

Cellulosic Polymers for Corrosion Protection of Aluminium

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Abstract— The corrosion inhibiting performance of hydroxyethyl cellulose (HEC) and hydroxypropyl methylcellulose (HPMC) on the acid corrosion of aluminium has been evaluated by gravimetric, electrochemical impedance spectroscopy (EIS), potentiodynamic polarization and quantum chemical calculation techniques. The gravimetric measurements reveal concentration-dependent effect of the inhibitors. The polarization study shows decrease in the corrosion current at both anodic and cathodic partial reactions. EIS measurements provided evidence of adsorption of the inhibitor on the metal surface. Quantum chemical calculations demonstrate that frontier orbitals of HEC and HPMC molecules are mainly located on the glucosidic rings, and HPMC molecules possess higher reactivity than HEC molecules.

Index Terms— Adsorption; Aluminium; Corrosion inhibition; Electrochemical techniques; Cellulosic polymers

I. INTRODUCTION

Aluminium is widely used in modern society for industrial applications such as in the construction industry (door and window frames, sidings), manufacture of aircraft, automobile parts, and in food packaging (aluminium foil, aluminium cans). Large electrical cables are made almost entirely out of aluminium; despite the fact that it is not as good a conductor as copper, this is offset by the lighter weight. These applications are possible due to the excellent corrosion resistance of aluminium arising from the presence of the barrier oxide film that is bonded strongly to its surface. However, in aqueous solution, aluminium generally exhibits passive behavior, which influences its corrosion susceptibility. Nevertheless, the adhesive passivating surface oxide film is amphoteric and hence cannot withstand strong acidic solutions. The breakdown of the surface film in such environments exposes bare aluminium surface sites to the corrodent, thereby accelerating the corrosion reaction [1], [2]. In efforts to ameliorate the dissolution of the protective surface of aluminium and consequently protect the integrity of the metal in aggressive media, some corrosion prevention and control measures have been exploited. Among these measures, the use of corrosion inhibitors still remains the most cost effective and flexible means of corrosion control in fluid systems, since the method can effectively isolate the metal surface from the corrosive agents [3], [4].

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Several investigations have been made into the corrosion inhibiting effect of some water soluble polymers on the aluminium dissolution [5], [6]. They were found to generally exhibit good inhibition efficiencies. This is due to the ease with which they form complexes with metal ions, through their functional groups. The complexes formed during the inhibitive reaction occupy a large surface area, depending on the concentration of the inhibitor, surface charge of the metal, as well as the number and nature of the active centers of adsorption on the inhibitor [7].

As a contribution to the current exploitation of environmentally friendly polymeric corrosion inhibitors, the present study appraises the corrosion inhibiting effect of two cellulosic polymers – hydroxyethyl cellulose and hydroxypropyl methylcellulose on aluminium corrosion in 1.0 M HCl solution using both experimental and theoretical measurements.

II. EXPERIMENTAL

Materials preparation. Weight loss experiments were conducted on aluminium sheets of the type AA 1060 and purity 99 percent which was mechanically press-cut into coupons of dimension, 2 X 4 X 0.2 cm. These were degreased in absolute ethanol, dried in acetone and warm air and subsequently stored in moisture-free desiccators prior to use. The inhibitors, HEC and HPMC (Sigma-Aldrich, product of China and Japan respectively), were used as sourced without further purification. Hydrochloric acid used was of Pro analysis AR grade. The halide salt (KI), used was from M&B Laboratory Chemicals. All other reagents used for the study were of analar grade and double distilled water was used for solution preparation. The blank corrodent was 1.0 M HCl solution. Four different test solutions, each of HEC and HPMC were prepared in the concentration range 500 - 2,000 mg/L. The effect of halide salt addition was also examined by incorporating 500 mg/L KI into each of the 2,000 mg/L HEC and HPMC.

Weight loss experiments. Pre-cleaned and weighed coupons were suspended in beakers containing the test solutions using glass hooks and rods. Experiments were conducted under total immersion conditions in 300 ml of the aerated and unstirred test solutions. To determine weight loss with respect to time, the coupons were retrieved from test solutions at 24 hours intervals progressively for five days, cleaned, dried, and reweighed. To study the effect of inhibitor injection on the inhibition efficiency, test solutions were prepared and metal coupons immersed in them and allowed to stay under aerated condition for seven weeks. For the seven weeks of this study, 20 ml of the inhibitor solutions were removed at the middle of every week and equal amount of freshly prepared one injected immediately. These coupons were retrieved and examined at the end of every week and returned into the test solution. The procedure was repeated for six weeks. The weight loss was taken to be the difference between the weight of the coupons

at a given time and its initial weight. All tests were run in triplicate and the data showed good reproducibility. Average values for each experiment were obtained and used in subsequent calculations.

