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Durability and synergistic effects of KI on the acid corrosion inhibition of mild steel by hydroxypropyl methylcellulose

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ABSTRACT

The performance of hydroxypropyl methylcellulose (HPMC) as safe corrosion inhibitor for mild steel in aerated 0.5 M H_2SO_4 solution was appraised by weight loss, impedance and polarization measurements. Results indicate that HPMC functions as a good inhibitor in the studied environment and inhibition efficiency increased with increasing concentration of inhibitor and temperature. Time-dependent effect of the inhibition efficiency reveals that inhibition efficiency increased with time up to the fourth day after which it waned, but improved on addition of KI. The synergism parameter evaluated confirmed the synergistic effect of KI and HPMC. Impedance results clearly show that HPMC inhibited the corrosion reaction via adsorption onto the metal/solution interface following Freundlich adsorption isotherm. Polarization results indicate that HPMC acts as a mixed-type inhibitor with predominant cathodic effect. Theoretical study using density functional theory was employed to establish the correlation between the structure (molecular and electronic) and the inhibition efficiency.

1. Introduction

Although corrosion is inevitable, its cost can be considerably reduced. Aside from its direct cost in economy, corrosion is a serious problem because it definitely contributes to the depletion of our natural resources, due to increase in the consumption of mineral resources used in the metal industry (Fontana, 2007).

Metals and their alloys are most times deployed in services that involve chemically challenged operations. Their contacts with aggressive environments affect their integrity resulting to conspicuous deteriorating effects. Some of the deleterious effects of corrosion are surface dulling, high maintenance and operating cost, contamination of product, plant shutdowns, loss of valuable products as well as effects on safety and reliability (Landolt, 2007).

To reduce the corrosion problem and thus save resources, different approaches to corrosion resistance abound (Cecchetto, Delabouglise, & Petit, 2007; Kim et al., 2006; Praveen, Venkatesha, Arthoba, Naik, & Prashantha, 2007; Subasria, Shinoharaa, & Morib, 2005). Among the different methods available, the use of corrosion inhibitors is usually the most appropriate and effective way to achieve this objective (Akpan & Offiong, 2012; Arthur, Jonathan, Ameh, & Anya, 2013; Arukalam, Madufor, Ogbobe, & Oguzie, 2013; Umoren, 2009). This involves isolation of a metal from corrosive agents via adsorption of compounds containing inhibiting molecules onto the metal surface which forms protective barrier (Arukalam, Madufor, Ogbobe, & Oguzie, 2014; Oguzie, Li, Wang, & Wang, 2011).

Compounds containing nitrogen, oxygen, sulphur and phosphorus in the conjugated system, as well as aromaticity have been reported as effective corrosion inhibitors (Obot, 2009; Oguzie et al., 2011; Umoren & Obot, 2008). The inhibitive characteristics of such compounds derive from the adsorption ability of their molecules, with the polar group acting as the reaction centre for the adsorption process. The resulting adsorbed film acts as a barrier that separates the metal from the corrodent and efficiency of inhibition depends on the mechanical, structural and chemical characteristics of the adsorption layers formed under particular conditions (Hussin & Kassim, 2010; Okafor, Ebenso, & Ekpe, 2010).

In effort to combat mild steel corrosion in acidic environments, there have been documented reports on the use of both synthetic and natural polymers as effective corrosion inhibitors (Dubey & Singh, 2007; Umoren & Ebenso, 2008). The functional groups of the polymers interact with the metal ions and form complexes which act as barrier that separates the aggressive solution from the metal surface. Hence, corrosion inhibition is achieved via adsorption (Kumpawat, Garg, & Tak, 2009; Umoren, 2008).

Co-adsorption of two or more additives otherwise referred to as synergistic effect on the inhibitors describes the enhancement of the performance of a corrosion inhibitor in the presence of

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another substance in small amount in the corrosion medium. This phenomenon could be thought of as an effective method of getting better performance or to decrease the amount of usage of the inhibitor (Musa, Mohamad, Kadhum, Takriff, & Tien, 2011; Sudhish, Ashish, Luteendo, Mwadham, & Eno, 2012). It is an acceptable fact that the presence of halide ions in acidic medium could synergistically increase or decrease antagonistically the inhibition efficiency of some organic compounds. Some previous reports have shown that among the inhibiting effect of halide ions studied, iodide ions have shown greater influence, which is attributable to its large ionic radius, high hydrophobicity and electronegativity, compared to other halide ions (Okafor, Oguzie, Iniama, Ikpi, & Ekpe, 2008; Umoren, Li, & Wang, 2010).

The present study, however, aims to appraise the inhibiting capability of hydroxypropyl methylcellulose (HPMC) on mild steel corrosion in 0.5 M H_2SO_4 solution using the above mentioned measurement techniques.

2. Experimental

2.1. Weight loss measurements

The experiments were performed on mild steel specimens having the following percentage chemical composition: Si: 0.02; C: 0.05; Mn: 0.18; Cu: 0.02; Cr: 0.02 and the remainder Fe. The mild steel sheet of thickness 0.05 cm was machined into test coupons of length, 3 cm and width, 2 cm and a small hole drilled at one end of the coupon to enable suspension into the test solution in the beaker. The metal specimens were polished with fine SiC emery paper up to 800 grits, degreased and cleaned as described elsewhere (Kumar, Sankar, Kumaravel, & Rameshkumar, 2013; Mani megalai, Ramesh, & Manjula, 2013). HPMC sourced from Sigma Aldrich chemical company, was used without further purification, at concentrations of 500, 1000, 1500 and 2000 mg/l. Blank sulphuric acid solution was prepared in the concentration of 0.5 M H_2SO_4. The potassium iodide, KI from BDH laboratory Supplies was used. 100 and 500 mg/l KI were prepared and used as inhibitors while 2000 mg/l HPMC in combination with 100 mg/l KI was also used as inhibited solution.

