"STUDIES ON POTENTIAL GREEN CORROSION INHIBITORS FOR MILD STEEL IN DIFFERENT MEDIA"

A

Thesis

Submitted to

University of Kota, Kota

For the Award of Degree of

DOCTOR OF PHILOSOPHY

In the Faculty of Science (Chemistry)

By

PRIYA BHARDWAJ

Under the supervision of

Dr. (Ms.) Seema Agarwal
(Co-supervisor)
Lecturer in Chemistry
P.G. Department of Chemistry
Govt. College Kota
Kota (Rajasthan)

Dr. (Mrs.) Kalpana
(Supervisor)
Lecturer in Chemistry
P.G. Department of Chemistry
Govt. College Kota
Kota (Rajasthan)

2017

DEDICATED TO MY FAMILY

Candidate's Declaration

I hereby certify that the work, which is being presented in this thesis, entitled "**STUDIES ON POTENTIAL GREEN CORROSION INHIBITORS FOR MILD STEEL IN DIFFERENT MEDIA**" in partial fulfilment of the requirement for the award of the Degree of Doctor of Philosophy, carried under the supervision of Dr. (Mrs.) Kalpana and co-supervision of Dr. (Ms.) Seema Agarwal and submitted to the (University Department of Chemistry/ University Research Center), University of Kota, Kota represents my ideas in my own words and where other ideas or words have been included I have adequately cited and referenced the original sources. The work presented in this thesis has not been submitted elsewhere for the award of any other degree or diploma from any Institution. I also declared that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that any violation of the above will be cause for disciplinary action by the University and can also evoke action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.

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Date: Dr. (Mrs.) Kalpana

Supervisor

P.G. Department of Chemistry

Govt. College Kota, Kota

University of Kota, Kota

Dr. (Ms.) Seema Agarwal

Co-supervisor

P. G. Department of Chemistry

Govt. College Kota, Kota

University of Kota, Kota

CERTIFICATE

I feel great pleasure in certifying that the thesis entitled **"STUDIES ON POTENTIAL GREEN CORROSION INHIBITORS FOR MILD STEEL IN DIFFERENT MEDIA"** submitted by **Ms. Priya Bhardwaj** is an original piece of research work carried out under our guidance and supervision. She has completed the following requirements as per Ph.D regulations of the university.

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(2) Residential requirements of the university (200 days).
(3) Regularly submitted annual progress report.
(4) Presented her work in the departmental committee.
(5) Published/accepted minimum of one research paper in a referred research journal.

We recommend the submission of thesis.

Date

Dr. (Mrs.) Kalpana
(Supervisor)
Lecturer in Chemistry
P.G. Department of Chemistry
Govt. College Kota
Kota (Rajasthan**)**

Dr. (Ms.) Seema Agarwal
(Co-supervisor)
Lecturer in Chemistry
P.G. Department of Chemistry
Govt. College Kota
Kota (Rajasthan)

ACKNOWLEDGEMENT

''सरस्वती नमस्तुभ्यं, वरदे कामरूपिणी।

विद्यारम्भं करिश्यामि, सिद्धिर्भवतु मे सदा''

"Saraswati Namastubhyam, Varde Kaamroopini

Vidyaarambham Karishyaami, Siddhir Bhavatu Me Sada"

First of all I thank to The Almighty for showering me his blessings, perserverance, internal strength, mental strength, wisdom for completion of my Ph.D thesis.

The present text in above Sanskrit shloka draws deep sense of profound gratitude and inestimated indebtedness toward my learned supervisor ***Dr. (Mrs.) Kalpana*** *Senior lecturer and co-supervisor* ***Dr. (Ms.) Seema Agrawal*** *Lecturer, Department of Chemistry, Govt. College Kota (Rjasthan) for their noble guidance, erudite inspiration, kind and affectionate advise and perpetual encouragement throughout the period of this piece of research work. She has always been an open person to me and I consider myself very fortunate to receive her able supervision and guidance. She always encouraged me in every stage of this research work and her constructive criticism during the course of investigations made this endeavour a success. She always encouraged me to frame new ideas and thoughts by acting on it leads to this thesis salvation as:* ***"Man's actions are the best interpreters of his thoughts."***

I owe to my heartfelt gratitude to her for being my mentor and the torchbearer for my doctoral degree research endeavour.

