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Corrosion Inhibiting Effect of Cetyl Pyridinium Chloride on Aluminium in Acid Media in Presence of KI

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Kalium iodide (KI) used as a synergist in the presence of cetyl pyridinium chloride (CPC) for corrosion inhibition of aluminium in 0.3 M HCl was evaluated through electrochemical and non-electrochemical techniques. From electrochemical analysis and gravimetric techniques, the efficiency of inhibition enhances with raising the CPC concentrations ($3.6\times10^{-5} – 2.3\times10^{-4}$M) in combination with 6×10^{-4} M KI and decreases with temperature rise. Curves of polarization suggest that the synergistic formulation behave as a commingled inhibitor, predominately cathodic nature. The addition of 6×10^{-4} M KI in 0.3M HCl with 2.3×10^{-4} N CPC raises the charge transfer resistance (R_{ct}) and diminishes double layer capacitance (C_{dl}), both are confirmed by electrochemical A.C Impedance analysis. The effect of activation energy, enthalpy and entropy on aluminium corrosion rates was discussed. Langmuir and El-Awady isotherms were checked the adsorption of CPC in the presence of KI. Confirmation of functional groups and formation of protective layer through vibrational spectroscopy study. The obtained results indicate that the KI acts as a good synergist corrosion inhibition of aluminium.

Keywords: Aluminium; Electrochemical, A.C Impedance analysis, Corrosive media; Charge transfer resistance; SEM; EDX

1. INTRODUCTION

In many industries, Hydrochloric acid is regularly employed as washing, and pickling for the deletion of corrosion products [1-5]. Aluminium is a popular building material used in many industries in the manufacture of reaction vessels, machinery, storage tanks, pipelines for petroleum industry and ore production, wherein it easily corroded in the presence of aggressive environment. In general, the use of inhibitors in acid solutions reduce aluminium corrosion in aggressive solution. A significant number of heterocyclic compounds have been analysed and assessed as effective acid organic inhibitors in a literature survey [6-9]. Various heteroatom containing compounds such as benzotriazole, pyridine, tetrazole, pyrazole, benzimidazole, triazole and derivatives of benzothiazole have been shown to be a very strong inhibition of aluminium in various media [10-17]. Among the different nitrogen and sulphur compounds tested as inhibitors, pyridine has been found to be biologically appropriate chemicals. Some substituted pyridine compounds as effective mild steel corrosion inhibitors in acidic media have recently been examined in considerable details [18-24]. Usually the protection efficacy of these chemical compounds is due to their contact by adsorption with the aluminium surface. Singh *et.al* stated that an improvement in the protection efficacy of chemical compounds in the presence of certain anions, specially X-(halide ions), was due to a synergistic effect [25]. Anions are thought to be able to enhance adsorption of the organic cations at the metal/positive end of the inhibitor interface through an intermediate bridge. Corrosion inhibition synergism is therefore the result of enhanced surface coverage as a result of interaction between the organic cations and anions. The aim of the present research is to study the CPC synergistic effect of halides on the corrosion of aluminium in 0.3 M HCl solutions. Corrosive inhibition of CPC with KI was verified by mass loss, effect of temperature, AC impedance measurements, Potentiodynamic polarization, FT-IR and SEM methods. Additionally, it evaluated thermodynamic and kinetic results.

2. EXPERIMENTAL

2.1. Mass loss and Electrochemical analysis

Aluminium specimens with a weight ratio composition: Cu = 0.1%, Fe = 0.6%, Mn = 0.2%, Mg = 0.05%, Ti = 0.08%, Zn = 0.1%, Si = 0.5%, Cr = 0.5% and remainder of Al. Mechanically, the steel specimens were cut into 40 ×10 × 0.2 mm in size for mass loss analysis. Aluminium specimens embedded in epoxy resin with an uncovered area of 1 cm^2.The working electrode (Al specimens) was polished using different sandpaper **(**4/0 grades). They were then rinsed with acetone, dried and kept in prior to corrosion tests in a moisture-free desiccator. Triple-distilled water and AR grade HCl is used to prepare 0.3 M HCl. Gravimetric approach is the best way to find the rate of corrosion and inhibition effectiveness. In our research, aluminium specimens were sinked in 0.3 M HCl (100 ml) alone and with various concentrations of CPC ($3.6\times10^{-5} - 2.3\times10^{-4}$ M), combination of different concentrations of CPC with 0.0006 M of KI at different temperatures (303-318K) for 2h. The specimens were taken out from the test solution after 2 h of immersion, rinsed with deionized water, dried and weighed thoroughly. The mass of aluminium specimens was measured using a balance Shimadzu AY62 model with a precision of 0.1mg before and after immersion. The triplicate tests were carried out and the mass losses were averaged and measured [26]. The measurement of mass loss is employed to determine corrosion rate as follows:

$$\text{Corrosion Rate} = \frac{\text{mass loss (g)}}{\left[\text{surface area of the specimen}\left(\text{cm}^2\right) \times \text{period of immersion(h)}\right]} \qquad (1)$$

Electrochemical analyzer Model Vertex. 100mA.D was used to record Tafel polarization curve and AC impedance spectra. The aluminium specimen (1 cm^2) was exposed to the 0.3 M HCl solutions in absence and presence of CPC, combination of CPC with 0.0006 M KI. All electrochemical measurements were performed in stationary condition. Before the Tafel polarization and AC impedance testing, the electrode was submerged in 0.3M HCl for 30 min to attain stable conditions. Tafel polarization curves recorded from -0.001 to +0.001 V_{SCE} with a scan rate of 5 mV.sec^{-1}. The EIS measurements was performed between 10 MHz to 1 Hz with an AC signal of 0.01V. The values of R_{ct} and C_{dl} were determined using the relationship [27]:

$$R_{ct} = \text{(Solution resistance + Charge transfer resistance) - Solution resistance} \qquad (2)$$

$$C_{dl} = \frac{1}{2\pi \times \text{Maximum frequency } (f_{max}) \times \text{charge transfer resistance}} \qquad (3)$$

2.2. SEM and Functional group analysis

Scanning Electron Microscope (VEGA 3 TESCAN with Bruker) was used to investigate formation of protective film on the surface of the aluminium specimen in 0.3 M HCl in alone and presence of CPC, combination of CPC with KI after 2h. The presence of adsorbed tested molecules ascertained using EDX (Energy dispersive X-ray) technique. Perkin-Elmer 1600 FTIR spectrophotometer recorded the FT-IR spectra for pure CPC and the insulated layer obtained on the aluminium surface.

3. RESULTS AND DISCUSSION

3.1. Mass Loss Analysis

3.1.1. Inhibitive action of Cetyl pyridinium chloride

The corrosion attitude of aluminium immersed in 0.3 M HCl alone and with different concentrations of CPC was measured at different temperatures (303-318K) using gravimetric method and the data are given in Fig.1a. The findings suggest that the speed of corrosion diminishes with the addition of CPC. This behaviour due to an increase in the adsorption of CPC on the aluminium surface takes place by nitrogen, aromatic ring which is active centre in CPC molecule. The highest inhibition efficiency is about 98.01% at the concentration of 0.00023 M CPC and 303K. The inhibition of corrosion is reinforced by increased CPC concentration cause increased adsorption of CPC on aluminium surface results isolating the aluminium surface effectively from aggressive media. Results of temperature studies reveal that the efficiency of inhibition diminishes with enhancing the examined temperature. This shows the desorption of CPC from aluminium surface at higher temperatures. This finding showed that the adsorption of CPC on aluminium surface might be due to physisorption [28, 29].