Weight loss experiments were conducted on test coupons under total immersion conditions in 200 ml of test solutions at ambient temperature, 28 ± 1 °C. The pre-cleaned and weighed coupons were suspended in 250 ml capacity beakers containing the test solutions using glass rods and hooks. All tests were made in aerated solutions and were run three times to ensure reproducibility. To determine weight loss with respect to time and additive concentrations, the coupons were retrieved from test solutions at 24-h interval progressively for 120 h (5 days). Also to study the effect of inhibitor's durability, tests were conducted at weekly interval for a total duration of seven weeks. The effect of periodic inhibitor injection was also conducted. Here tests were conducted for seven weeks. At the middle of every week of the seven weeks under study, 20 ml of the test solution was removed and immediately replaced with equal amount of a freshly prepared one. The coupons were examined at the end of every week. Temperature test was also conducted using thermostatic water bath in the range, 30–60 °C for 6 h. At the end of the tests, the weight losses were taken to be the mean value of the difference between the initial and final weights of the coupons for the three determinations at a given time. The corrosion rates of mild steel in 0.5 M H_2SO_4 solution and the acid solution containing the additives; HPMC, KI and HPMC + KI were calculated using the expression (Arukalam, Madu, Ijomah, Ewulonu, & Onyeagoro, 2014):

$$\text{Corrosion rate, } R_c \ \ (\text{g m}^{-2}\,\text{h}^{-1}) = \left[\frac{\Delta W}{At}\right] \quad (1)$$

Table 1
Calculated values of corrosion rates (g m^{-2} h^{-1}) for mild steel corrosion in 0.5 M H_2SO_4 in the absence and presence of different concentrations of HPMC from weight loss measurements.

System	Corrosion rate (g m^{-2} h^{-1})				
	Day 1	Day 2	Day 3	Day 4	Day 5
Blank	61.80	64.77	56.16	49.18	44.64
500 mg/l	46.27	32.00	26.31	21.20	18.17
1000 mg/l	25.60	19.77	15.20	12.47	17.12
1500 mg/l	20.60	16.40	12.38	10.63	13.44
2000 mg/l	9.40	6.60	5.47	4.47	4.13

where ΔW, A, t are weight loss in gram, surface are of the test coupon in cm^2 and time of exposure in the test solution in hour, respectively.

The inhibition efficiency was taken to represent the surface coverage (θ). The percentage inhibition efficiency was calculated using Eq. (2):

$$\text{I.E.\%} = \left(\frac{CR_o - CR_{inh}}{CR_o}\right) \times 100 \quad (2)$$

where both CR_o and CR_{inh} are the corrosion rates in the uninhibited and inhibited solutions respectively.

2.2. Electrochemical measurements

2000 mg/l concentration of the inhibitor was chosen to study the kinetics of the corrosion inhibition process as well as the cathodic and anodic partial reactions occurring in the process. In the electrochemical studies the coupons were machined in such a way that only 1 cm^2 surface area was exposed. Before the measurements, the samples were polished using different grade emery papers followed by washing in ethanol, acetone and finally with distilled water. Electrochemical tests were carried out in a conventional three-electrode configuration with graphite rod as counter electrode and saturated calomel electrode (SCE) as the reference electrode. The working electrode (mild steel of 1 cm^2 surface area) was first immersed in the test solution and after establishing a steady state OCP (open circuit potential), the electrochemical measurements were carried out in a *VERSASTAT 3* computer controlled electrochemical workstation. The frequency range of 10 kHz to 10 Hz with amplitude of 10 mV (RMS) using a.c. signals at open circuit potential was used. The potentiodynamic polarization curves were obtained in the potential range of ±250 mV at a sweep rate of 0.5 mV/s.

All theoretical quantum chemical calculations were performed using the density functional theory (DFT) electronic structure programmes – Forcite and $DMol^3$ as contained in the Materials Studio 4.0 software.

3. Results and discussion

3.1. Weight loss results

3.1.1. Weight loss, corrosion rates and inhibition efficiency

The corrosion rates of the mild steel coupons were assessed using Eq. (1) and the corresponding values for the different test solutions are given in Table 1. It was also observed that the metal corroded in the free acid solution but the weight lost from the coupons decreased on addition of HPMC in the corrodent (Table 1). The assays further present the effect of addition of HPMC at different concentrations on the corrosion of mild steel in 0.5 M H_2SO_4 at ambient temperature, 28 ± 1 °C. The results show that corrosion rates decreased in the presence of HPMC and decreased further with increasing concentration of HPMC. This implies that the HPMC retarded the dissolution of mild steel in the acidic environments,

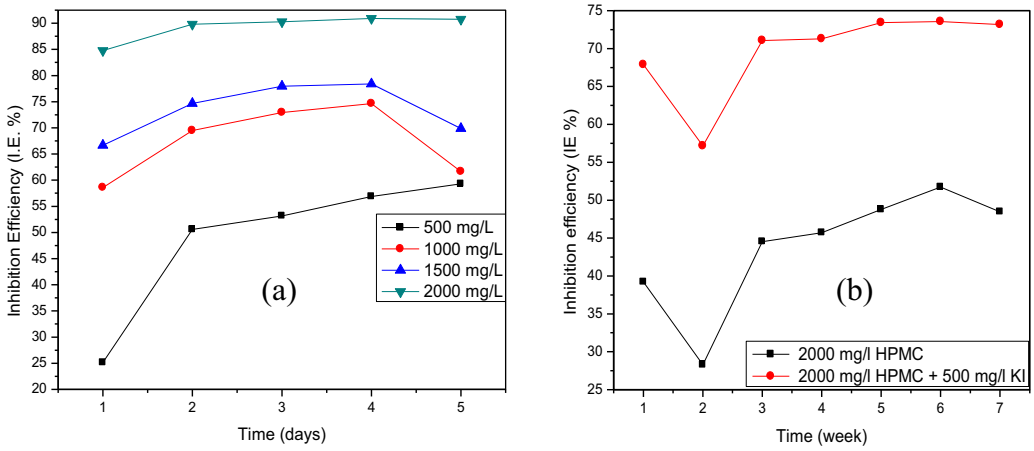

Fig. 1. Inhibition efficiency against time for (a) 5 days and (b) 7 weeks, for mild steel corrosion in 0.5 M H_2SO_4, in the absence and presence of different concentrations of HPMC.