Electrochemical experiments. Electrochemical experiments were performed using a VERSASTAT 3 Advanced Electrochemical System Operated with V³ Studio electrochemical software. A conventional three-electrode glass cell was used for the experiments. Test coupons with 1 cm² exposed surface area were used as working electrode and a graphite rod as counter electrode. The reference electrode was a saturated calomel electrode (SCE), which was connected via a Luggin's capillary. The working electrode was immersed in

test solution for 30 minutes to attain a stable open circuit potential prior to electrochemical measurements. All experiments were undertaken in 300 ml of stagnant aerated solutions at 29 ± 1 °C. Each test was run in triplicate to verify the reproducibility of the systems. Electrochemical impedance spectroscopy (EIS) measurements were made at corrosion potentials (E_{corr}) over a frequency range of 100 kHz-10 mHz, with a signal amplitude perturbation of 5mV. Spectra analyses were performed using Zsimpwin software. Potentiodynamic polarization studies were carried out in the potential range -250 to +1600 mV at a scan rate of 0.333mV/s.

Computational details

Complete geometrical optimization of the investigated molecule was performed using DFT (Density Functional Theory) electronic structure programs – Forcite and DMol³ as contained in Materials Studio 4.0 software (Accelrys Inc.). Electronic parameters for the simulation include restricted spin polarization using DNP basis set and Perdew Wang (PW) local correlation density functional. This approach is shown to yield a favourable geometry for the molecule. This basis set gives good geometry optimisation.

III. RESULTS AND DISCUSSION

Weight loss measurements. Corrosion rates and Inhibition efficiency.

The surface of aluminium was uniformly corroded in 1.0 M HCl, with corresponding reduction in thickness of the metal coupons. The results given in Table 1 clearly show corrosion susceptibility of aluminium metal in the uninhibited acid solution. These results further show that the corrosion rates of aluminium in 1.0 M HCl decreased on addition of the inhibitor. The corrosion rates decreased further with increase in the concentration of the inhibitor. This indicates that HEC and HPMC actually afforded corrosion inhibition of aluminium in 1.0 M HCl solution. The percentage inhibition efficiency (P %) on the electrochemical corrosion of aluminium in 1.0 M HCl solution was evaluated by comparing the weight losses in the presence and absence of inhibitor as follows:

$$P\% = \left[1 - \frac{C_r^{inh}}{C_r^{blk}} \right] \times 100 \quad (1)$$

where C_r^{inh} and C_r^{blk} are corrosion rates of aluminium in the presence and absence of inhibitor, respectively.

The calculated values of inhibition efficiency for aluminium corrosion in 1.0 M HCl in the absence and presence of the inhibitor are also given in Table 1. From the Table 1, the trend of inhibition efficiency as a function of inhibitor concentration shows that efficiency of inhibition improved with increase in the concentrations of inhibitor.

Table 1: Calculated values of corrosion rates (mm/yr) and inhibition efficiency (P.%) for Aluminium corrosion in 1 M HCl in the absence and presence of different concentrations of HEC and HPMC from weight loss measurements.

Inhibitor	System Conc.	Corrosion Rate (mm/yr)					Inhibition Efficiency (P %)				
		Day 1	Day 2	Day 3	Day 4	Day 5	Day 1	Day 2	Day 3	Day 4	Day 5
	Blank	4.77	3.44	2.50	2.05	1.70	-	-	-	-	-
HEC	500 mg/L	3.25	2.07	1.42	1.14	0.93	27.65	36.18	39.66	40.94	41.92
	1000 mg/L	2.45	1.57	1.10	0.90	0.74	48.50	54.28	56.02	56.12	56.39
	1500 mg/L	1.27	0.86	0.60	0.49	0.44	72.51	74.01	75.10	75.25	73.18
	2000 mg/L	0.82	0.64	0.48	0.39	0.34	83.25	81.91	81.43	81.51	80.73
HPMC	500 mg/L	4.49	2.88	2.04	1.61	1.34	6.16	16.45	18.47	21.14	21.23
	1000 mg/L	2.38	1.32	0.93	0.73	0.75	49.29	60.86	62.25	63.66	55.06
	1500 mg/L	0.76	0.53	0.37	0.29	0.26	83.10	83.77	84.24	84.91	83.84
	2000 mg/L	0.71	0.48	0.38	0.30	0.29	84.68	85.53	84.54	84.82	82.59