3.1.2. Effect of KI on Inhibition efficiency of CPC

The influence of I^- on the protection efficacy of various concentrations of CPC**,** the corrosion of aluminium in 0.3 M HCl was investigated by gravimetric analysis. The maximum inhibition effect is obtained for a KI concentration of 0.0006 M. Addition of CPC with 0.0006 M KI causes the values of CR decreases and % IE increases and it is shown in Fig.1b. From Fig. 1b, it is noted that presence of I^- improves protection efficacy of CPC and retard the corrosion of aluminium in HCl solution. The maximum inhibition efficiency (98.57%) was noticed at maximum CPC concentration of 0.00023 M in combination with 0.0006 M of KI. Higher inhibition efficiency of the reaction may be reason for this result as synergistic effect between CPC and I^- ions. However, the corrosion rate enhances with increase in temperature. This indicates that the augmentation of temperature leads to the acceleration of the dissolution process. The findings shown in the Fig. 1b suggest that, with a raise in CPC concentration, the synergistic parameter increases and is more than 1, that clearly indicates that the inhibition of corrosion caused by CPC along with I^-. The stabilization of adsorbed cations on the surface of aluminium by electrostatic interactions of CPC molecules with iodide ions cause synergistic effect. This contributes to higher surface coverage and thus provides greater metal protection. However, the greater influence of I^- over CPC at 303K may be caused by its high hydrophobicity, larger ionic radius, and low electro negativity [30].

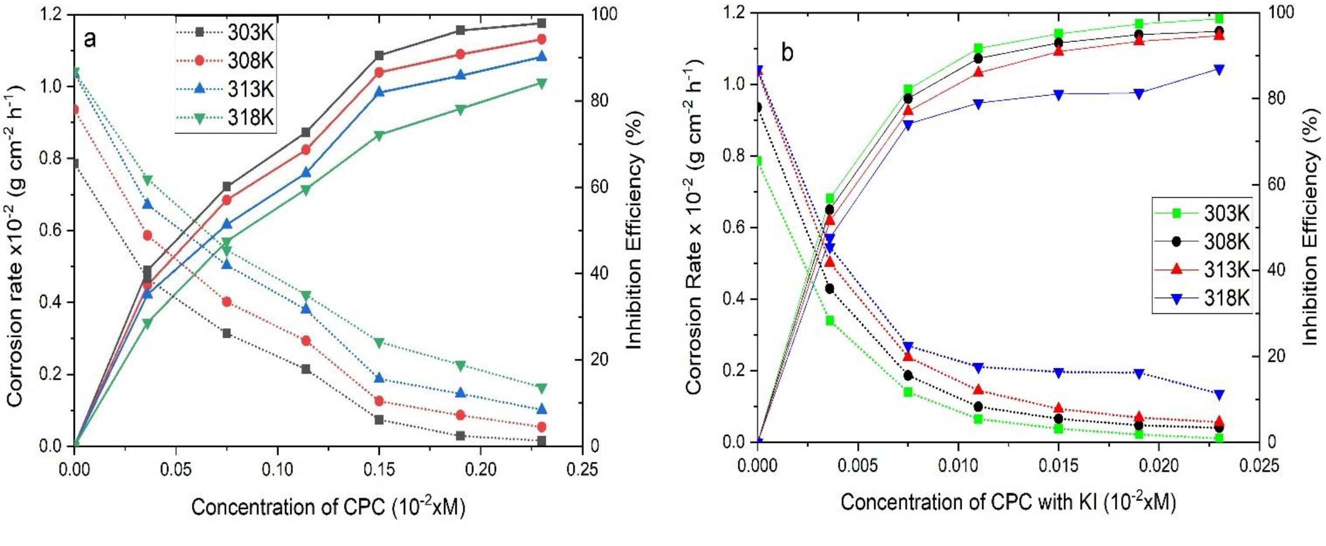


Figure 1. (a) Corrosion rate (…) and Inhibition efficiency (-) of Al specimens immersed in 0.3M HCl without and with various concentrations of CPC and (b) CPC-KI mixtures at 303, 308, 313 and 318 K.

3.1.3. Effect of variation of Concentration of the corrosive medium.

The effect on protection efficacy of the tested inhibitor by varying the concentration of the acid medium is **e**valuated and results are shown in Fig.2. The protection efficacy of inhibitor system (0.00023 M CPC + 0.0006 M KI) increases with increasing concentration of hydrochloric acid up to 0.3 M HCl. The inhibition efficiency decreases while increasing the concentration of acid above 0.3 M HCl. The inhibitor system (0.00023M CPC + 0.0006 M KI) is found to be effective at 0.3 M HCl. However, the maximum inhibition efficiency of 98.01% is obtained for 0.3 M HCl.

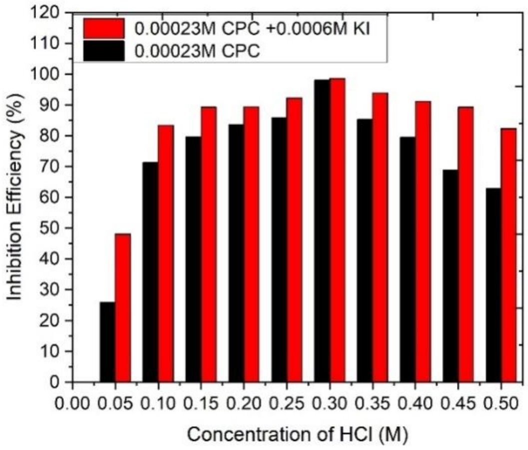


Figure 2. Variation of inhibition efficiency with divergent concentrations of HCl at 0.00023 M CPC system and 0.00023 M CPC with 0.0006 M KI system

3.1.4. Effect of Immersion time

The influence of exposure time on the protection efficiency of optimum concentration of CPC and their mixtures (0.00023 M of CPC with 0.0006 M KI) is also studied and the results are shown in Fig.3. Perusal of the results from Fig.3 reveals that inhibition efficacy slightly diminishes with raise in duration of exposure time. However even after 5 hours there is 96.56% inhibition efficiency which shows that the inhibitor mixtures are strongly adherent on the surface of the aluminium and with stand the attach of corrosive medium and thus inhibits corrosion.

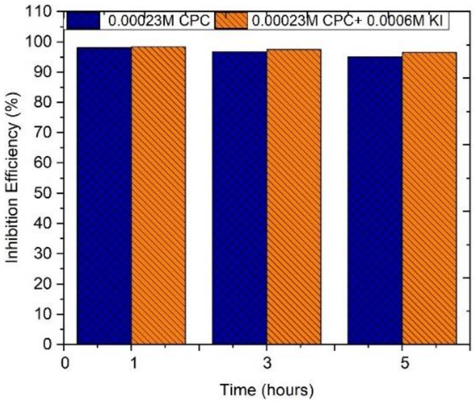


Figure 3. Inhibition efficiency of CPC and CPC with KI as a function of time in 0.3 M HCl solution.