I feel extremely grateful to ***Principal,*** *Govt. College Kota and* ***Head,*** *P.G. Department of Chemistry, Govt. College Kota for providing me all the necessary facilities and support for carrying out this research work.*

My special thanks to all ***staff members*** *of Chemistry Department, Govt. College Kota for their kindness, encouragement, assistance and invaluable suggestions during this critical period.*

I am highly indebted to ***Dr. Suman Sharma, Dr. Krishna Rani Kapoor, Dr. Sadhana Chittora, Dr.S.M. Nafees, Dr. Nitin Gupta*** *for their help and boosting my morale time to time.*

Words can hardly express the deep sense of gratitude: I express my appreciation to all my research colleagues especially ***Mr. Anilesh Yadav*** *and* ***Ms. Preeti Singhal*** *for helping me in innumerable ways and positive attitude at the time of critical need.*

*I would also like to thank **Lab incharges**, **Lab staff** members and **Library staff** members for their help and support.*

*I owe the highest debt of gratitude to my loving mother **Smt. Shakuntala Bhardwaj** and my father **Shri Birdhi Lal Bhardwaj** for their blessings, moral support and best wishes which maketh me to have courage and perserverance to complete this work however difficult it may be and one day it will award me with flamboyant colours.*

*I am also highly indebted to my brother **Mr. Akash Bhardwaj**, who has spent his valuable time in typing of this thesis and solving the technical problems related. I am at a loss of words to acknowledge his indispensible help received. Without his contribution this thesis would not have been in this form.*

*I owe a lot of thanks to my Didi **Mrs. Prachi Pareek** and Jijaji **Mr. Krishna Kant Pareek** for their encouragement and best wishes.*

Lastly I thank to one and the all who helped me directly or indirectly in smooth conduction of my research programme and who have been inadvertently forgotten at this moment and end my words with these truly, beautiful and golden lines:

"Laboratories are temple of the future, of wealth and of walfare; in them humanity grows greater, stronger and better"

Ms. Priya Bhardwaj

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CHAPTER – 1

INTRODUCTION AND REVIEW OF LITERATURE

Mild steel is the commonly used alloy in the industries due to its remarkable features such as low cost, easy availability, high strength, durability etc. It is largely used in designing of various reaction vessels, tanks, for handling of various corrosive liquids, various aggressive solutions like acidic solutions, basic solutions, salt solutions etc. Acid solutions are generally used for descaling, acid cleaning, acid pickling, and in various petrochemical processes. Hydrochloric acid, acetic acid and sulphuric acids are widely used in the pickling process [53]. These acids are also largely used for drilling fracturing and acid simulations at various stages in oil exploration, production and descaling operations and with many industrial applications [100]

Acidic environment corrode mild steel easily. Corrosion is a natural and electrochemical phenomenon caused by potential difference between metal and acid [12]. H^+ ions and dissolved oxygen are named natural motors of corrosion [26] Corrosion results large economic loss of any country across a year. Corrosion is a continuous process and cannot be stopped completely. Therefore application of corrosion inhibitors in industries and in different other fields, is the most effective method to protect the metal from corrosion [17]. Corrosion inhibitors are compounds those cause lowering in the corrosion rates of a metal, when added in suitable amounts without significantly changing the concentration of other agents [245].

A great number of corrosion inhibitors have been studied for mild steel in acidic media. Most of the well known corrosion inhibitors are those organic compounds which containing N, O, S, P and multiple bonds or aromatic rings in their structure [104, 211, 212, 219]. The loosely bonded π electrons and lone pairs in these functional groups are key feature which determine the corrosion inhibition efficiency [46, 112, 231]. The organic compounds present in the inhibitor adsorb on the metal surface and block the active sites and thus reduce the corrosion rate considerably [194]. Besides having good corrosion inhibition property they are costly, non biodegradable and harmful for human beings and environment. The above drawbacks of synthetic corrosion inhibitors provoked the researchers to search for the new

cheap non-toxic, eco-friendly, green, naturally occurring plant products as corrosion inhibitors. Natural products have been reported as corrosion inhibitor for different metals [52, 75, 190, 257]. Extracts of plant roots, seeds, leaves, bark, fruits etc. have been reported in acidic media as corrosion inhibitors [3, 169,170, 173]. The inhibitive action of natural plant products is due to the presence of organic compounds such as tannins, alkaloids, steroids, amino acids, flavanoids etc. [55, 73, 148]. Researchers have studied that inhibitive effect of some plant extracts is due to the adsorption of some phytochemicals present in the extract and formation of protective film on the metal [74, 167, 250].

Metallic corrosion has been studied in different acidic, basic and neutral medium using different gravimetric and electrochemical methods and different techniques. Hesham T.M. Abdel-Fatah et al. reported Miswak (*Salvadora persica*) aqueous root extract in 1.0 N sulfamic acid solution using mass loss and EIS techniques at 303-313 K temperature [2]. Pandian Bothi Raja et al. studied *Neolamarckia cadamba* extract in 1M HCl medium using PDP, EIS & SEM technique [191]. Aqueous extract of LD (*Lavandula dentata)* was investigated in 1M HCl solution by weight loss, EIS and Potentiodynamic polarization measurements and obtained 95% efficiency at 2wt% extract concentration. Polarisation studies indicate the phytochemical compounds present in LD extract acts as mixed type inhibitor [47].

