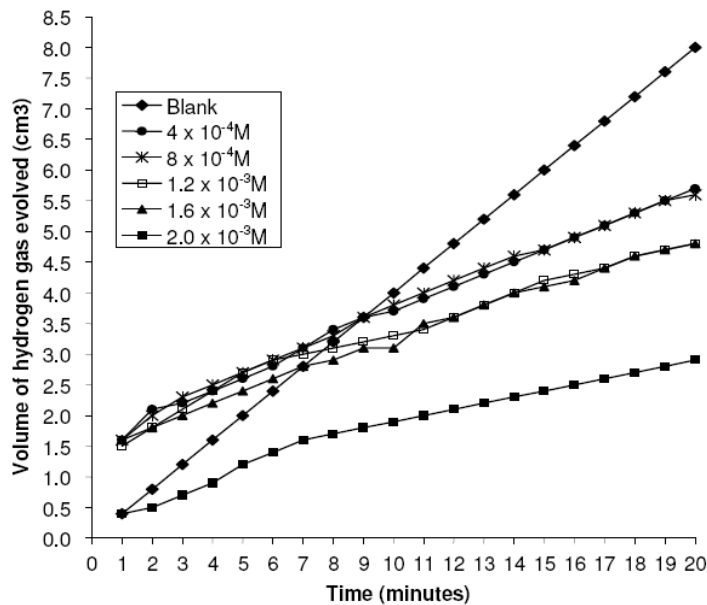


Figure 2. Variation of volume of hydrogen gas evolved with time for the corrosion inhibition of mild steel at various concentrations of methocarbamol at 303 K.

Fig. 4 shows the variation of inhibition efficiency against the different concentrations of methocarbamol at both 303 and 333 K. The significant difference between values of inhibition efficiency of methocarbamol obtained at 303 and 333 K suggests that the mechanism of adsorption of inhibitor on mild steel surface is by physical adsorption. For a physical adsorption mechanism, inhibition efficiency of an inhibitor decreases with temperature, while for a

chemical adsorption mechanism, values of inhibition efficiency increase with temperature [34-36]. Comparing values of inhibition efficiency obtained from thermometric and gasometric methods, it is seen that values obtained at 303 K from thermometric method were comparable at all concentrations of methocarbamol with those obtained from the gasometric methods.

Thermodynamic and adsorption considerations

In order to study the effect of temperature on the corrosion reaction of mild steel in the presence of methocarbamol as inhibitor, Arrhenius equation was used (equation 5) [37]:

$$\log \frac{CR_2}{CR_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \tag{5}$$

where E_a is the activation energy of the reaction, R is the gas constant, T is the temperature and, considering a change in temperature from 303 K (T_1) to 333 K (T_2), the corresponding values of the corrosion rates at these temperatures are CR_1 and CR_2 , respectively. The values of E_a for the inhibited corrosion reaction of mild steel have been calculated and recorded in Table 2. Values of E_a ranged from 68.94 to 71.16 kJ/mol. These values are higher than the value of 51.17 kJ/mol obtained for the blank indicating that the corrosion reaction of mild steel is retarded by methocarbamol [38]. It also supports the phenomenon of physical adsorption.

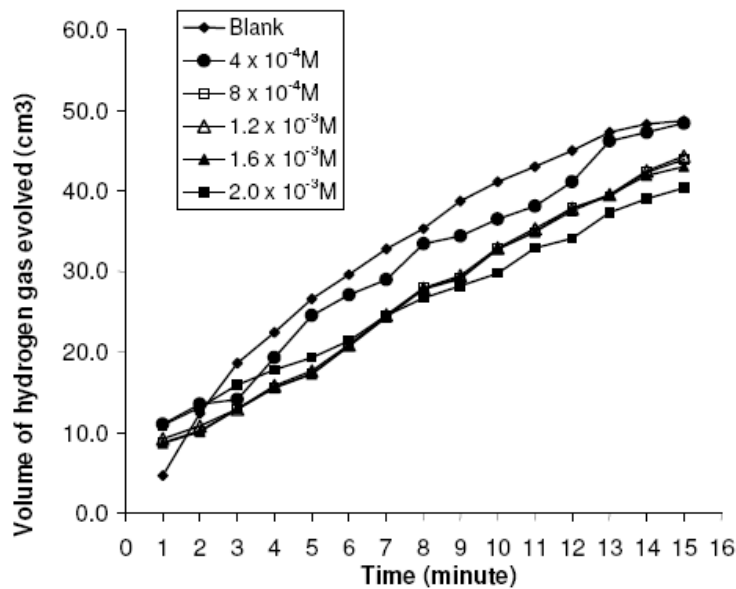


Figure 3. Variation of the volume of hydrogen gas evolved with time during the inhibition of the corrosion of mild steel by various concentrations of methocarbamol at 333 K.