3.1.5. Study of Kinetics and Thermodynamic Parameters on the Corrosion process

The Arrhenius equation represents the relationship between the temperature (T) and corrosion rates (CR).

$$\log CR = \frac{-Ea}{2.303RT} + \log \lambda \qquad (4)$$

The relationship between CR/T and temperature (T) is expressed via the theory of transition state.

$$CR = \frac{RT}{Nh} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{-\Delta H^* ads}{RT}\right) \qquad (5)$$

Here the apparent effective activation energy is E_a, λ is the pre-exponential factor, R is the universal gas constant, Planck's constant is h, Avogadro's number is N, the activation enthalpy is ΔH* and the activation entropy is ΔS*. A plot of log of CR versus 1/T gives a straight line and is shown in Fig.4a &b (Arrhenius state plot). The Transition state plot of log CR/T vs 1/T is shown in Fig.5a&b. The values of ΔS^*, $\Delta H^*$and E_a obtained from Transition and Arrhenius state plot are shown in Table 1. When E_a at different concentrations are compared, it is found that the activation energy of the process of corrosion increases upon the addition of CPC. It is clearly shown that corrosion process is inhibited on addition of CPC when the value of E_a is higher. Lower rate of corrosion is corresponding to the greater value E_a. Rise in CPC concentration is proportionate to the decrease in the rate of corrosion and it is indicative of the fact that the deciding factor in influencing the rate of corrosion is $E_{a.}$ [31]. Endothermic dissolution of aluminium reflected by the positive sign of ΔH^* both in the absence and presence of different concentrations of CPC. When the value of $\Delta H^*$is increased with respect to blank it is deciphered that the dissolution of aluminium is strenuous in the presence of CPC. In the presence of CPC the value ΔH* is greater than in its absence.

Table 1. Activation parameter and thermodynamic parameters of aluminium in 0.3M HCl in various concentration of CPC with [KI] = 0.0006 M.

Concentration of CPC (M)	E_a (KJ mol^{-1})	ΔH* (KJ mol^{-1})	ΔS* (J mol^{-1} K^{-1})	Concentration of CPC with KI (0.0006 M)	E_a (KJ mol^{-1})	ΔH* (KJ mol^{-1})	ΔS* (J mol^{-1} K^{-1})
0	15.05	12.54	-1.086	0	15.05	12.54	-1.086
0.000036	24.25	21.75	-1.06	0.000036	24.94	22.47	-1.06
0.000075	29.81	27.28	-1.04	0.000075	34.63	32.10	-1.03
0.000114	36.67	33.54	-1.02	0.000114	61.02	58.51	-0.95
0.00015	70.36	67.83	-0.92	0.00015	81.47	79.30	-0.89
0.00019	106.49	103.96	-0.81	0.00019	107.75	105.17	-0.81
0.00023	121.81	119.30	-0.76	0.00023	123.47	120.95	-0.76

Higher energy barrier of the reaction may be the reason for this result as it plays a clear role in the increase in the enthalpy of the corrosion process. [32]. Negative value is shown by the entropy of activation of the corrosion process in free acid solution. It is suggestive of the idea that transition state reflects better arrangement than that of the reactants and the addition of CPC effects shift in the value of

ΔS* to a lesser negative value. And it is observed that there is an increase in the randomness of the transition state CPC is added. As presented in Table 1, the comparison of the activation of energies of blank with inhibitor system is indicative of the result that the presence of the additives goes on to increase the activation energy (E_a) While the activation enthalpy (ΔH^*) is increased a corresponding shift of the activation entropy (ΔS^*) to a lesser negative value for the corrosion process is noticed. And it is observed that the value of E_a^* are modified with the addition of CPC which shows adsorption of CPC onto surface of Al and this adsorption forms a barrier and the corrosion reaction energy barrier raises as the CPC concentration increases and thus % IE increases. This implies that the corrosion process is controlled by activation. The entropy of activation (ΔS^*) is negative for 0.3 M HCl and CPC, showing that the activated complex represents association rather than dissociation step.

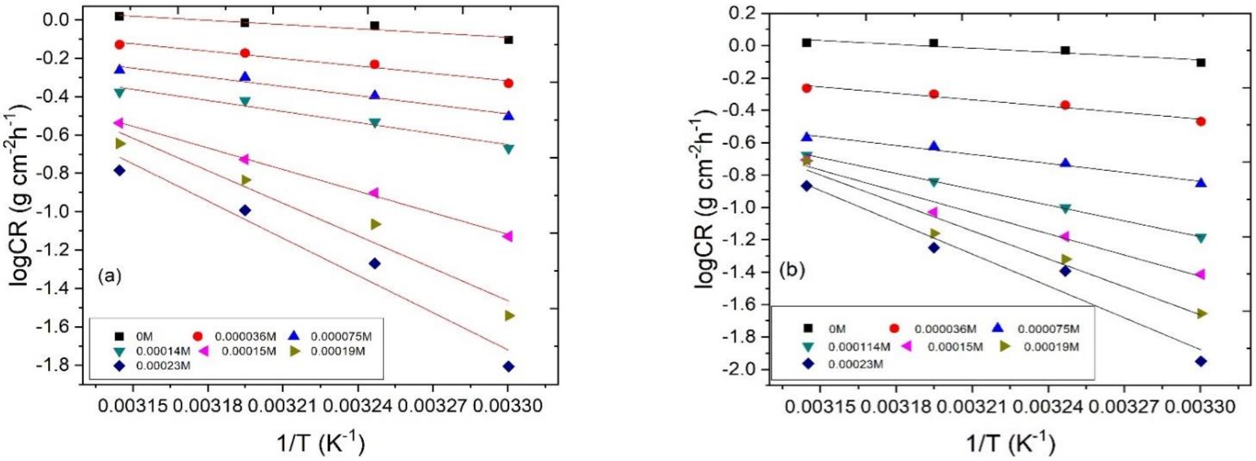


Figure 4. Arrhenius (1/T vs log CR) curves of aluminium in 0.3 M HCl (a) CPC (b) CPC+ KI.

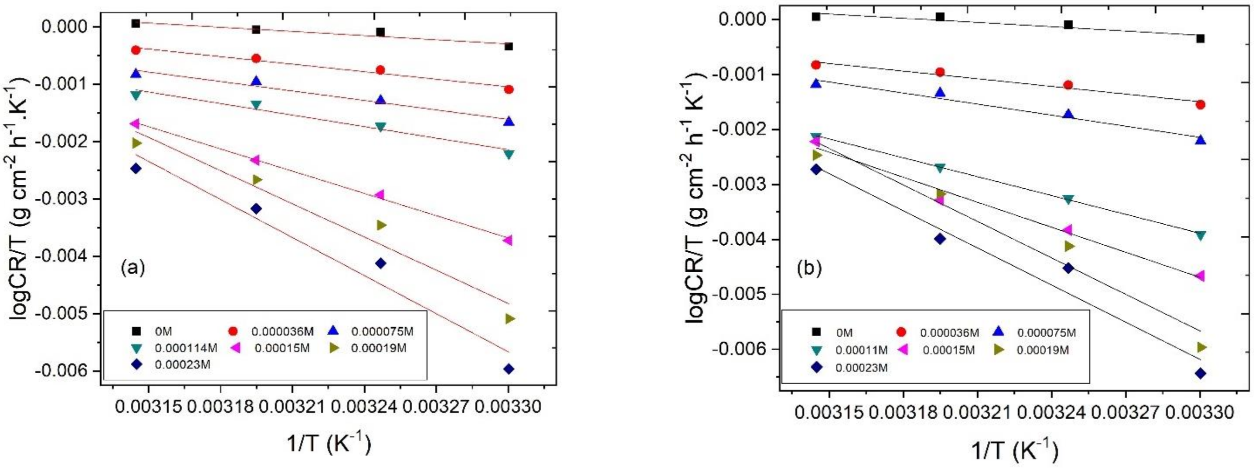


Figure 5. Transition state (1/T vs log CR/T) curves of aluminium in 0.3 M HCl (a) CPC (b) CPC + KI.

Addition of KI to the inhibitor further increases the energy of activation and the enthalpy of activation and thus make the dissolution process more difficult and hence corrosion rate is diminished to a greater extent and protection efficiency enhances and a maximum inhibition efficiency of 98% is achieved at room temperature. However, at higher temperature the inhibition efficiency decreases for the inhibitors with and without KI. This may be due to the acceleration of desorption process at higher temperatures.