Raphia hookeri (RH) gum exudates was studied in H_2SO_4 solution by weight loss and hydrogen evolution technique and 71.9% efficiency was obtained at 0.5g/L at 30^0C [231]. Ehteram A Noor investigated fenugreek leaves extract in 2M HCl & 2M H_2SO_4 solution and found Langmuir adsorption in HCl and Temkin adsorption isotherms in H_2SO_4 solution [159]. *Hibiscus cannabinus* extract inhibitor for mild steel corrosion is reported by M.Ramananda Singh et al. in 0.5 M H_2SO_4 [218]. Ecofriendly Quinazoline derivative was studied by A.S. Fouda et al. in 2M HCl solution using EIS, PDP, electrochemical frequency modulation weight loss technique and 93.8% efficiency was obtained at 30^0C [81].

Sesbania sesban extract (SSE) for carbon steel was reported as inhibitor in 1M HCl. 91.08% efficiency was obtained at 2.00 g/L at 25^0C [22]. *Mentha rotundifolia* leaves extract for steel in 1M HCl in the range 298K-338 K was studied as corrosion inhibitor [113]. Inhibitive effect of gramine was studied in 1M HCl by PDP, EIS & gravimetric measurements [185]. *Calotropis gigantea* leaves extract was studied by using weight loss and electrochemical techniques in 1M HCl solution [62]. P.S. Desai investigated *Hibiscus rosa sinensis* leaves extract for mild steel in 1M HCl using gravmetric & electrochemical techniques [61]. Eddy and Mamza studied ethanolic extract of seeds and leaves of *Azadirachta indica* in H_2SO_4 solution using gravimetric, gasometric and IR methods [68]

90% inhibition efficiency was obtained in mild steel corrosion inhibition in 1N H_2SO_4 solution using *Nyctanthes arbortristis* leaves extract [197]. Aqueous extract of *Ammodaucus leucotrichus* fruit was reported as inhibitor for C38 steel in 1M HCl solution using EIS, EDP & weight loss method [145]. Maria V. Fiori Bimbi et al. studied pectin as eco friendly corrosion inhibitor [80]. Bei Ojan studied inhibitive effect of tannic acid on mild steel corrosion in sea water wet/dry cyclic conditions using weight loss & electrochemical methods [184]. Banana peel extract gave 98% inhibition efficiency at Zn^{+2} (15ppm) by weight loss method [196].

Alka Singh and Kalpana S. have reported corrosion inhibition of iron surfaces by fenugreek leaves in CH_3COOH & citric acid solution by weight loss method [215,216]. Leaves extract of *Gossipum hirsutum L.* was studied by Olusegun K. Abiola et al. as green corrosion inhibitor for Al in HCl solution. They employed weight loss method for corrosion inhibition studies and 92% inhibition efficiency was obtained at 30^0C [8].

Corrosion inhibitor for mild steel in 0.5M H_2SO_4 and 1M HCl solution was investigated by P.R. Vijayalakshmi, R. Rajakshmi and S. Subhashini using weight loss and electrochemical measurement techniques. The plant material taken was *Borassus flabellifer Linn.* (palmyra palm) shell

extract. 97.65% and 98.11% inhibition efficiency was obtained in 0.5 M H_2SO_4 and 1M HCl solutions at 3% (v/v) concentration of extract [240].

The inhibitive effect of *Aloe vera barbadensis* gel was studied on copper metal in hydrochloric acid solution using weight loss technique [92]. The inhibitive effect of leaves extract of African bread fruit in 1M H_2SO_4 solution was investigated by P.M. Ejikeme et al. for mild steel and aluminum metal [70]. They obtained 70.55% inhibition efficiency for mild steel and 78.56% inhibition efficiency for Al at 30^0C in 5g/L concentration of BLE.

Extract of areal parts *Daucus carota* plant was investigated as green corrosion inhibitor for mild steel in hydrochloric acid medium using weight loss method and on theoretical analysis [111]. Maximum 95.72% inhibition efficiency was achieved at 2% (v/v) DCA extract at 5h of immersion at 30^0C. Cantaloupe (*Cucumis melo*) juice and seed extracts has been investigated for cast iron corrosion inhibition in 1M hydrochloric acid solution [77] using hydrogen evolution measurements (HEM) and mass loss measurements. Adsorption process followed Langmuir adsorption isotherm.

It has been found that *Polyalthia longifolia* leaves extract is a good corrosion inhibitor for mild steel. 92% inhibition efficiency was obtained at 1.5% (v/v) concentration of extract in sulphuric acid medium and 87% inhibition efficiency was obtained at 1.5% (v/v) concentration of extract in hydrochloric acid medium [236,237]. I.J. Alinnor and P.M. Ejikeme investigated aqueous, ethanolic and acidic leaves extract of *Ocimum gratissimum* for corrosion inhibition of aluminum in hydrochloric acid medium using gravimetric method [20]. Narayana Hebbar et al. revealed the anticorrosion behavior of anti inflamatory ketosulfone drug for Zn in acidic medium by polarization and AC-impedance technique at 303-333K. Tafel plots were drawn in experiments which indicated that the drug is a mixed type inhibitor [93].