Values of heat of adsorption of methocarbamol on mild steel surface were calculated using equation 6 below [39]:

$$Q_{ads} = 2.303R \left[\log \left(\frac{\theta_2}{1-\theta_2} \right) - \log \left(\frac{\theta_1}{1-\theta_1} \right) \right] \times \left(\frac{T_1 \times T_2}{T_2 - T_1} \right) \text{kJmol}^{-1} \quad (6)$$

Values of Q_{ads} (see Table 2) calculated were negative and ranged from -32.53 to -52.61 kJ/mol, indicating that the adsorption of methocarbamol on mild steel surface is exothermic.

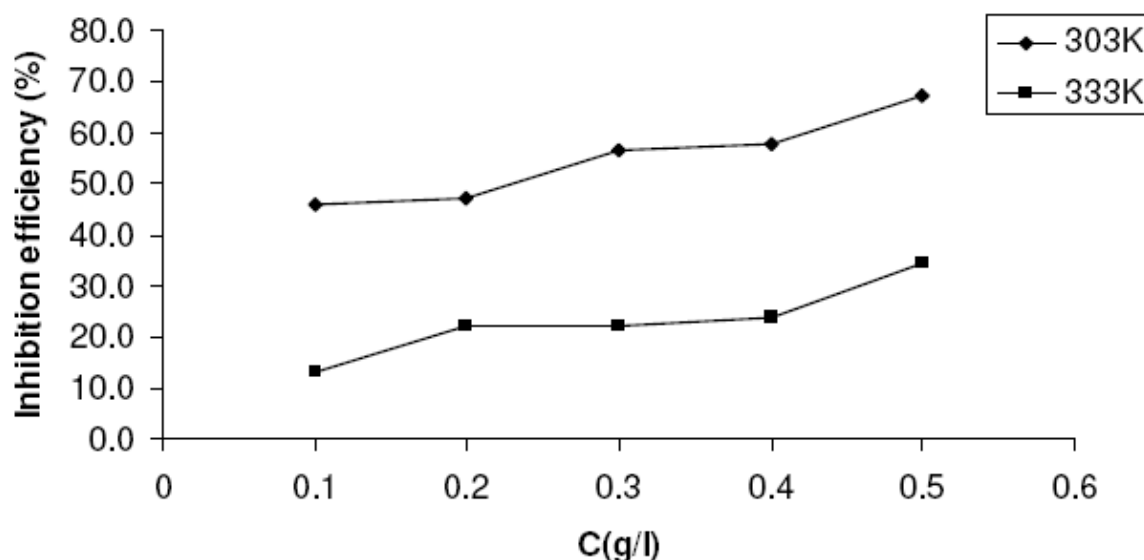


Figure 4. Variation of inhibition efficiency with the concentration of methocarbamol.

Table 2. Some thermodynamic parameters for the adsorption of methocarbamol on mild steel surface.

Conc. of methocarbamol (M)	E_a (kJ/mol)	Q_{ads} (kJ/mol)
Blank(2.5 M H ₂ SO ₄)	51.17	
4×10^{-4}	71.14	-48.00
8×10^{-4}	68.94	-32.53
1.2×10^{-3}	74.25	-42.53
1.6×10^{-3}	74.55	-41.55
2.0×10^{-3}	77.16	-37.78

Values of free energy of adsorption of methocarbamol on mild steel surface were calculated from the plot of the isotherms in Fig. 5. Calculated values of ΔG_{ads} are recorded in Table 3. These values are negative and are -12.50 kJ/mol at 303 K and -15.01 kJ/mol at 333 K for the Langmuir isotherm plot. The values obtained indicate that adsorption of methocarbamol is spontaneous and occurs via physical adsorption mechanism. Generally, values of ΔG_{ads} up to -20 kJ/mol (as obtained in this study) are consistent with electrostatic interaction between the charged metal and charged molecules, which signifies physical adsorption, while values more negative than -40 kJ/mol signify chemical adsorption [34-36, 40-41].