3.1.6. Adsorption isotherms

In order to get information about nature of metal-inhibitor interaction is given by Adsorption. Adsorption is greatly influenced by chemical structure of inhibitor, number of metal surface active sites, charge density and size of inhibitor molecule. Adsorption isotherms are taken important role in the investigation of organic molecules in electrochemical corrosion, the most commonly used isotherms are Langmuir and the El- Awady isotherms [33]. The surface coverage (θ) values were fitted graphically to various adsorption isotherms such as the Langmuir and the El- Awady isotherms. According to the Langmuir isotherm, the data fit for the adsorption of CPC on aluminium surface (θ) is related to the inhibitor concentration, by the following equation

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{6}$$

Where K_{ads} is the equilibrium constant of adsorption process, C is concentration of the inhibitor and θ is degree of surface coverage. C/θ is plotted against C at temperatures 303, 308, 313 and 318 K (Fig. 6a). The values of K_{ads} are calculated from the intercept of the graph.

$$K_{ads} = \frac{1}{\text{intercept}} \tag{7}$$

The K_{ads} is related to the standard free energy of adsorption ΔG°_{ads} by the formula

$$\Delta G^{\circ}_{ads} = -2.303\ RT \log (K_{ads} \times 55.55) \tag{8}$$

The adsorption parameters obtained from the straight lines of C/ θ versus C at various temperatures are given in Table 2. From the table 2 it is found that the R^2 values for CPC are closer to unity. The slope value is found to be less than 1 means that there is no contact between adsorbed molecules on the surface of the metal. The values of ΔG^0_{ads} are negative, it lies between -25.64 to -25.38 kJ mol^{-1} for CPC. The negative values indicate that the adsorption of the inhibitors on the aluminium surface is spontaneous. ΔG^0_{ads} values less than -40 kJ mol^{-1} is indicative of physical adsorption and greater than -40 kJ/mol is indicative of chemical adsorption. Here for CPC, ΔG°_{ads} values lie between -20 kJ mol^{-1} to -40 kJ mol^{-1} which shows that the mode of adsorption is mixed type. Hence it is suggested that chloride molecules are first adsorbed on the sites first making the surface negative and the protonated inhibitor are held on the surface by electrostatic interaction [34]. The plot of C versus C/θ for corrosion of Al in 0.3 M HCl containing various concentrations of CPC with fixed concentration of KI are displayed in Fig. 6b. The adsorption parameters calculated from Langmuir isotherm are given in Table 2. The R^2 values are closer to unity at 303, 308, 313 and 318 K respectively. The slope value is closer to 1 up to 313 K temperature and this indicates that there is one to one adsorption as assumed by Langmuir.

Although the Langmuir adsorption isotherm gives a linear plot with high correlation coefficient (R^2 closer to unity**)**, the deviation of the slopes from unity necessitated the fitting of the experimental surface coverage, θ values into El-Awady's kinetic thermodynamic model. It is expressed as

$$\log\left(\frac{\theta}{1-\theta}\right) = \log K + y \log C \tag{9}$$

Table 2. Adsorption parameters of CPC and CPC with KI

Inhibitor	T(K)	R^2	$K_{ads}(M^{-1})$	ΔG^0_{ads} (KJ mol^{-1})
CPC	303	0.984	476	-25.64
	308	0.985	400	-25.59
	313	0.977	344	-25.65
	318	0.998	270	-25.38
CPC+KI	303	0.997	833	-27.03
	308	0.996	667	-26.89
	313	0.997	588	-27.02
	318	0.993	526	-27.15

Here, the number of inhibitor molecules sharing one active site is y, the inhibitor concentration is C and surface coverage is $\theta.k_{ads}=k^{1/y}$, K_{ads} is the adsorption process equilibrium constant and 1/y reflects the number of active sites of the metal surface occupied by one CPC molecule. The log $(\frac{\theta}{1-\theta})$ is plotted against logC and can be seen in Fig. 7a. The adsorption parameters calculated from the model of El-Awady *et.al*., are shown in the Table 3. The 1/y value obtained greater than unity, suggesting that the CPC is bound to more than one active site on the aluminium surface [35].

The plot of log $(\frac{\theta}{1-\theta})$ versus logC corrosion of aluminium in 0.3 M HCl containing different concentrations of CPC with fixed concentration of KI at various temperatures are shown in Fig. 7b. The adsorption parameters calculated from El-Awady *et.al* isotherm are given in Table 3. The R^2 values are closer to unity showing that it obeys El-Awady isotherm at all temperature. The value of 1/y which gives the number of sites to which one molecule is attached is found to be greater than one and increases with increase in temperature. This shows that at higher temperature interaction between surface site and inhibitor molecules increases with increase in temperature.

Table 3. Adsorption parameters calculated from the El-Awady *et.al*., adsorption isotherm for CPC and CPC with KI

Inhibitor	T(K)	R^2	1/y	K_{ads} (M^{-1})	ΔG^0_{ads} (KJ mol^{-1})
CPC	303	0.214	0.810	1270	-28.09
	308	0.271	0.947	1006	-27.95
	313	0.288	1.064	820	-27.86
	318	0.309	1.189	595	-27.46
CPC + KI	303	0.986	6.062	812	-26.97
	308	0.996	0.620	868	-27.59
	313	0.999	0.658	809	-27.86
	318	0.927	1.040	838	-28.00

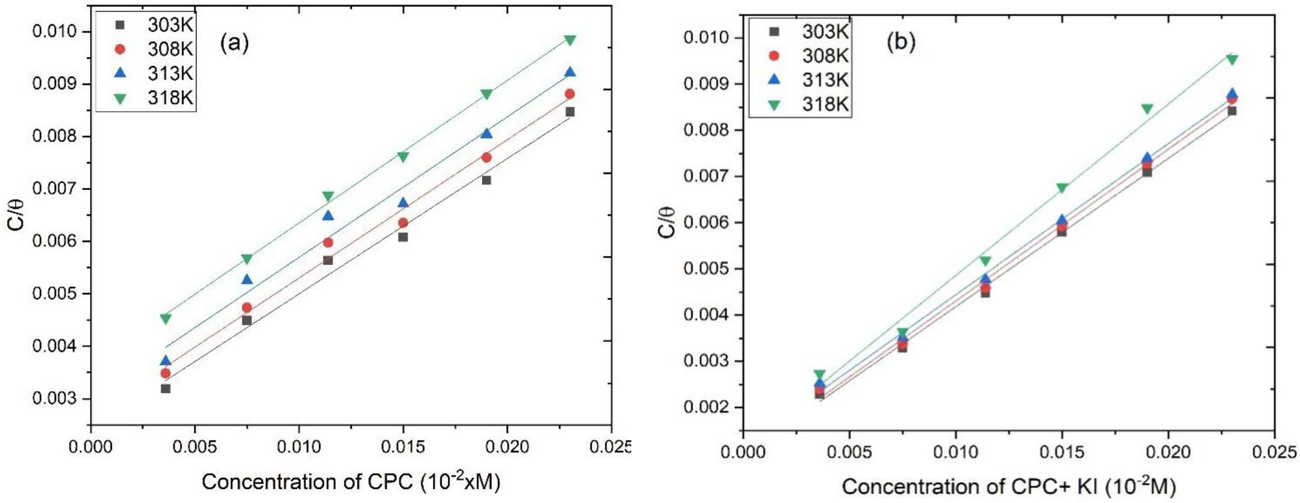


Figure 6. Langmuir adsorption isotherm model for corrosion of aluminium in 0.3 M HCl (a) CPC (b) CPC + KI.