S. Aejitha, P.K. Kasthuri and P.Geethamani studied the corrosion inhibition efficiency of acidic leaves extract of C*ommiphora caudata* (CC) in

1M HCl and 1M H_2SO_4 solutions separately using weight loss and electro chemical techniques [11]. Results showed that inhibitive property of CC is greater in hydrochloric acid solution.

D.G. Ladha et al. evaluated corrosion inhibition properties of aqueous extract of fenugreek seeds (FSE) (*Trigonella foenum graecum*) for aluminum in hydrochloric acid medium using gravimetric, galvanostatic polarization and EIS techniques. Results showed that inhibitive properties are due to the presence of phytochemical constituents such as trigonelline and sites present in extract. Adsorption process follows Langmuir adsorption isotherm [128].

Anticorrosive behavior of *Glycine max* (*L*.) oil is investigated in 2M H_2SO_4 solution by Bhawsar Jeetendra et al. using weight loss method for mild steel. 47.98% inhibition efficiency was obtained for 20 g/L at 298 K [44]. Abdulrasoul Salih Mahdi and Shymma Kadhem Rahem studied inhibitive properties of aqueous leaves extract of herb *Thymus vulgarize* (thyme) for reinforced steel in simulated chloride contaminated concrete pore solution (SCP) using open circuit potential and potentiodynamic polarization technique [140].

R. Karthik et al. studied the anticorrosion activity of *Cassia senna* for mild steel in 1M hydrochloric acid using weight loss, potential dynamic polarization, electrochemical impendance spectroscopy (EIS), scanning electron microscopy (SEM), UV-visible spectroscopy and x-ray diffraction (XRD) studies [108].

Nutan Kumpawat et al. reported the anticorrosive behavior of *Holy Basil* (Tulsi) for tin metal in HNO_3 solution by using leaves and stem extracts of different varieties by weight loss technique [127]. It has been reported by Kanchan Agarwal that *Fenugreek* leaves and Lemon peel extracts are good corrosion inhibitor for mild steel in 1M HCl solution using weight loss and electrochemical methods [13]. Inhibitive effect of seed extract of Kuchla

(*Strychnos nuxvomica*) has been reported for mild steel in hydrochloric acid solution by Ambrish Singh et al. [25].

Extract of rice husk ash was studied as a good corrosion inhibitor for mild steel in 1M H_2SO_4 and HCl solutions. The study was carried out using mass loss and atomic absorption spectroscopy (AAS) [18]. Iroha et al. revealed anticorrosive behavior of acetone extract of red onion skin for aluminum in 2 M hydrochloric acid solution using weight loss method. [101].

Yaro and Ibraheem revealed the inhibitive effect of Peach juice on low carbon steel corrosion in hydrochloric acid at different temperatures using weight loss and polarization techniques. 91% inhibition efficiency was obtained at 50^0C in 50cm^3/L inhibitor concentration [248]. E.E.Oguzie studied corrosion inhibitor effect of leaves extract of *Sansevieria trifasciata* on aluminum metal by gasometric technique [168].

It has been reported by L.Y.S. Helen et al. that *Aquilaria crassna* leaves extract is a good corrosion inhibitor for mild steel in 1M HCl medium using gravimetric method (weight loss method) [95]. Potato peel extract was investigated as an effective naturally available corrosion inhibitor for mild steel in 2M HCl by Taleb H. Ibrahim et al. [100].

Gopal Ji et al. studied corrosion inhibition effect of root extract of C*hlorophytum borivilianum* on mild steel in HCl and H_2SO_4 solution using various techniques viz. weight loss, electrochemical impedance spectroscopy, Tafel polarization and scanning electron microscopy [88].

Inhibition effect of biomass extract of *Petersianthus macrocarpus* plant was revealed by gravimetric electrochemical impedance and potentiodynamic methods on mild steel corrosion in HCl and H_2SO_4 solutions [17]. Saedah R. Al-Mhyawi found anticorrosive behavior of J*uniperus* plant extract for mild steel in H_2SO_4 solution using chemical (HE and WL) and electrochemical (PDP and EIS) methods [21].

M. Dekmouche et al. investigated corrosion inhibition effect of ethyl acetate extract of *Pistacia atlantica* gals in hydrochloric acid solution for mild steel using weight loss, polarization and AC impedance methods [60]. O. Benali et al. revealed the corrosion inhibition effect of tannin extract of *Chamaerops humilis* plant and potassium iodide on the corrosion of mild steel in 0.5 M H_2SO_4 solution using electrochemical methods [40]. S.A. Umoren et al. investigated synergistic inhibition effect between naturally occuring exudate gum and halide ions on mild steel corrosion in H_2SO_4 medium by hydrogen evolution techniques [234].