the degree of inhibition depending on the concentration of the HPMC.

The experimental data plotted in Fig. 1(a) clearly show that the inhibitive effect of HPMC on mild steel corrosion in 0.5 M H_2SO_4 is very satisfactory. It is evident that all concentrations of the additive exhibited significant inhibition efficiency. The inhibitive action of the organic substance during mild steel corrosion could be reasoned to be based on the adsorption ability of the molecules, where the resulting adsorption film isolates the metal surface from the corrosion medium. Consequently, in inhibited solutions, the corrosion rate is indicative of the number of free corrosion sites remaining after some sites have been effectively blocked by adsorption of inhibitor.

Assuming that corrosion is restricted to the uncovered sites on the coupons, such that the covered sites by the inhibitor have negligible rates, the degree of surface coverage can be evaluated using the expression

$$\theta = 1 - \frac{CR_{inh}}{CR_o} \quad (3)$$

The parameters retain their previous meanings.

The surface coverage and inhibition efficiency data of HPMC at different concentrations are also given in Table 1. The results suggest that the HPMC exhibited good inhibition during mild steel corrosion in the corrodent.

3.1.2. Effect of immersion time/durability test

Plots of inhibition efficiency versus time (in days) of immersion of test coupons in the presence of test solutions are also shown in Fig. 1(a). They reveal that inhibition efficiency increased with time but decreased after the fourth day, except for 500 mg/l concentration of inhibitor which increased progressively with time. This is the critical point beyond which the strength of the inhibiting molecules waned. It is worth noting that the adsorption of HPMC onto the mild steel surface is found to be slow, suggesting that the adsorption process is time-dependent. This behaviour is characteristic of polymers where, by virtue of their macromolecular nature, will be soluble, depending on the nature of the solvent (HCl solution) and solute (HPMC), viscosity of the medium, polymer texture and molecular weight (Katchy, 2000). At 2000 mg/l HPMC, inhibition efficiency can be seen to maintain almost steady values at $t > 48$ h, suggesting stability of the inhibitor action.

The time-dependence of the inhibiting effect is particularly pronounced at high HPMC concentration, where inhibition efficiency maintained low values at the initial stages of immersion and gradually augmented with prolonged immersion. The optimum inhibition efficiency is 90.92% at 2000 mg/l HPMC after 4 days of exposure.

To further elucidate on the time-dependent inhibiting effect of HPMC to ascertain its durability over time, experiments were conducted with 2000 mg/l HPMC for seven weeks and the results of the assays are presented in Fig. 1(b). From the plots, the inhibition efficiency of HPMC decreased in comparison with what was obtained at lower immersion time as seen in Fig. 1(a). On addition of KI to HPMC, the inhibition efficiency increased considerably. A further look at the plots show that HPMC is durable even after the seven weeks of study, only that the inhibition efficiency is low which was improved on addition of KI. However, there is a marked decrease in inhibition efficiency at $t > 1$ week which later resumed at $t > 2$ weeks and gradually increased with time. The characteristic decrease in inhibition efficiency could be due to agitation from external influence which resulted to temporary desorption of the adsorbed inhibitor. As the agitation died down, the coiled molecules of the polymer continued to unwind and adsorption resumed leading to increase in inhibition efficiency.

3.1.3. Effect of temperature

The effect of temperature on the corrosion behaviour of mild steel in the free acid solution and in the solution containing different concentrations of HPMC was investigated at 30, 40, 50 and 60 °C. The results obtained for a 6-h immersion period are presented in Table 2. The data indicate that the corrosion rate in uninhibited acid increased with rise in temperature, whereas that in the presence of HPMC decreased as the temperature rises from 30 to 50 °C, but shows rapid increase as the temperature rose to 60 °C. The observed decrease in corrosion rate with rise in temperature from 30 to 50 °C could be reasoned to be due to insufficient kinetic energy required to achieve molecular mobility of HPMC. However, at 60 °C, the corrosion rate increased substantially, since temperature elevation which results to increase in kinetic energy usually accelerates corrosive processes. Accordingly, inhibition efficiency increased with rise in temperature as depicted in Fig. 2.

Table 2
Calculated values of corrosion rates ($g\,m^{-2}\,h^{-1}$) for mild steel corrosion in 0.5 M H_2SO_4 in the absence and presence of different concentrations of HPMC at different temperatures from weight loss measurements.