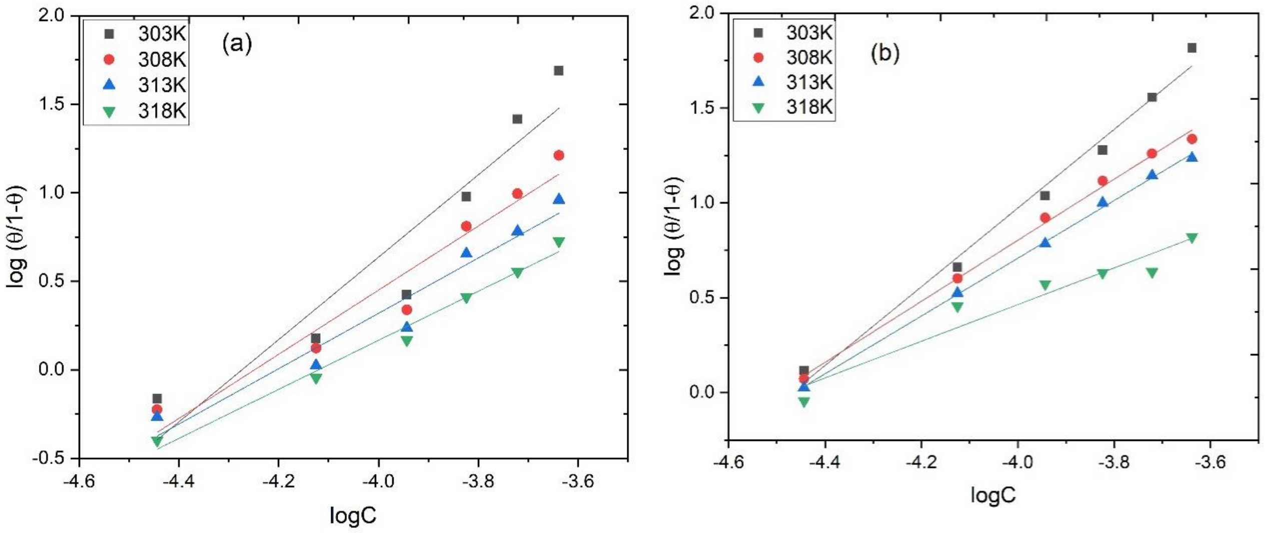


Figure 7. El-Awady *et.al*., adsorption n isotherm plot for corrosion of aluminium in 0.3 M HCl (a) CPC (b) CPC + KI

3.2. Electrochemical Measurements

3.2.1. Potentiodynamic Polarization

Tafel plots of Al in 0.3 M HCl in the absence and presence of CPC with KI are displayed in Fig 8. Table 4 offers polarization parameters such as Tafel slopes, corrosion potential (E_{corr}) and current density (i_{corr}) in 0.3 M HCl containing CPC with KI. It is observed from the Tafel curve that there is a large reduction in the I_{corr} value which is a measure of the corrosion rate on the addition of inhibitor system (CPC + KI). The E_{corr} value has shifted towards more negative value on the addition of inhibitor system (CPC + KI) and there is a large shift in the cathodic slope. This shows that the inhibitor predominately acted as cathodic inhibitor but it controls both the processes [36].

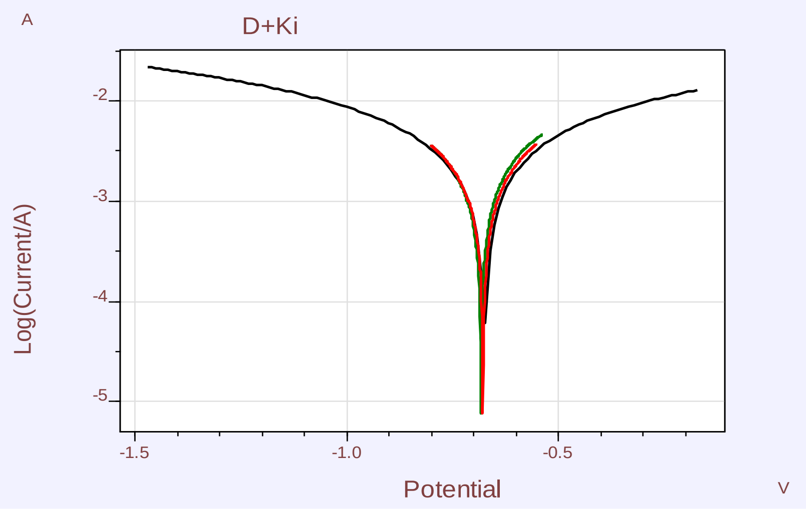


Figure 8. Tafel curves of aluminium in 0.3 M HCl in the presence and absence of CPC with KI

3.2.2. *EIS Measurements*

The impedance spectra of Al in 0.3 M HCl in the presence and absence of CPC with KI are shown in Fig 9. The impedance parameters (R_t and C_{dl}) for inhibitor system (CPC + KI) are given in Table 4. It is clear from the Fig. 7 that the charge transfers resistance (R_t) value increase on the addition of inhibitor system CPC + KI, but the value of C_{dl} decreases as a result of a diminish in the local dielectric constant and enhance in thickness of the electrical double layer, resulting in CPC deposition at the metal solution interface. The percentage inhibition efficiency calculated from the above data (98.59%) is found to be in argument with the inhibition efficiency calculated from the mass loss method [37].