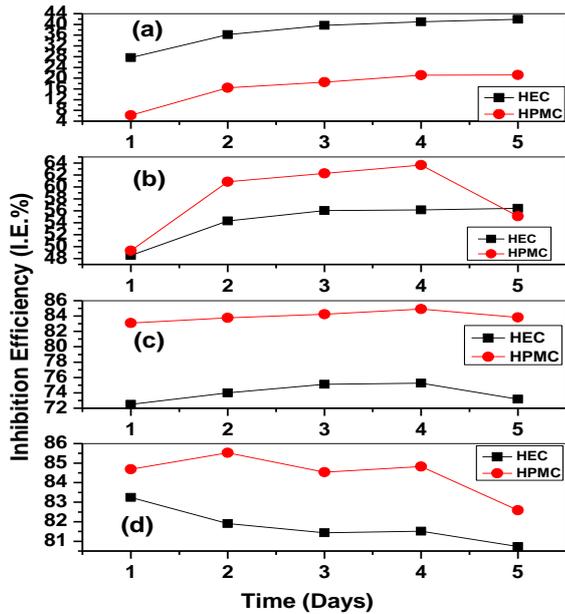


Figure 1: Comparative effect of HEC and HPMC on Corrosion inhibition of aluminium in 1 M HCl against time at different inhibitor concentrations: (a) = 500 mg/L; (b) = 1000 mg/L; (c) = 1500 mg/L; (d) = 2000 mg/L

Figure 1 compares the inhibition efficiencies of HEC and HPMC as a function of time and clearly shows that the inhibitive effect of HEC on aluminium corrosion in 1.0 M HCl was lower than that of HPMC, except for Figure 1(a) where the reverse is the case. The higher $P\%$ of HPMC for Figure 1 (b), (c) and (d) is possibly due to higher molecular size and weight. For Figure 1(a), the concentration of HPMC was not sufficient to form the viscosity required to give a better adsorption layer, hence the lower inhibition efficiency.

Effect of periodic inhibitor injection on the inhibition efficiency. The experimental data in Figure 2 compares the inhibitive effect of inhibitor system in the test solution allowed unperturbed throughout the duration of the test and inhibitor system where there was mid-week removal of certain quantity of the test solution with immediate injection of freshly prepared inhibitor system. These assays also provide information on the durability of the inhibitor systems. The results clearly show improved inhibition efficiency for systems where there was periodic injection of the inhibitor system. As a function of time, $P\%$ did not show significant decrease with time. This implies that the adsorbed inhibitor film is stabilized and could be durable under the prevailing experimental conditions. This could be explained on the basis of macromolecular nature of HEC and HPMC whose effect is pronounced at increased concentration.