System	Corrosion rate ($g\,m^{-2}\,h^{-1}$)			
	30 °C	40 °C	50 °C	60 °C
Blank	53.07	55.20	72.00	106.13
500 mg/l HPMC	20.26	20.00	17.60	25.60
2000 mg/l HPMC	16.27	14.40	12.80	18.67

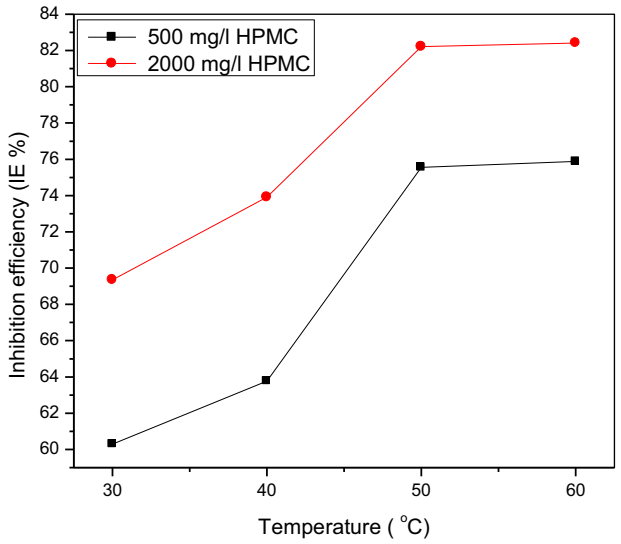

Fig. 2. Inhibition efficiency against temperature for mild steel corrosion in 0.5 M H_2SO_4, in the absence and presence of different concentrations of HPMC.

Such increase in inhibition efficiency with rise in temperature implies that the adsorbed inhibitor is chemisorbed on the metal surface (Banerjee et al., 2011; De Souza & Spinelli, 2009). It is therefore interesting to note here that the obtained value of inhibition efficiency at maximum HPMC concentration for a 6-h immersion period at 60 °C (82.41%) is close to that obtained after 24-h of immersion at room temperature (84.71%), confirming increased molecular action at elevated temperature. This is substantiated by the fact that polymer solubility and its diffusion is a slow process, especially at room temperature. The reason is due to the presence of macro-molecules in polymers.

3.1.4. Adsorption/thermodynamic considerations

Adsorption of organic inhibitor molecules on a corroding metal surface and subsequent metal–inhibitor interaction may be regarded as a displacement reaction process, wherein the inhibitor molecules displace water molecules pre-adsorbed on the mild steel surface. To understand the mechanism of adsorption of HPMC and extrapolate vital information regarding the nature of interaction between the HPMC and the corroding mild steel surface, adsorption isotherms are quite useful. The data in Table 1 were used to evaluate the adsorption of HPMC on mild steel surface and was found to follow Freundlich adsorption isotherm given by

$$\theta = K_{ads} C^n \tag{4}$$

This is written in logarithmic form as

$$\log \theta = \log K_{ads} + n \log C \tag{5}$$

where $0 < n < 1$; θ is the degree of surface coverage, C is the concentration of the inhibitor and K_{ads} is the equilibrium constant of adsorption–desorption process while n represents the number of pre-adsorbed water molecules replaced by inhibitor molecule. The plots of $\log\theta$ versus $\log C$ are shown to be linear as presented in Fig. 3(a) for mild steel corrosion.

K_{ads} is obtained from the intercept of the plot. Generally, K_{ads} denotes the strength between adsorbate and adsorbent. Large values of K_{ads} imply more efficient adsorption and hence better inhibition efficiency. For mild steel in H_2SO_4, $K_{ads} = 1.107$, 1.110, 1.063 and 1.061 at 30, 40, 50 and 60 °C respectively. This confirms the good inhibition of mild steel dissolution in H_2SO_4 by HPMC.

Table 3
Calculated values of enthalpy ΔH° and entropy ΔS° of activation for mild steel corrosion in 0.5 M H_2SO_4 solution in the absence and presence of HPMC.

System	ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K)
Blank	6.876	−0.074
500 mg/l	0.881	−0.097
2000 mg/l	0.407	−0.100

Adsorption enthalpies ΔH° and adsorption entropies ΔS° could be calculated from the transition state equation (Eq. (6)) (Arukalam et al., 2013) and presented in Table 3.

$$CR = \left(\frac{RT}{Nh}\right) e^{(\Delta S^\circ/R)} \cdot e^{(-\Delta H^\circ/RT)} \tag{6}$$

where h is the Planck's constant, N is the Avogadro's number, T is the absolute temperature and R is the universal gas constant. A plot of $\log(CR/T)$ versus $1/T$ gives straight lines (Fig. 3(b)). ΔH° and ΔS° were estimated from the slope and intercept respectively from the linear function. The positive values of ΔH° reflect the endothermic nature of mild steel corrosion in the presence of the HPMC and the negative values indicate exothermic reaction of the mild steel/H_2SO_4 in the presence of HPMC. The negative values of ΔS° in corrosive medium show an increase in the system order.

The standard Gibbs free energy of adsorption of the inhibitor (ΔG°_{ads}) on mild steel surface can be evaluated with the following equation (John, Joseph, Balakrishnan, Aravindakshan, & Joseph, 2010):

$$\Delta G^\circ_{ads} = -RT \ln\left(\frac{55.5\theta}{C(1-\theta)}\right) \tag{7}$$

where C is the concentration of inhibitor in g/l. From Eq. (7), the values of ΔG°_{ads} for 500 mg/l HPMC were calculated to be −12.885, −13.753, −15.743 and −16.230 kJ mol^{-1} at temperatures of 303 K (30 °C), 313 K (40 °C), 323 K (50 °C) and 333 K (60 °C) respectively. Whereas ΔG°_{ads} for 2000 mg/l HPMC obtained are −10.387, −11.370, −12.996 and −13.399 kJ mol^{-1} for the four temperatures of study. The calculated standard Gibbs free energy of adsorption values for the two concentrations of HPMC examined reveal lower values than −20 kJ mol^{-1} which is an indication of physical adsorption, but show tendency towards chemical adsorption as evidenced in the increase in ΔG°_{ads} values (more negative) with increasing temperature (Hussin & Kassim, 2010). The low values of ΔG°_{ads} could be reasoned to be due to short immersion period. Hence, it is believed that longer immersion period will favour chemical adsorption especially at low inhibitor concentration, since the mobility of polymer molecules such as HPMC is sensitive to temperature, time and solvent. This could be explained on the basis that at lower concentration, there is increased inhibitor mobility which enhanced its adsorption on the mild steel surface forming protective adsorption film of polymers. The observed physical adsorption experienced with higher inhibitor concentration is due to reduced molecular mobility arising from increased viscosity of the system. Therefore, the decrease in ΔG°_{ads} at high concentration of inhibitor shows that there was desorption of the adsorbed inhibitor molecules due to instability arising from mere mechanical screening of the steel surface (Obot & Obi-Egbedi, 2010):