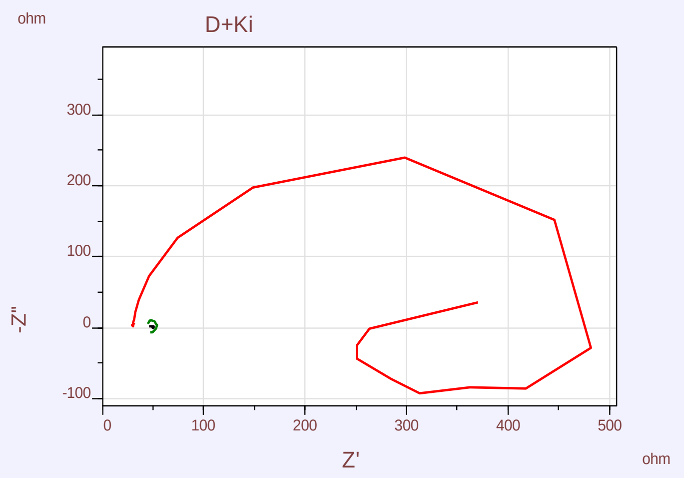
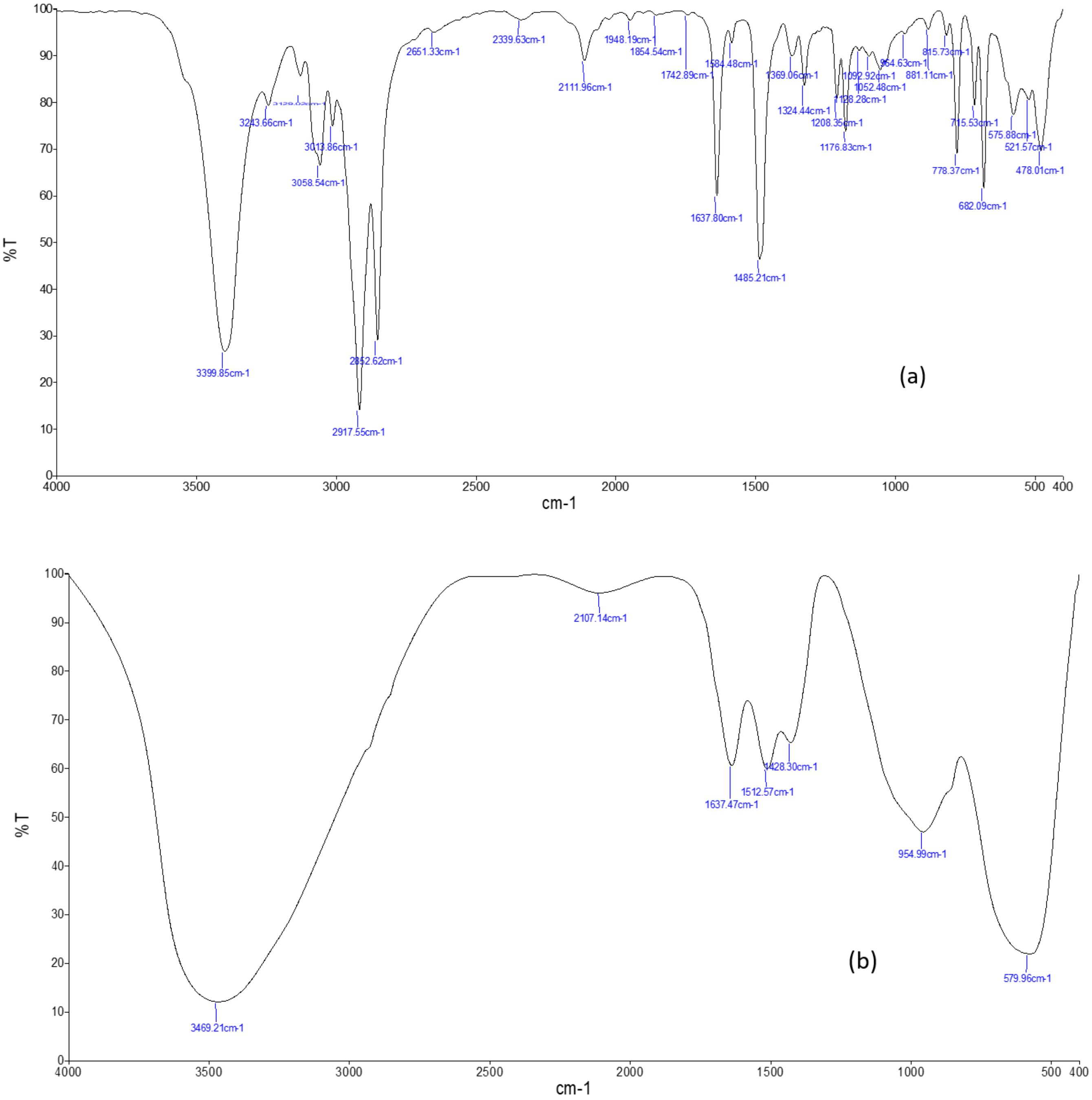


Figure 9. Nyquist plots of Al in 0.3 M HCl alone and with CPC + KI

Table 4. Electrochemical parameters of Al exposed in 0.3 M HCl and presence of CPC with KI.

Test solutions	Tafel polarization parameters					Impedance parameters			
	E_{corr}(V)	I_{corr}(A/cm^2)	β_a (V/dec)	β_c (V/dec)	IE %	$R_{s(ohm)}$	$R_{ct(ohm)}$	C_{dl} (F)	IE%
Blank	-0.673	0.003218	0.604	0.950	-	47	3.557	1.686	-
CPC+ KI	-0.689	0.000758	0.172	0.141	76.44	47.91	252.3	0.0000073	98.59



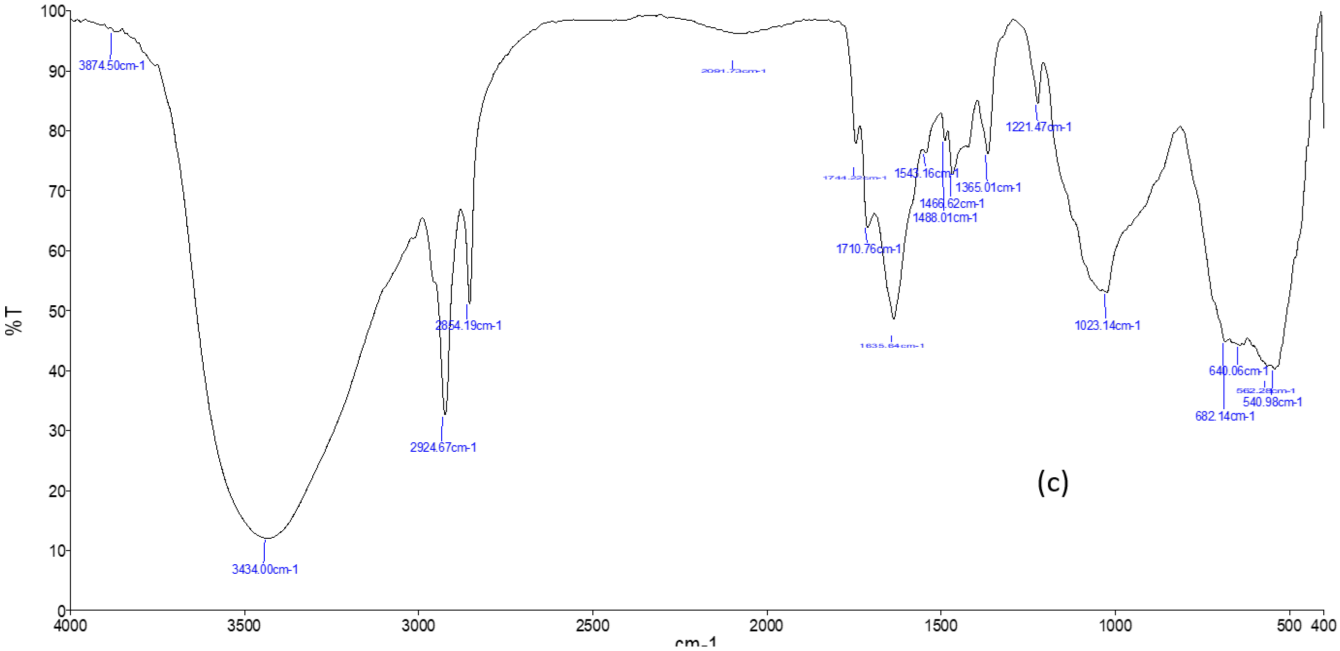


Figure 10. (a) FT-IR spectrum of pure cetyl pyridinium chloride (b) FT-IR spectrum of scraped material of CPC (c) FT-IR scraped material of CPC with KI.

3.3. FT-IR Spectroscopic study

FT-IR studies are performed to prove the adsorption of inhibitors on aluminium surface IR spectrum of CPC, the thin film on the aluminium surface after immersion in 0.3 M HCl containing CPC and the film formed on the surface after immersion in 0.3 M HCl containing CPC and KI are shown in Fig. 10(a-c). Fig. 10(a) shows the FT-IR spectrum of pure sample of CPC. Fig. 10(b) shows the spectrum of scrapped material of CPC from the metal surface. Fig. 10(c) shows the spectrum of scrapped material of CPC with KI from the metal surface. In the IR spectrum of CPC there are bands at 1637, 1584 and 1485 cm^{-1} due to aromatic –C=C–. These bands are shifted to 1637, 1512 and 1428 cm^{-1} in the film containing CPC alone and 1635, 1543 and 1488 cm^{-1} in the film containing CPC and KI. This is due to the weak interaction of л electrons of the inhibitor with the surface of the aluminium [38].