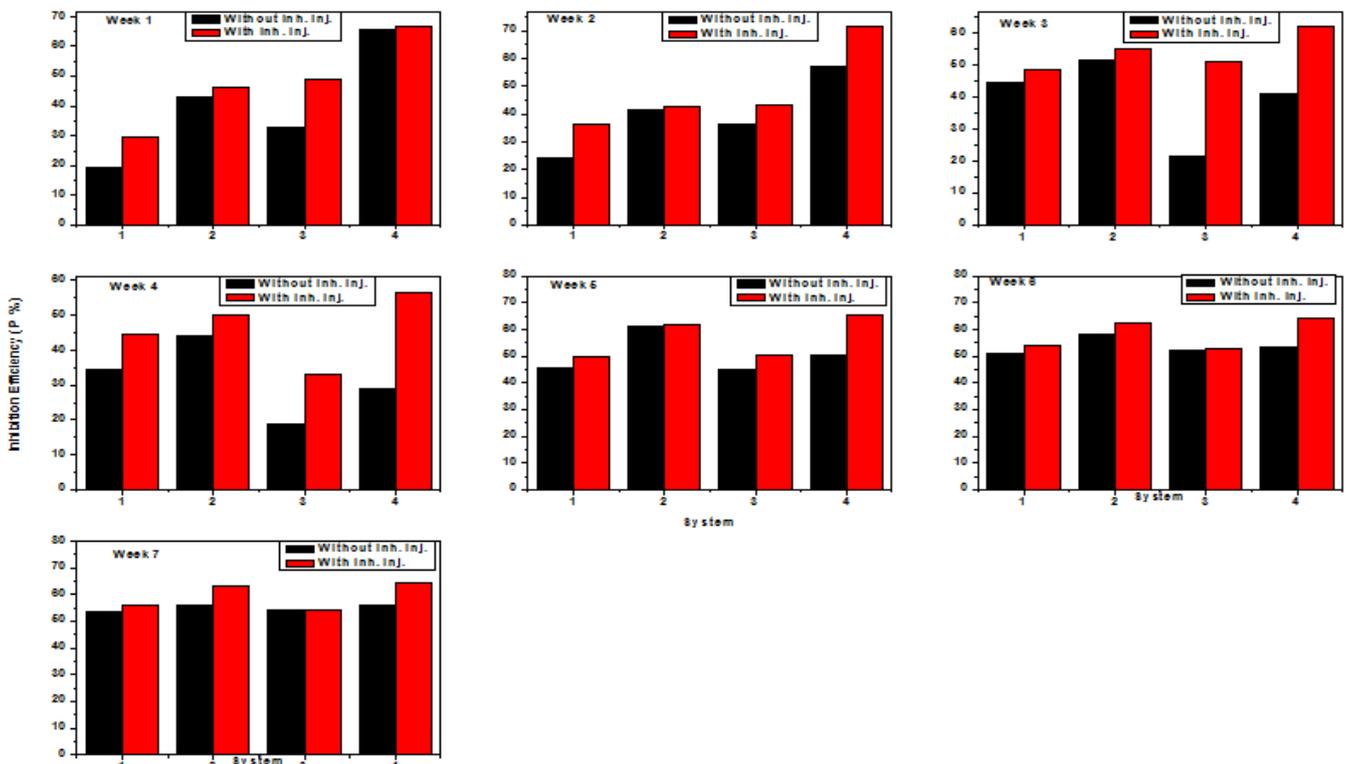


Figure 2: Inhibition efficiency against different Inhibitor systems for Aluminium corrosion in 1 M HCl, for 1-7 weeks of exposure. 1 = 2000 mg/L HEC; 2 = 2000 mg/L HEC + 500 mg/L KI; 3 = 2000 mg/L HPMC; 4 = 2000 mg/L HPMC + 500 mg/L KI.

Generally, the observed corrosion inhibition may be attributed to the adsorption of HEC or HPMC molecules at the metal/solution interface; where the adsorption film isolates the metal surface from the corrosive 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 the inhibitor adsorption.

Adsorption considerations. Assuming a direct relationship between $P\%$ and θ [$P\% = 100 \times \theta$] for different inhibitor concentrations, data obtained from our measurements were adapted to determine the adsorption characteristics of HEC (or HPMC) on aluminium/1.0 M HCl solution. The

dependence of θ on HEC or HPMC concentration was further assumed by theoretical fitting to different adsorption isotherms, and the adsorption of HEC or HPMC on the aluminium was found to follow adsorption isotherm of Freundlich, given by

$$\log \theta = \log k_{ads} + n \log C \quad (2)$$

where θ , k_{ads} , C and n are the degree of surface coverage, equilibrium constant of adsorption-desorption process, concentration of the inhibitor and number of pre-adsorbed water molecules substituted by the inhibitor molecule respectively. Plotting $\log \theta$ against $\log C$ gave a straight line (Figure 3), indicating compliance with the Freundlich isotherm. This indicates that HEC or HPMC functions by adsorption on the corroding aluminium surface and the observed increase in surface coverage with HEC or HPMC

concentration results from enhanced inhibitor adsorption on the metal surface.