3.1.5. Effect of inhibitor injection

2000 mg/l HPMC was chosen to study the effect of inhibitor injection on the inhibition efficiency of HPMC for mild steel corrosion in 0.5 M H_2SO_4 solution. The data obtained from the assays are presented in Table 4. Fig. 4 shows the plots of the effect of inhibitor injection for mild steel corrosion in 0.5 M H_2SO_4 without and with HPMC and KI. The data reveal higher corrosion rate for mild steel in the solution with inhibitor injection than solution without inhibitor

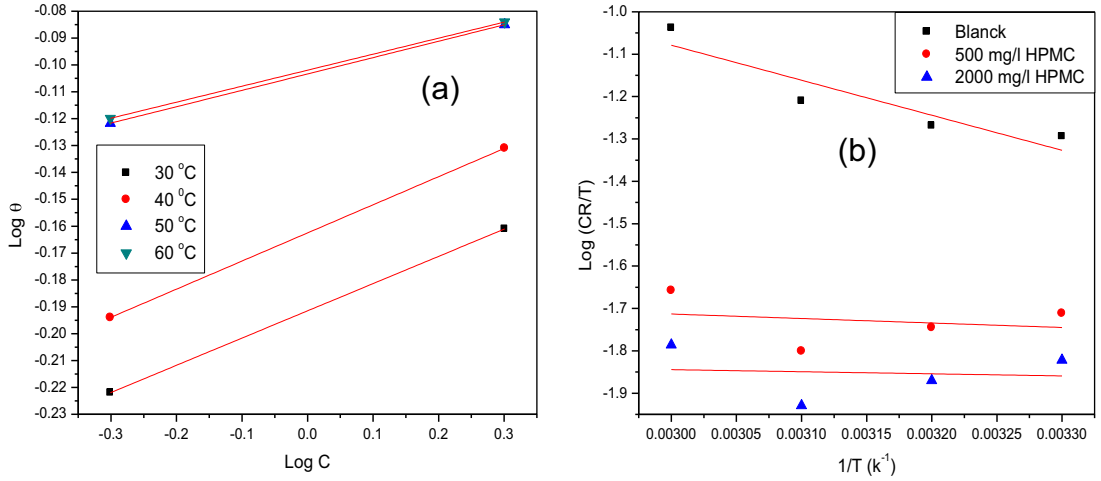

Fig. 3. (a) Plots of Freundlich adsorption isotherm and (b) plots of transition state for HPMC adsorption on mild steel in 0.5 M H_2SO_4 solution.

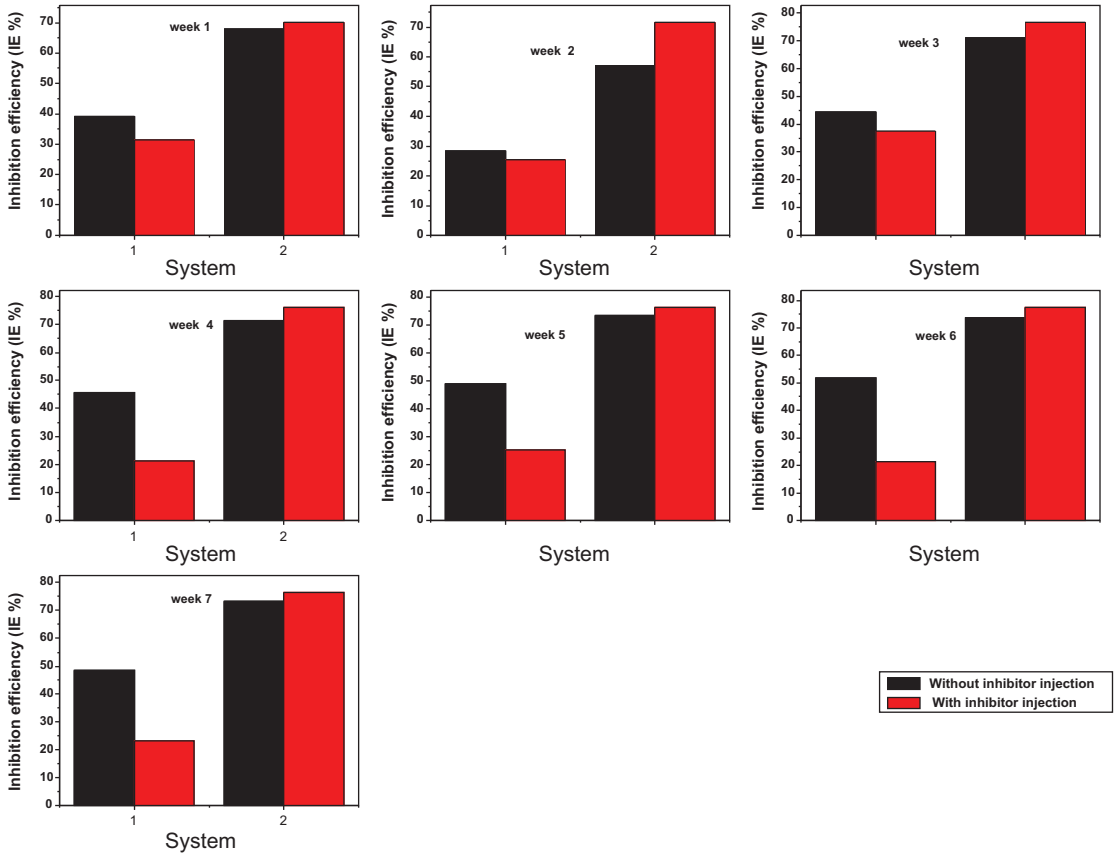

Fig. 4. Inhibition efficiency against inhibitor systems for mild steel corrosion in 0.5 M H_2SO_4, for 1–7 weeks of exposure. 1 = 2000 mg/l HPMC; 2 = 2000 mg/l HPMC + 500 mg/l KI.