3.4. SEM and EDX analysis

The metal pieces are exposed in 0.3 M HCl in absence and presence of CPC, in combination of KI for one hour and SEM images of the smooth surface of Al and after soaked in 0.3 M HCl with and without CPC are taken and shown in Fig. 11(a-d). In order to see the changes occurred during the corrosion of aluminium in the absence and the presence of CPC, SEM images of samples are recorded. Fig. 11b indicates that aluminium immersed in 0.3 M HCl are badly damaged; it can be implied that the Al surface is highly corroded in 0.3 M HCl. Fig. 11c and d display a smooth surface with deposited CPC and an inhibitor system (CPC + KI) on the aluminium surface. SEM images clearly demonstrate that the surface defects due to corrosion are absent on the aluminium surface and the surface is almost free from corrosion in the presence of inhibitor system (CPC + KI) [39].

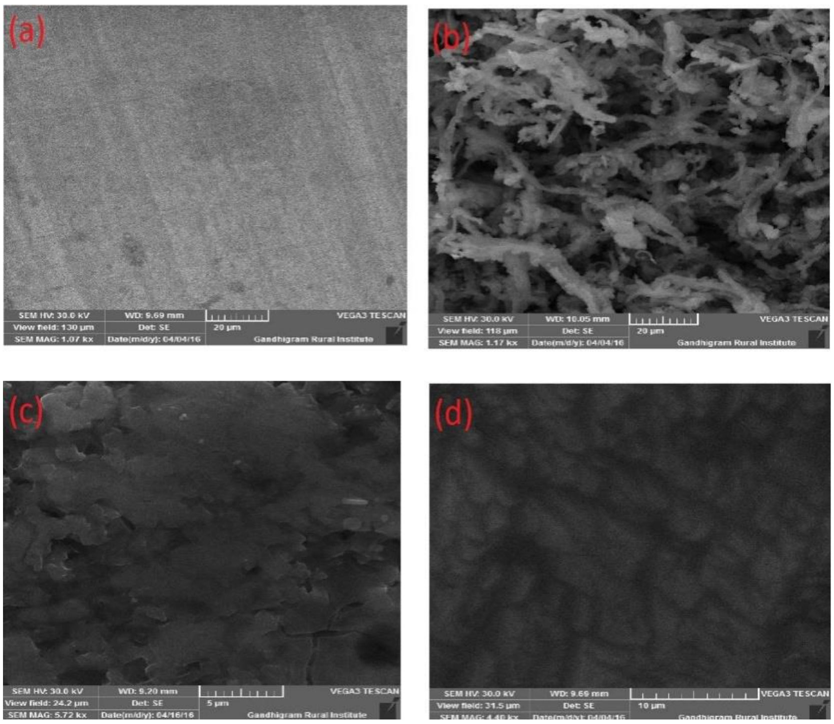


Figure 11. SEM images of aluminium (a) Polished aluminium (b) Aluminium immersed in 0.3 M HCl (c) Aluminium immersed in 0.3 M HCl with presence of 0.0023 M CPC (d) Aluminium immersed in 0.3 M HCl with presence of 0.0023 M CPC and 0.0006 M KI.

Table 5. Elemental composition of Aluminium surface and aluminium immersion in 0.3M HCl and aluminium immersion in 0.3 M HCl with 0.0023 M CPC + 0.0006 M KI for 1 hour.

System	Atomic percentage							
	Al	Cr	Fe	C	Cl	O	N	I
Aluminium	99.30	0.14	0.40	-	-	-	-	-
Aluminium in 0.3 M HCl	59.61	0.11	0.21	-	5.58	34.49	-	-
Aluminium in 0.3 M HCl + CPC	68.44	0.04	0.34	18.39	-	8.37	4.46	-
Aluminium in 0.3 M HCl + CPC + KI	67.75	0.00	0.20	9.30	0.68	18.48	3.44	0.04

Energy Dispersive X-ray analysis is used to investigate CPC molecules adsorbed on the aluminium surface. Fig. 12(a-d) shows the EDX spectra for the polished aluminium and aluminium in 0.3 M HCl containing inhibitor system. The elemental composition of aluminium and aluminium in 0.3 M HCl and inhibitor system are given in the Table 5. The EDX data indicate the absence of chloride ion on the metal surface on the inhibited surface. The presence of chloride ion in the blank (Fig. 12b) and the absence of chloride ion in the presence of inhibitor system, the presence of iodide ion on the metal

(Fig. 12c) and the presence of nitrogen, carbon and oxygen on the surface when inhibitor system is added clearly demonstrate that the adsorption of I^- and CPC causing diminishes of aluminium corrosion in acid medium. It can be clearly inferred from these finding that CPC and KI forma barrier layer on the surface of aluminium and retards the corrosion [40].

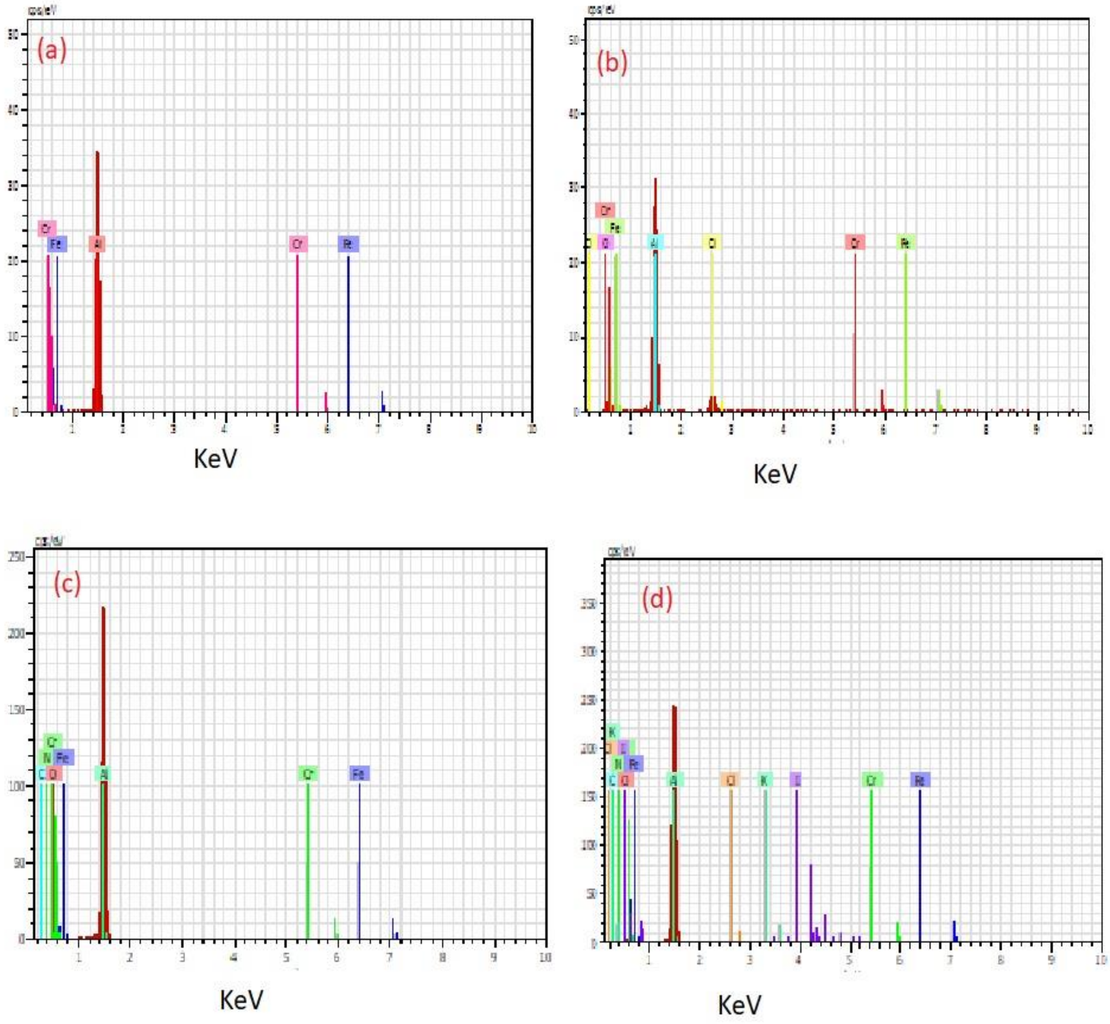


Figure 12. EDX images of aluminium (a) Polished aluminium (b) immersed in 0.3 M HCl (c) immersed in 0.3 M HCl + 0.0023 M CPC (d) immersed in 0.3 M HCl + 0.0023 M CPC + 0.0006 M KI