L. Afia et al. studied anticorrosive property of Argan Oil (AO) on corrosion of C38 steel by weight loss, electrochemical polarization and EIS methods [12]. Taleb Ibrahim et al. revealed that Thyme leaves extract showed 84% corrosion inhibition efficiency in 2M HCl solution for mild steel by using weight loss measurements and various electrochemical techniques [99].

Osmanthus fragran leaves extract was studied as corrosion inhibitor for carbon steel in hydrochloric acid medium using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FTIR) and quantum chemical calculations [135]. Bamboo leaf extract was studied by Xianghong Li et al. as corrosion inhibitor for steel in HCl and H_2SO_4 solutions [133]. Xianghong Li et al. also studied bamboo leaves extract as corrosion inhibitor in citric acid solution for steel and zinc using weight loss, potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) methods. [134].

M. Faustin et al. investigated corrosion inhibition of C38 steel by *Geissospermum* leave alkaloids extract in hydrochloric acid solution using electrochemical studies [79]. Long chain alkyl carboxylates like stearate, palmitate and myristate were investigated as green corrosion inhibitor for magnesium alloy ZE41 corrosion in aqueous salt solution using potentiodynamic polarization, EIS, SEM and EDX analyses [64]. Black pepper extract was studied by M.A. Quraishi, Dileep Kumar Yadav and

Ishtiaque Ahamad as corrosion inhibitor for mild steel in hydrochloric acid solution using mass loss measurements, PDP, Linear polarization resistance and EIS [187]. Corrosion inhibition of aluminum by *Salvia judica* extract was investigated in 1M NaOH solution by E.M. Nawafleh et al. using weight loss method at different temperatures [154].

Deepa prabhu and Padmalatha Rao found *Garcina Indica* extract (GIE) as novel green inhibitor for aluminium and 6063 aluminium alloy in 1.0 M H_3PO_4 solution using potentiodynamic polarization, Tafel extrapolation technique and EIS technique [182].

Olasehinde E.F. et al. studied corrosion inhibition effect of *Musa Sapientum* peels extract in HCl solution for mild steel using weight loss method [174]. I.E. Uwah, P.C. Okafor, V.E. Ebiekpe investigated corrosion inhibition effect of leaves bark and roots exract of *Nauclea latifolia* on mild steel in H_2SO_4 solution using weight loss and gasometric techniques [243].

L. Bammou et al. reported *Chenopodium ambrosiodes* extract as good corrosion inhibitor for steel in sulphuric acid solution using weight loss method, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements 94% inhibition efficiency was obtained at 4g/L [33].

M.Dhamani et al. investigated black pepper extract and its piperine as a corrosion inhibitor for C38 steel in 1M HCl by weight loss method [57]. J. Halambek et al. reported natural oil extract from *Lavandula angustifolia L.* as corrosion inhibitor for Al-3Mg alloy by weight loss, polarization measurements and SEM [91].

Corrosion inhibition effect of *Phyllanthus amarus* extracts from leaves and seeds for mild steel corrosion in acidic media has been studied by P.C. Okafor et al. [172]. M. Lebrini et al. reported *Oxandra asbeckii* alkaloids extract as an good corrosion inhibitor for C38 steel in 1M hydrochloric acid

medium using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) [130].

A.K. Satapathy et al. have been investigated the corrosion inhibition of mild steel by extract of *Justicia gendarussa* plant in hydrochloric acid solution by weight loss and electrochemical techniques. 93% inhibition efficiency was achieved with 150 ppm extract at 25^0C [199]. Shivakumar and Mohana reported *Centella asiatica* extracts as green corrosion inhibitior for mild steel in 0.5 M sulphuric acid medium using gravimateric, polarization and EIS measurements. 95.08% inhibition efficiency was obtained at 303K [210]. *Spirulina platensis* was reported as green corrosion inhibitor for mild steel by C. Kamal and M.G. Sethuraman using weight loss, PDP method, EIS and SEM analysis [106].

3-[(4-amino-2-methyl-5-pyrimidinyl) methyl]-5-(2-hydroxyethyl)-4-methylthiazoliumchloride hydrochloride was reported as green corrosion inhibitor for copper in HNO_3 solution by Olusegun K. Abiola et al. using weight loss method [7]. M. Behpour et al. investigated two aleo-gum resin exudates from *Ferula assa-foetida* and *Dorema ammoniacum* as corrosion inhibitor for mild steel corrosion in acidic medium using weight loss, PDP and EIS methods [37]. Mahendra Yadav et al. reported synthesized thiourea derivatives for mild steel corrosion inhibition in 15% HCl solution using weight loss, PDP, EIS techniques [246]. Punita Mourya, Sitashree Banerjee and M.M. Singh reported *Tagetes erecta* (marigold flower) extract as green corrosion inhibitor for mild steel in 0.5 M H_2SO_4 solution using gravimetric, PDP and EIS measurements [151]. N.O. Obi-egbedi et al. investigated extracts of *Spondias mombin L.* as green corrosion inhibitor for aluminium in sulphuric acid medium using standard gravimetric technique [162].