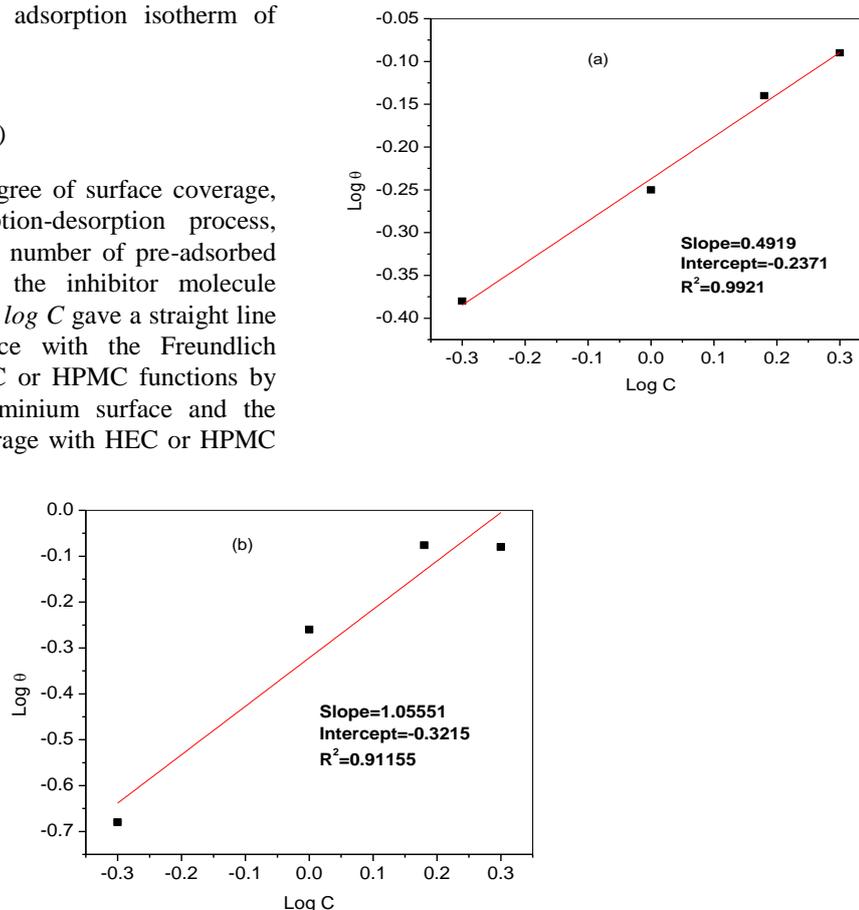


Figure 3: Freundlich isotherms for (a) HEC and (b) HPMC adsorption on Aluminium in 1 M HCl solution.

Generally, the cellulosic polymers are endowed with electron-rich centres which facilitate the adsorption to the surface of the metal. The adsorption of HEC and HPMC on the metal surface can occur directly via donor-acceptor interactions between the p-electrons and free pair electrons of the heterocyclic compound and the vacant d-orbitals of surface aluminium atoms [8].

The polymer may be adsorbed on the metal surface in the form of neutral molecules involving the replacement of pre-adsorbed water molecules from the metal surface and sharing of electrons between the oxygen atoms as well as atoms of the glucosidic ring and the metal surface [9].

It may result from the fact that amount of adsorption and the coverage of the polymers on the aluminium electrode surface increases with increasing concentration of the polymer. Consequently, the metal surface is efficiently isolated from

the corrosive medium. It could be interesting to point out here that the presence of the cellulosic polymer inhibitor does not significantly alter the character of the impedance spectra, suggesting similar mechanisms for the aluminium dissolution in HCl solution in the absence and presence of the cellulosic polymer inhibitor. The imperfect impedance spectra is an indication of inhomogeneity of the metal surface and redox reaction effect.

Electrochemical impedance spectroscopy results

The effect of HEC and HPMC on the corrosion behavior of aluminium in 1.0 M HCl was studied by EIS measurements at room temperature (29±1 °C) after an exposure period of 30 minutes (time taken to reach open circuit potential) and results are given in Table 2.

Table 2: Impedance parameters for aluminium in 1 M HCl in the presence and absence of HEC and HPMC.

System	R _{ct} (Ω)	n	I.E. %	CPE (F) x 10 ⁻⁵	C _{dl} (uF cm ⁻²) x 10 ⁻⁵	E _{corr} (mV(SC E))	I _{corr} (μA cm ⁻²)
Blank	15.68	0.9999	-	2.581	3.21	-776.27	1683.5
HEC	167.3	0.9471	90.63	2.173	1.90	-731.84	186.65
HEC + KI	270.3	0.9454	94.20	2.112	1.86	-691.31	125.49
HPMC	128.5	0.9370	87.80	3.792	3.11	-743.13	268.1
HPMC + KI	180.8	0.9476	91.33	3.271	2.21	-752.82	146.06