3.5. Mechanism of corrosion inhibition

Halide ions are known to be greatly enhancing the corrosion inhibition ability of organic moiety to inhibit corrosion by synergistic action. The increased surface coverage resulting from the anion-cation interactions between KI and CPC has been thought to generate synergistic corrosion inhibition. Two potential mechanisms have been put forward to describe the adsorption on the metal surface of such ion pairs [41]. It is assumed in one mechanism that the ion pair is formed in the acid medium before being adsorbed as represented in Eqs. (10) and (11).

$$CPCs + I_s = (CPCI)_s \qquad (10)$$

$$(CPCI)_s = (CPCI)_{ads} \qquad (11)$$

In the second one, adsorbed I^- ions on to surface of aluminium and the electrical double layer is recharged. The CPC is then drawn into the double layer through Van der Waals interaction with the adsorbed iodide ions, forming ion pairs directly on the Al surface as indicated in Eqs. (12) and (13).

$$I_s = I_{ads} \tag{12}$$

$$CPC_s + I_{ads} = (CPCI)_{ads} \tag{13}$$

where CPC, I_s and $(CPCI)_s$ in the test solution represent an antioxidant, iodide ion and ion pair respectively, while CPC_s, I_s and $(CPCI)_s$ in the adsorbed state refer to the same species. The findings of the present study obviously demonstrate that the protection efficiency of CPC is greatly increased by adding iodide ions. Any understanding of interaction between CPC and the aluminium surface involves the effect of KI. The aluminium dissolution process in 0.3 M HCl described by Bokris *et. al* [42]. In this case, CPC atoms can be joined with the adsorbed intermediates to frame a metal-CPC complex. The subsequent complex either catalyses or hinders further aluminium disintegration relying upon its dissolvability [43]. Fig.13 depicts the schematic route of CPC with KI adsorbed onto Al surface. Stabilization of KI through interaction with CPC leads to increased surface coverage and thus to increased efficiency of inhibition. Further to affirm the presence of synergism between CPC and KI towards adsorption of CPC on Al surface, Aramaki and Hackerman [44] suggested an equation for the synergism parameter S_θ

$$S_\theta = \frac{1-\theta_{1,2}}{1-\theta'_{1,2}} \tag{14}$$

The synergistic parameter is calculated using eqs (14). The calculated values for the different concentrations of CPC with fixed concentration of KI at 303 K are presented in Table 6. The findings shown in the Table 6 demonstrate that the synergistic parameter raises with increase in the concentration of CPC and are greater than 1, which clearly indicates that the corrosion inhibition induced by CPC in combination with I^- ions.

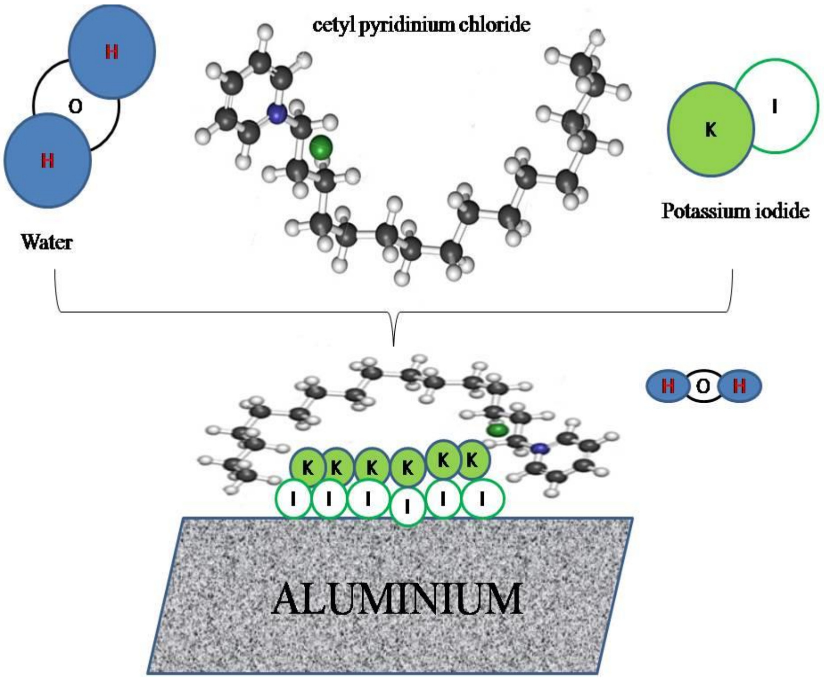


Figure 13. Schematic illustration of CPC with KI adsorption process

The effect between CPC and KI is due to electrostatic interactions between cetyl pyridinium ion and I^- and the stabilization of adsorbed cations of the organic compounds on the surface of aluminium by electrostatic interactions of CPC molecules with iodide ions. This leads to higher surface coverage and hence provides greater protection to Al. However, its large ionic radius, low electro negativity and high hydrophobicity can be due to the greater influence of I^- over chloride at 303K [45]. The strong attraction of I^- ions on the Al surface caused by the synergistic effect of I^- ions and protonated CPC [46]. As the I^- ion bigger in size than Cl^- ion, the adsorption increases and also it is more stable compound to chloride ion and thus inhibition efficiency increases.

Table 6. The percentage of inhibition efficiency at different concentrations of CPC with KI for the corrosion of Al after 1h of immersion in 0.3 M HCl at 303 K.

Concentrations of CPC (M)	% IE	KI (M)	% IE	θ_{1+2}	Combined IE %	S_θ
0	-	-	-	-	-	-
0.000036	40.72	0.0006	12.4	0.567	56.79	1.19
0.000075	60.11	0.0006	12.4	0.821	82.15	1.94
0.000114	72.76	0.0006	12.4	0.916	91.69	2.84
0.00015	90.53	0.0006	12.4	0.950	95.08	1.66
0.00019	96.34	0.0006	12.4	0.973	97.32	1.18
0.00023	98.01	0.0006	12.4	0.985	98.57	1.13

4. CONCLUSION

In this work, the inhibitive effect of CPC alone and tested mixture (CPC + KI) on the corrosion of aluminium in 0.3 M HCl were investigated. The experimental results reveal that % IE enhances with an increase in CPC concentration with optimum concentration of KI. The IE of CPC diminishes with a temperature increase. The endothermic reaction of corrosion is confirmed by the positive sign of enthalpy of activation (ΔH^*). The negative sign of ΔG^*_{ads} indicates that adsorption is a spontaneous process. The negative value of enthalpy of activation (ΔH^*_{ads}) suggests that the adsorption is an exothermic process. The electrochemical method of potentiodynamic polarization techniques reveal that the CPC and KI controls cathodic reaction by blocking the cathodic sites of the aluminium and thus the inhibitor acts as a cathodic types. FT-IR, SEM and EDX analysis affirmed the development of barrier layer on the Al surface.

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