L. Bammou et al. studied the corrosion inhibition effect of eco friendly cheap natural substance *Harmal* extract on C-steel in hydrochloric acid solution [32]. They used weight loss and electrochemical methods. Ambrish Singh et al. reported extract of *Zanthoxylum schinifolium* as an

effective corrosion inhibitor for N80 steel in CO_2 saturated 3.5% NaCl solution by using EIS,PDP, XRD, SEM techniques [24].

Mohammad Ismail et al. have been investigated the ethanolic leaves extract of soild waste of Genus Musa (Banana), Gemus Saccharum (Sugarcane) and *Citrullus lanatus* (water melon) as a corrosion inhibitor for mild steel in HCl medium, using weight loss technique [102]. M. Lebrini et al. have been studied effect of alkaloids of plant *Isertia coccinea* on corrosion inhibition of C38 steel in 1M HCl solution using EIS and potentiodynamic polarization techniques [129].

Ambrish Singh et al. studied the corrosion inhibitive influence of *Gingko biloba* leaves extract on J55, N80, P110SS and C110 steels in 3.5 wt% NaCl solution with CO_2 using static high pressure high temperature (HPHT) autoclave. The steel surface was studied by XRD, SEM and contact angle measurement technique [23].

N. Soltani and M. Khayatkashani revealed corrosion inhibition property of leaf extract of *Gundelia tournefortii* plant on mild steel in 2M HCl and 1.0 M H_2SO_4 solutions using weight loss method, PDP, EIS techniques [222]. Inhibition effect of *Cnidoscolus chayamansa* leaves extract was investigated for Zn metal in 1N HCl by weight loss measurements by Bright et al. The Protective film on metal surface was studied by UV, FTIR, XRD and SEM-EDX techniques. [51]. Corrosion inhibition effect of leaves extract of *Artemisia holodendron* on mild steel was revealed by electrochemical potentiodynamic polarization measurements and EIS techniques [96].

A. Chetouani et al. revealed the corrosion inhibition property of jojoba oil on corrosion of iron in HCl solution using weight loss measurement and electrochemical polarization methods. [54]. A.A. Rahim et al. studied inhibitive action of mangrove tannins and phosphoric acid of pre- rusted steel in 3.5% NaCl solution [188]. Essential oils obtained from *Thymus satureioides* was tested as green corrosion inhibitor for template in 0.5M HCl solution by L. Bammou et al. [31]. Inhibitive effect of fruit peel extract of *Eugenia*

jambolana on zinc were reported by P.D.Rani et al. in 1N HCl medium using mass loss measurements [194]. Olusegun K. Abiola and A.O. James studied corrosion inhibiting effect of *Aloe vera* leaves extract by weight loss techniques, on the corrosion of zinc in 2M HCl solution [6].

F. Silvio de Souza et al. evaluated caffeine as green corrosion inhibitor for copper using PDP and EIS techniques in aerated 0.1M H_2SO_4 solution [214]. A.S. Yaro et al. showed the inhibitive properties of Apricot juice in 1M phosphoric acid to protect mild steel from corrosion using weight loss technique at different temperatures [249]. S. Sathiya, K. Bharathi and S. Geetha revealed corrosion inhibition of Al metal by *Datura metel* leaves extract in 1M HCl using chemical and electrochemical techniques [201].

S. Anath Kumar et al. studied aqueous extract of *Magnolia champaca* flower [123] as corrosion inhibitor for mild steel in 0.5 M H_2SO_4 solution and *Magnolia champaca* stem extract [124] using weight loss, PDP, EIS methods for metal steel in 1M HCl. *Tectona grandis* acid seed extract has showed a green corrosion inhibitor for mild steel in HCl solution by G.R. Thusnavis et al. [229]. Gopal ji et al. studied corrosion inhibititive effect of *Argemone mexicana* plant leaves extract [89], *Capsicum annum* fruit extract [87], *Parthenium hysterophorus* plant leaves extract [86] for mild steel in HCl solution.