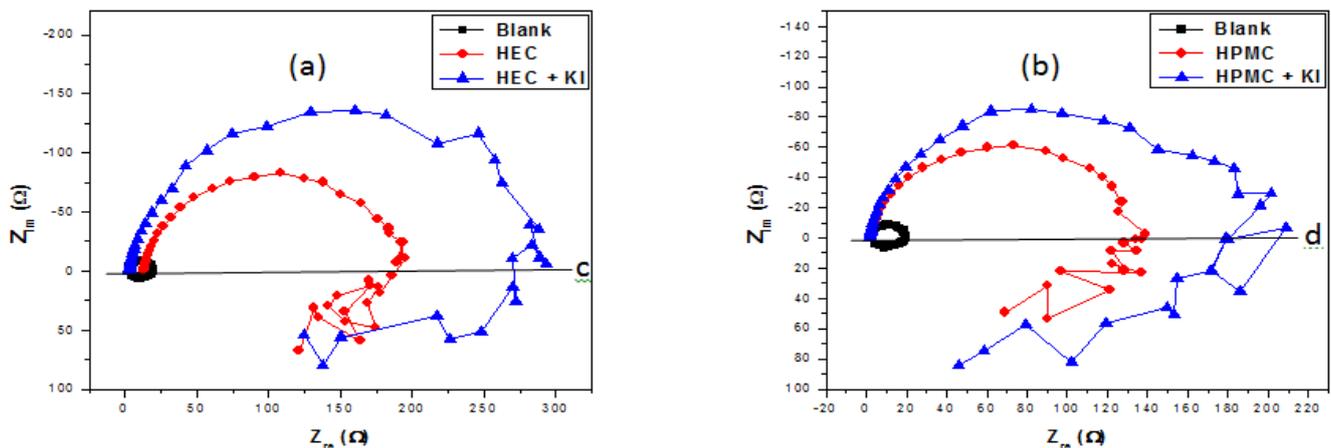


Figure 4: Nyquist impedance plot of Aluminium corrosion in 1 M HCl for (a) HEC and (b) HPMC, in the absence and presence of KI.

The Nyquist plots of the impedance behavior of aluminium in 1.0 M HCl solution in the absence and presence of the inhibitors as shown in Figure 4. The existence of a single semicircle shows the presence of single charge transfer process during dissolution which is unaffected by the presence of inhibitor molecule. The depressed dispersion has been attributed to roughness and other inhomogeneities of the solid electrode [10], [11]. The charge transfer resistance (R_{ct}) and the interfacial double layer capacitance (C_{dl}) values are derived from these curves. The diameter formed by the intercept of these semicircles and the horizontal Zreal axis gives the R_{ct} , it is found that the value of R_{ct} is a measure of electron transfer across the metal/solution interface and is inversely proportional to corrosion rate. Hence, a large R_{ct} value indicates strong resistance against corrosion. A further look at Figure 4 reveals presence of large capacitive loops at high frequencies and small inductive loops at low frequency values below lines c and d. At lines c and d are the points of intersection between the inductive loops and the real axis which is represented by $R_s + R_p$, where R_p is the polarization resistance, which is defined as the DC limit of the impedance [9]. The low frequency inductive loops in Figure 4 have been ascribed previously [12] for aluminium in the presence of chloride ions to localized corrosion reaction arising from the electrode adsorbing or generating hydrogen gas. This may lead to surface reaction or chemical modification of the electrode.

The inhibition efficiency was estimated from the relation:

$$P\% = \left[1 - \frac{R_{ct}}{R_{ctinh}} \right] \times 100 \quad (3)$$

where R_{ct} and R_{ctinh} are the charge transfer resistance in the absence and presence of inhibitor respectively.

The interfacial double layer capacitance (C_{dl}) values were calculated using the expression:

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \quad (4)$$

where f_{max} is the maximum frequency and other terms retain their previous meanings. Table 2 reveals that addition of HEC and HPMC into the acid solution caused reduction of the double layer capacitance. This effect becomes more pronounced on addition of KI to HEC and HPMC. The decrease in C_{dl} values resulting from a decrease in the

dielectric constant and /or increase in the adsorbed interfacial film thickness can be attributed to the adsorption of HEC and HPMC on the metal/solution interface and reduces the corrosion rates of the metals in the acid corrodent. This assertion can be justified by Helmholtz model [13] which is given as

$$C_{dl} = \epsilon \epsilon_o A / \delta \quad (5)$$

where ϵ and ϵ_o are the dielectric constants of the medium and permittivity of vacuum respectively, A is the surface area of the electrode and δ the thickness of the adsorbed interfacial layer.

An equivalent circuit of this polymer has been used in simulation of the impedance data, as previously reported (Chetouani et al., 2011). In this circuit, C_{dl} is the double layer capacitance, R_i is the interfacial charge-transfer resistance, L is the inductance, and R_L is the inductive resistance. When an inductive loop is present, the polarization resistance R_p can be calculated from Eq. (6) [14]:

$$R_p = \frac{R_L \times R_i}{R_L + R_i} \quad (6)$$

It has been observed that derivations from the results expected for the equivalent circuits [9] are for real, corroding systems.

Potentiodynamic Polarization results

Polarization experiments were conducted to gain insight into the effect of HEC and HPMC on the kinetics of anodic and cathodic partial reactions occurring on the aluminium electrode in 1.0 M HCl solution. The resulting polarization curves are given in Figure 5. It follows from Figure 5 that addition of inhibitor decreased the dissolution rate of aluminium in 1.0 M HCl. The inhibited solution containing 2000 mg/l of the inhibitors produced a significant inhibitive effect showing decrease in I_{corr} values. For inhibited solution containing 2000 mg/l of the inhibitor in admixture with KI, the inhibitive effect was not as pronounced as the former. The observed behaviour on the inhibitive system containing KI suggests obvious interference of KI with the stability of the passive film, rendering it less protective. This result is corroborated by the fact that halide ions exhibit adverse influence on passivity [10]. However, in Figure 5, there is a protrusion from the anodic arm of the polarization curves of the inhibited systems (circled region). This is a clear

confirmation of localized corrosion reaction earlier suggested by the impedance results. Furthermore, the addition of inhibitor shifted the E_{corr} values to 44.43 and 84.96 mV for HEC and HEC +KI respectively whereas 33.14 and 23.45 mV

are for HPMC and HPMC + KI respectively in the cathodic direction, compared to the blank, which is an indication that the inhibitors acted as mixed-type inhibitors with predominant cathodic effect.