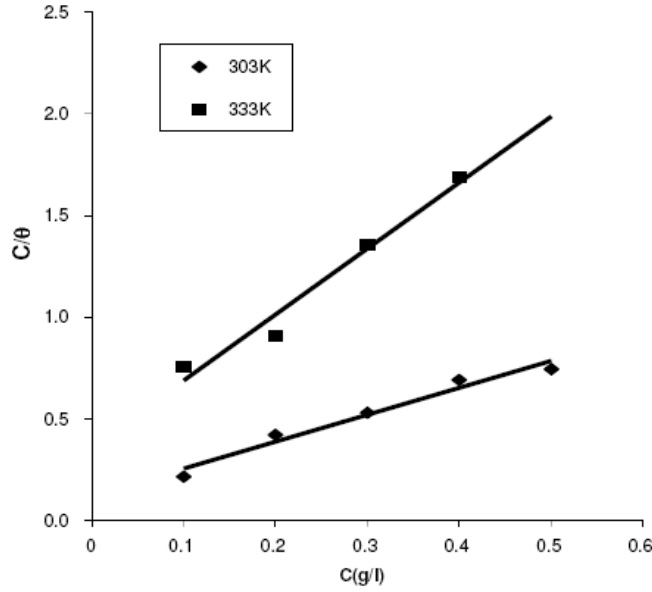


Figure 5. Langmuir adsorption isotherm for methocarbamol adsorbed on mild steel surface in 2.5 M H₂SO₄ solution.

Table 3. Values of Langmuir parameters.

Temperature (K)	log K	Slope	ΔG _{ads} (kJ/mol)	R ²
333	0.84	0.50	-15.01	0.9769
303	0.41	0.77	-12.50	0.9859

Adsorption isotherms are very important in understanding the mechanism of inhibition of corrosion reaction of metals and alloys. The most frequently used adsorption isotherms are Frumkin, Temkin, Freundlich, Flory Huggins, Bockris – Swinkel, El-Awardy and Langmuir isotherms. All these isotherms can be represented as follows,

$$f(\theta, x) \exp(-2a\theta) = k C \tag{7}$$

where $f(\theta, x)$ is the configuration factor which depends upon the physical model and the assumptions underlying the derivation of the isotherm. θ is the degree of surface coverage, C is the inhibitor concentration in the electrolyte, X is the size ratio, a is the molecular interaction parameter and k is the equilibrium constant of the adsorption process. Attempts to fit data obtained from gasometric measurement into different adsorption isotherms reveal that the data best fitted Langmuir adsorption isotherm.

Assumptions of Langmuir relate the concentration of the adsorbate in the bulk of the electrolyte (C) to the degree of surface coverage (θ) according to equation 8 below:

$$\frac{C}{\theta} = \frac{1}{K} + C \tag{8}$$

where K is the equilibrium constant of adsorption. By plotting values of C/θ versus values of C , straight line graphs were obtained (see Fig. 5), which proves that Langmuir adsorption isotherm is obeyed. Comparing the degree of linearity

of Langmuir adsorption isotherms as measured by values of R^2 (Table 3), it is seen that Langmuir adsorption isotherm is best applicable at 303 K than at 333 K. This confirms that the adsorption behaviour of the inhibitor is strongly influenced by temperature. Also values of the slope at 303 K are greater than the values obtained at 333 K, indicating that the strength of the attractive behaviour of the inhibitor decreases with temperature. The slopes of the C/θ versus C plots show deviation from unity, which means non-ideal simulating [42] and unexpected from the Langmuir adsorption isotherm. They might be the results from the interactions between the adsorbed species on the mild steel surface [43, 44].

Conclusions

Methocarbamol is a good inhibitor for mild steel corrosion. The inhibitor functions by being adsorbed on mild steel surface. Methocarbamol is a better inhibitor at lower temperature. The phenomenon of physical adsorption is proposed from the obtained thermodynamic parameters. The experimental data fit the Langmuir adsorption isotherm.

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