Table 4
Calculated values of corrosion rates (g m^{-2} h^{-1}) for mild steel corrosion in 0.5 M H_2SO_4 with and without inhibitor injection from weight loss measurements.

System	Corrosion rate without inhibitor injection (corrosion rate with inhibitor injection) (g m^{-2} h^{-1})						
	Wk 1	Wk 2	Wk 3	Wk 4	Wk 5	Wk 6	Wk 7
Blank	69.32	39.78	39.78	31.04	28.93	25.92	23.51
2000 mg/l HPMC	35.56 (44.60)	24.11 (27.73)	18.68 (23.21)	14.16 (22.90)	12.36 (20.19)	10.55 (18.99)	10.25 (16.88)
2000 mg/l HPMC + 500 mg/l KI	19.59 (19.59)	15.07 (10.85)	10.25 (8.74)	7.84 (7.23)	6.63 (6.63)	6.03 (5.73)	5.42 (5.42)

Table 5
Synergistic effect of KI on HPMC adsorption on mild steel in 0.5 M H_2SO_4 solution.

System	Corrosion rate ($g\,m^{-2}\,h^{-1}$)					Inhibition efficiency (I.E.%)				
	Day 1	Day 2	Day 3	Day 4	Day 5	Day 1	Day 2	Day 3	Day 4	Day 5
Blank	77.15	82.58	71.12	62.99	55.45	–	–	–	–	–
100 mg/l KI	42.79	41.59	35.56	28.93	25.01	44.53	49.64	50.00	54.07	54.89
500 mg/l KI	17.48	14.79	12.66	11.15	9.34	77.34	82.12	82.20	82.30	83.15
2000 mg/l HPMC	11.75	8.44	6.93	5.73	5.12	84.76	89.78	90.25	90.91	90.76
2000 mg/l HPMC + 500 mg/l KI	8.44	6.63	5.12	4.22	3.32	89.06	91.97	92.80	93.30	94.02

injection. This behaviour is traceable to the fact that solutions without inhibitor injection show reduction in the aggressive strength while solutions with freshly prepared inhibitor injection have more active acid molecules. As such the active molecules in the latter solution have more potency to corrode leading to higher corrosion rate of mild steel in 0.5 M H_2SO_4 solution. However, in the presence of KI, solution with inhibitor injection shows lower corrosion rate than those without inhibitor injection. The reason is due to synergistic effect of KI with HPMC for mild steel in 0.5 M H_2SO_4 as earlier reported. The complex formed by inhibitor–KI on the metal surface reduced the available area for corrodent attack, thereby increasing the surface area covered by the inhibitor system.

3.1.6. Effect of halide ion addition

Halide ions are known to enhance adsorption of organic cation-type inhibitors in solution by forming intermediate bridges between the metal surface and the positive end of the organic inhibitor. Accordingly, tests to evaluate the cooperative effect of KI and HPMC were undertaken in this study. Table 5 shows the effect of 100 and 500 mg/l of KI on the corrosion of mild steel in 0.5 M H_2SO_4 solution. Also shown in Table 5 is the effect of 500 mg/l KI on 2000 mg/l HPMC. It could be observed that addition of KI synergistically improved the inhibition efficiency of HPMC. This phenomenon is attributed to the stabilization of the adsorption of inhibitor on the mild steel surface caused by the interaction between $HPMC^+$ and I^- which leads to more surface coverage and hence, greater corrosion inhibition. This result suggests that the iodide ions have played an important role in stabilizing the adsorbed HPMC molecules and the two species (I^- and HPMC) seem to compete for active sites of adsorption. The process is similar to the phenomenon of anion-induced adsorption (Oguzie, Unaegbu, Ogukwe, Okolue, & Onuchukwu, 2004) and may be represented as follows:

$$I_s \rightarrow I_{ads} \tag{8a}$$

$$Org_s + I_{ads} \rightarrow OrgI_{ads} \tag{8b}$$

where I_s and Org_s are the halide ion and organic inhibitor, respectively in the bulk solution; I_{ads} and $OrgI_{ads}$ refer to the halide ion and ion-pair respectively in the adsorbate state. This ion-pair interaction consequently increases the surface coverage thereby reducing metal dissolution.

Synergism of corrosion inhibitors has been assessed in terms of a synergism parameter (S_I) according to the following equation:

$$S_I = \frac{1 - I_{1+2}}{1 - I'_{1+2}} \tag{9}$$

where $I_{1+2} = (I_1 + I_2)$; I_1 is the inhibition efficiency of the halide, I_2 is the inhibition efficiency of HPMC and I'_{1+2} is the inhibition efficiency of HPMC in combination with the halide. Calculated values of S_I are 1.46, 1.52, 1.52, 1.56 and 1.56 respectively for the 5 days of study. Synergism parameter greater than unity as observed, suggests that the increased inhibition efficiency resulting from the addition of halide to the inhibitor is only due to the synergistic effect.