S. Ananth Kumar et al. also studied the leaves extract of *Oxystelma esculentum* plant as corrosion inhibitor for mild steel in 0.5 M H_2SO_4 solution using weight loss, EIS and polarization techniques [125]. It has been shown that ethanolic extract of *Ricinus communis* leaves is good corrosion inhibitor for mild steel in 100 ppm NaCl solution [202]. Vitamin B-12 solution was tested by S. Ananth Kumar et al. as corrosion inhibitor in 0.5 M H_2SO_4 for mild steel using weight loss, PDP and EIS measurements [27]. A.M. Al-Fakih, M.Aziz and H.M.Sirat were reported the acidic extract of turmeric and ginger rhizomes separately as corrosion inhibitor for mild steel in 1M HCl solution using weight loss and PDP measurements. [19]. Aqueous extract of ginger has also been reported as inhibitor for mild steel in 1M HCl

by weight loss, open circuit potential (OCP), linear and Tafel polarization techniques [76].

Methanolic extract of *Alpina galinga* was tested against mild steel in 0.5 N H_2SO_4 for corrosion inhibition by S.Ananth Kumar et al. using weight loss, PDP and electrochemical impedance measurements [126].

Bryophyllum pinnatum Leaves extract has been proved as a corrosion inhibitor for mild steel in 0.5 M HCl solution by Dakeshwar Kumar Verma and Fahmida Khan using gravimetric and scanning electron microscope technique [238]. Leaves extract of *Millingtonia hortensis* for mild steel corrosion in 1N HCl and 1N H_2SO_4 solutions using mass loss measurements was studied by S. Kulandai Therese and V.G. Vasudha [119].

E.I. Ating et al. also studied leaves extract of *Ananas Sativum* as green inhibitor for aluminum in HCl solutions using weight loss and hydrogen evaluation method [28]. *Cocos nucifera* petiole extract was investigated as inhibitor of corrosion for mild steel in 0.5M H_2SO_4 and 1M HCl solution using mass loss, polarization and electrochemical impedance techniques [241]. The leaves extract of *Carcia papaya* and *Camellia sinensis* (green tea) extract were investigated as green corrosion inhibitors for α β (duplex) brass in 1M Nitric acid solution using weight loss and potential measurement techniques [138]. Extract of leaves and berries of *Solanum nigrum* were investigated as green inhibitor for zinc in 0.5N HCl [176] using weight loss, thermometric and gasometric methods. *Vernonia amygdalina* (bitter leaf) was tested for zinc plate corrosion inhibitor in 2M HCl solution by weight loss, gasometric and potentiostatic polarization [180].

A.Y. El-Etre et al. studied aqueous extract of *Lawsonia* (heena) leaves as corrosion inhibitor for C-steel, nickel and zinc in acidic, neutral and alkaline medium using polarization technique [73]. *Morinda tinctoria* leaves extract has shown corrosion inhibition property for mild steel in HCl medium using weight loss and AC impedance studies [118].

The corrosion controlling capacity of beet root extract was investigated in well water in the absence and presence of Zn^{+2} ion for carbon steel by mass loss method [205]. *Azadiractha indica*, ethanolic extract of leaves and seeds were tested as corrosion inhibitor for mild steel in H_2SO_4 solution using weight loss and gasometric techniques [68]. A.S. Founda et al. studied methanolic extract of barks and rhizomes of *curcum* plant as a green inhibitor for steel in 3.5% NaCl and 16ppm Na_2S solution by PDP, EIS, electro chemical frequency modulation (EFM) techniques [82]. Corrosion inhibition by *Ficus abutilifolia* plant extract on N-80 oil well tubular steel was studied by weight loss technique by G.Abubakar et al. [10] in 15% HCl solution. *Cassia auriculata* flowers extract was tested as corrosion inhibitor for Al and mild steel in 2M HCl solution by weight loss, polarization and impedance studies by A. Rajendran and C. Karthikeyan [192]. *Ginseng* root extract has been proved as eco-friendly corrosion inhibitor for AA 1060 aluminum alloy in HCl solution by weight loss method [164].

Hui Cang et al. studied *Aloes* leaves extract for mild steel corrosion in 1M HCl solution by weight loss PDP, EIS techniques [97]. S.M. Mahdi showed pomegranate peel powder as inhibitor for mild steel in 5% HCl and 5% H_2SO_4 solutions using weight loss method [141]. *Solanum trilobatum* was tested as green inhibitor for aluminum corrosion in 1M NaOH medium using weight loss, hydrogen evaluation, EIS and polarization methods [84]. F.S. de souza and A. Spinelli studied naturally occurring biological molecule caffeic acid as corrosion inhibitor for mild steel in 0.1 M H_2SO_4 solution using weight loss, PDP, EIS and Raman sopectroscopy [59]. M.Znini et al. revealed the corrosion inhibition effect of essential oil obtained from *Salvia aucheri mesatlantica* for mild steel corrosion in 0.5 M H_2SO_4 solution using weight loss and electrochemical polarization measurements [254].