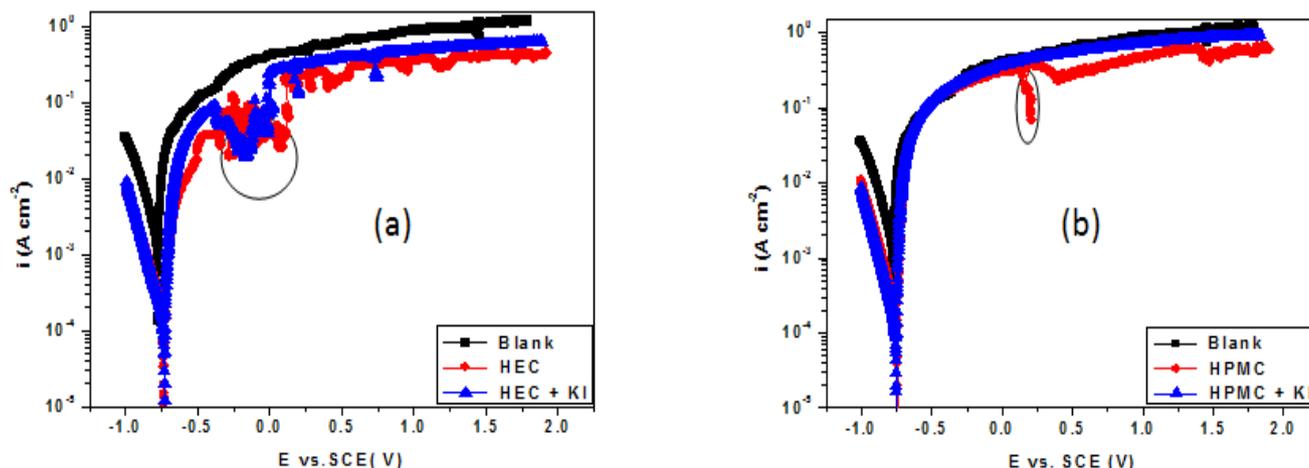


Figure 5: Polarization curves of Aluminium corrosion in 1 M HCl for (a) HEC and (b) HPMC, in the absence and presence of KI.

Quantum chemical computation

Figure 6 shows the electronic structure of the inhibitors – HEC and HPMC. The relationship between inhibitive effectiveness of inhibitors and their electronic structures have been correlated with the quantum chemical parameters such as HOMO (Highest Occupied Molecular Orbital), LUMO (Lowest Unoccupied Molecular Orbital), and the energy gap ($\Delta E = E_{LUMO} - E_{HOMO}$) [15]. The energy of HOMO, as a measure of electron donating ability of a molecule explains the adsorption on metallic surfaces by way of delocalized

pair of pi – electrons. A high energy of HOMO value expresses intrinsic electron donating tendency to an appropriate acceptor, i.e., any molecule with lower HOMO energy and empty molecular orbital while, the energy of the lowest unoccupied molecular orbital signifies the electron receiving tendency of a molecule. Accordingly, the calculated difference ($\Delta E = E_{LUMO} - E_{HOMO}$) demonstrates inherent electron donating ability and measures the interaction of the inhibitor molecule with the metal surface.