3.2. Electrochemical impedance spectroscopy results

Electrochemical impedance spectroscopy analyses provide insight into the kinetics of electrode processes as well as the surface characteristics of the electrochemical system of interest. Fig. 5(a) presents the impedance spectra measured at E_{corr} after 30 min immersion, and exemplify the Nyquist plots obtained for mild steel in 0.5 M H_2SO_4 solution in the absence and presence of HPMC and HPMC + KI. The observed increase in the impedance parameters in inhibited solutions is associated with the corrosion inhibiting effect of HPMC. The Nyquist plots for all systems generally have the form of only one depressed semicircle, corresponding to one time constant, although a slight sign of low-frequency inductive behaviour can be discerned. The depression of the capacitance semicircle, with centre below the real axis suggests a distribution of the capacitance due to inhomogeinities associated with the electrode surface.

To obtain the numerical values of the above impedance parameters, the impedance spectra were analyzed by fitting to the equivalent circuit model $R_s(C_{dl}R_{ct})$. These electrically equivalent circuits are generally used to model the electrochemical behaviour and to calculate the parameters of interest such as electrolyte resistance (R_s), charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) (Khaled, 2009). The CPE is used in place of a capacitor to compensate for deviations from ideal dielectric behaviour arising from the inhomogeneous nature of the electrode surfaces. The impedance of the CPE is given by

$$Z_{CPE} = Q^{-1}(j\omega)^{-n} \tag{10}$$

where Q and n represent the magnitude and exponent of the CPE respectively, j is an imaginary number and ω is the angular frequency in rad s^{-1}. The corresponding electrochemical parameters are presented in Table 6 and reveal that the magnitude of R_{ct} value increased in inhibited systems, with corresponding decrease in the double layer capacitance (C_{dl}). The double layer capacitance values were calculated using the expression:

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \tag{11}$$

where f_{max} is the maximum frequency. The obtained values of C_{dl} are presented in Table 6.

Lower double layer capacitance suggests reduced electric charge stored, which is a consequence of increased adsorption layer that acted as a dielectric constant. The increase in R_{ct} values in inhibited systems, which corresponds to an increase in the diameter of the Nyquist semicircle confirms the corrosion inhibiting effect of HPMC and HPMC + KI and is much more pronounced in the latter system, implying that KI synergistically enhanced the corrosion inhibiting effect of HEC. In other words, lower C_{dl} values correspond to reduced double layer capacitance, which, according to the Helmholtz model (Eq. (12)) results from a decrease in the dielectric constant (ε) or an increase in the interfacial layer thickness (δ).

$$C_{dl} = \frac{\varepsilon \varepsilon_o A}{\delta} \tag{12}$$

where ε is the dielectric constant of the medium, ε_o the vacuum permittivity, A the electrode area and δ, the thickness of the

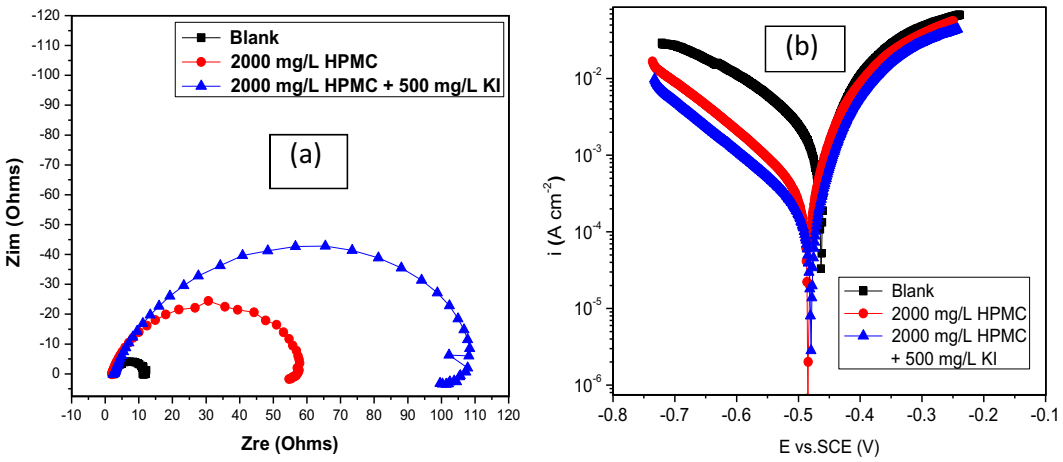

Fig. 5. (a) Nyquist impedance plots and (b) polarization curves for mild steel corrosion in 0.5 M H_2SO_4 solution in the absence and presence of KI and HPMC.

Table 6
Impedance and polarization parameters for mild steel corrosion in 0.5 M H_2SO_4 in the presence and absence of HPMC and HPMC + KI.

Conc./system	R_{ct}	n	C_{dl} ($\times 10^{-4}$ uF cm^{-2})	E_{corr} (mV SCE)	I_{corr} (μA cm^{-2})	I_{Rct}%
Blank	12.09	0.82	168.70	−463.54	1711.50	–
HPMC	55.35	0.86	47.56	−484.79	710.90	71.81
HPMC + KI	107.28	0.82	14.87	−479.93	293.84	91.18

interfacial layer. This result indicates a decrease in the reactive surface area caused by the adsorption of the inhibitor on the mild steel surface, and it suggests that the corrosion process became hindered.