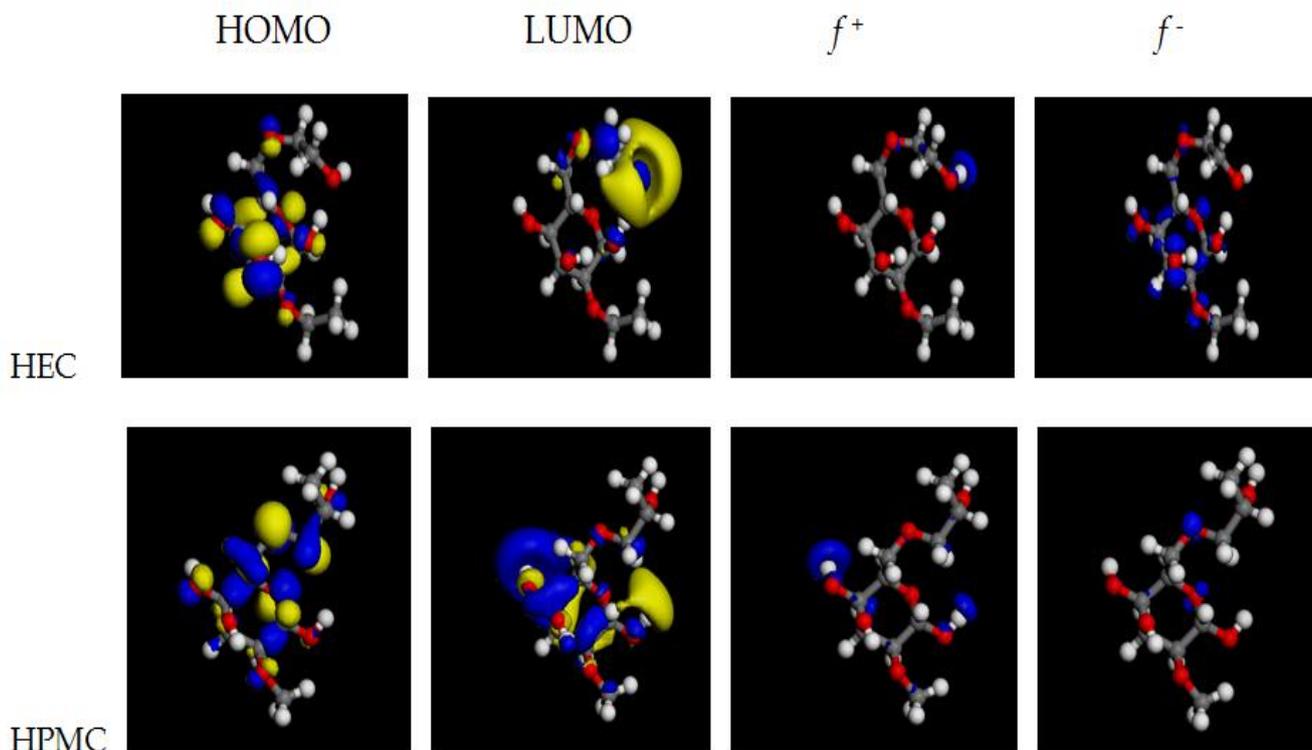


Figure 6: Electronic structures of Hydroxyethyl cellulose (HEC) and Hydroxypropyl methylcellulose (HPMC) [C, grey; H, white; O, red]

In Table 3, certain quantum chemical parameters related to the molecular electronic structure are presented. According to the calculated properties for each molecule, the inhibitive effectiveness order for the molecules are HPMC > HEC. The calculated results are in agreement with experimental results.

Table 3: Calculated values of quantum chemical properties for the most stable conformations of HEC and HPMC.

Property	HEC	HPMC
E_{HOMO} (eV)	-5.589	-0.352
E_{LUMO} (eV)	-0.139	0.313
$E_{\text{LUMO-HOMO}}$ (eV)	5.450	0.665
Maximum f^+ (Mulliken)	0.015 O(12)	0.014 O(8)
Maximum f^- (Mulliken)	0.165 O(12)	0.173 O(8)

The local reactivity was analyzed by means of the condensed Fukui function which allows us to distinguish each part of the molecule on the basis of its distinct chemical behavior due to the different substituent functional groups. Thus, the site for nucleophilic attack will be the place where the value of f^+ is a maximum. In turn, the site for electrophilic attack is controlled by the maximum value of f^- . Inspection of the Fukui functions values given in Table 3 shows the zones for nucleophilic and electrophilic attack for both molecules. In general, the results show that HPMC has more susceptible sites for adsorption on the aluminium surface, which again reflects its higher inhibition performance.

IV. CONCLUSION

The results obtained reveal that HEC and HPMC inhibited aluminium dissolution in 1.0 M HCl, and inhibition efficiency depends on the concentration of the inhibitor. On the effect of periodic inhibitor injection on the inhibition efficiency, the assay shows improved inhibition efficiency with inhibitor injection. Impedance results shows there was adsorption of HEC and HPMC on the aluminium surface following Freundlich adsorption isotherm. Polarization measurements indicate that the two inhibitors were of mixed-type with predominant cathodic effect. Quantum chemical parameters obtained shows that the active region responsible for the adsorption of the inhibitors is located around the oxygen atoms and the glucosidic ring of the molecules. Consequently, the inhibitive effectiveness of the HPMC molecule is greater than HEC and these are in agreement with experimental findings.

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