3.3. Potentiodynamic polarization results

Fig. 5(b) illustrates the polarization curves of mild steel dissolution in 0.5 M H_2SO_4 solution in the absence and presence of 2000 mg/l HPMC and 2000 mg/l HPMC + 500 mg/l KI. The obtained polarization data are given in Table 6. Introduction of HPMC and HPMC + KI into the acid solution is observed to shift the corrosion potentials of both inhibited systems slightly in the negative direction and in both cases inhibited the anodic metal dissolution reaction as well as the cathodic hydrogen evolution reaction. Since the E_{corr} is not altered significantly, the implication is that the corrosion inhibition process is under mixed control with predominant cathodic effect. In addition, report (Satapathy, Gunasekaran, Sahoo, Amit, & Rodrigues, 2009) has it that when displacement in E_{corr} is >85 mV, the inhibitor can be regarded as a cathodic or anodic type inhibitor and if the displacement in E_{corr} is <85 mV, the inhibitor can be seen as mixed type. In the present study, the displacement in the corrosion potential (E_{corr}) in the presence of HPMC and HPMC + KI shifted 21.25 and 16.39 mV respectively in the cathodic direction, compared to the blank, which is a confirmation that the inhibitor acts as a mixed-type inhibitor with predominant cathodic effect.

3.4. Quantum chemical computations

This is one of the useful approaches to investigate the mechanisms of reaction in the molecule and its electronic structure levels. In this study, the structure and electronic parameters have been analyzed by means of theoretical calculations using the density functional theory (DFT) computational methodology. The geometry optimized structure of the inhibitor in its ground state, as well as the nature of their molecular orbitals, HOMO (homo occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) are involved in the property of activity of inhibitors and shown in Fig. 6.

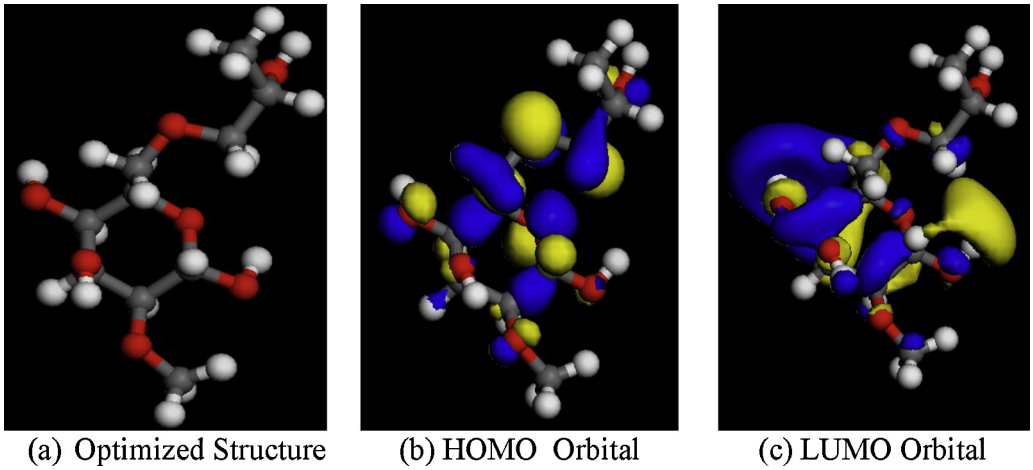

Fig. 6. Electronic properties of one molecule of hydroxypropyl methylcellulose (HPMC) [C, grey; H, white; O, red]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

According to the frontier orbital theory, the energy of HOMO (E_{HOMO} = −0.352 eV) is often associated with the electron donating ability of a molecule. High values of E_{HOMO} (less negative) indicate a tendency of the molecule to donate electrons to appropriate acceptor molecules with low-energy, empty electron orbital. Similarly, the energy of LUMO (E_{LUMO} = 0.313 eV) represents the ability of the molecule to accept electrons. The lower the values of E_{LUMO}, the more probable it is that the molecule would accept electrons (Issa, Awad, & Atlam, 2008). The difference of E_{LUMO} and E_{HOMO} (ΔE = 0.665 eV) is another important factor that should be considered. It demonstrates inherent electron donating ability and measures the interaction of the inhibitor molecule with the mild steel surface. It has been reported that low values of ΔE will provide good inhibition efficiency, because the energy for removing an electron from the last occupied orbital will be low (Khaled, 2008). However, from Fig. 6 it could be observed that the glucosidic ring and the oxygen atoms are saturated with electrons and illustrate the region from where electrons are donated to the empty *d*-orbital of the metal. In a similar manner, the lowest unoccupied molecular orbital is seen around the glucosidic ring close to HOMO regions. This suggests that centres from which electrons are donated to metals have adjacent centres for accepting electrons from metals. This explains the importance of glucosidic ring as a strong adsorption centre for hydroxypropyl methylcellulose.

4. Conclusion

Results of weight loss showed that hydroxypropyl methylcellulose inhibited mild steel corrosion in 0.5 M H_2SO_4 solution. The inhibition efficiency was found to increase as the inhibitor concentration and temperature increased. The time-dependent effect of inhibition efficiency showed that inhibition efficiency increased with time but waned after the fourth day. Addition of KI improved the durability of the inhibitor. Values of Gibbs free energy of adsorption suggest physical adsorption with tendency towards chemical adsorption. For the study of the effect of inhibitor injection, the data reveal higher corrosion rate for mild steel in the solution with inhibitor injection than solution without inhibitor injection. However, in the presence of KI, solution with inhibitor injection shows lower corrosion rate than those without inhibitor injection. Generally, KI synergistically improved the inhibition efficiency of HPMC.

Polarization measurements have shown that HPMC inhibited both the cathodic and anodic partial reactions with predominant cathodic effect. EIS measurements confirmed the adsorption of the inhibitor following Freundlich adsorption isotherm. Calculated values of some quantum chemical descriptors (E_{HOMO} and E_{LUMO}) show that the HPMC molecule should be readily adsorbed on a corroding metal surface.

Conflict of interests

The author hereby declares that there was no conflict of interests regarding the publication of this paper.

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