A.S. Abdulrahman et al. have investigated corrosion inhibition of mild steel in sulphuric acid solution by leaves extract of *African prequentina* using gravimetric, gasometric and thermometric measurements [4].

Seed extract of *Psidium guajava* fruit (guava) was studied by K.P. Vinod Kumar et al. as inhibitor for carbon steel in HCl medium using weight loss measurement [120]. S. Leelavathi and R. Rajalakshmi revealed the corrosion mitigating property of leaves extract of *Dodonaea viscosa L.* on mild steel corrosion in 1M HCl and 0.5M H_2SO_4 using mass loss and electrochemical measurements [131]. Nasrin Soltani et al. studied leaves extract of S*alvia officinalis* as inhibitor for 304 stainless steel in 1M HCl solution using weight loss, PDP, EIS and Tafel polarization studies [224]. M. Sangeetha et al tested aqueous extract of asafoetida for protection of mild steel corrosion in sea water using weight loss method [195]. Bentiss et al. studied 4H-1,2,3-triazole derivatives as corrosion inhibitors for mild steel in normal HCl solution by using weight loss and AC impedence measurements and polarisarion curves. Results showed that 4H-1,2,3-triazole derivatives obeys Langmuir adsorption model on mild steel surface [41].

The corrosion inhibition efficiency of pyridazine compounds in 0.5M H_2SO_4 medium were studied by Bouklah et al. using weight loss method at various temperatures and revealed that inhibition efficiency increases with increase in concentration. Pyridazine compounds followed Langmuir adsorption isotherm on mild steel surface [48]. Corrosion inhibition of Armco iron in HCl solution was studied by using four surfactants: tetradecyl trimethyl ammoniumiodide (TTAI), tetradecyl trimethyl ammoniumbromide (TTAB), hexadecyl trimethyl ammonium bromide (HTAB) and dodecyl trimethyl ammonium bromide (DTAB). They observed that protection efficiency increases with increase in inhibitor concentration and length of alkyl chain and these surfactants followed Langmuir adsorption isotherm on Armco iron surface [50].

Cristofari et al. studied essential oil extracted from *Pulicaria mauritanica* as corrosion inhibitor for mild steel in 0.5M H_2SO_4 medium. They employed weight loss, EIS, electrochemical polarization methods. Carvatan acetone was found predominant component in essential oil in 87.3%. 91.5% inhibition efficiency was found at 2g/L essential oil

concentration. Spontaneous adsorption of inhibitor was observed and adsorption followed Langmuir adsorption isotherm [56].

Eddy investigated corrosion prevention properties of ethanolic extract of *Garcinia kola* and *Cola nitida* using weight loss and thermometric methods for mild steel in H_2SO_4 medium. Physical adsorption mechanism was proposed from inhibition efficiency trend with temperature and Langmuir adsorption isotherm was followed by inhibitor [69]. Ekanem et al. studied pineapple leaves extract as mild steel corrosion inhibitor in HCl solution at 30^0C- 60^0C temperature range using weight loss and hydrogen evolution methods. Inhibition efficiency increases with increase in temperature. Extract adsorption followed Langmuir isotherm and chemisorption is also proposed by the trend of inhibition efficiency with temperature [71].

4-phenylsemicarbazide (4PSC) and semicarbazide (SC) were found significant corrosion inhibitors for mild steel in HCl solution by Ita and Offiong. They used weight loss and hydrogen gas evolution measurements and found that 4PSC showed 82% inhibition efficiency and SC showed 66% inhibiton efficiency [103].

Mimosa tannin was tested as corrosion inhibitor for low carbon steel in sulphuric acid medium by using weight loss method in the range of 20^0C to 60^0C temperatures and observed that adsorption of tannin followed Temkin, Freumkin and Freundlich adsorption isotherms [147]. Tryptamine (TA) was found as effective corrosion inhibitor for ARMCO iron in 0.5 M deaerated H_2SO_4 solution in 25°C-55^0 C temperature range. They employed potentiodynamic curves and electrochemical impedence spectroscopy (EIS) methods. TA adsorption followed Bockris – Swinkels' adsorption isotherm (X=1) [150].

Corrosion inhibition efficiency of aqueous extract of fenugreek leaves and seeds were studied by Ehteram A. Noor in HCl and H_2SO_4 solution for mild steel and revealed that both extract act as anodic type

inhibitors. He observed that inhibition efficiency was found greater in HCl than in H_2SO_4 solution. He employed electrochemical impedence spectroscopy and potentiodynamic polarization measurements for study [158].

Okafor et al. studied leaves (LV), root (RT) and seeds (SD) extract of *Azadirachta indica* as corrosion inhibitor for mild steel in H_2SO_4 solution using weight loss and gasometric techniques. Inhibition efficiency followed SD> RT> LV trend and increases with increase in extract concentrations. Adsorption followed Freundlich adsorption isotherm [171].

Leaves extract of *Bridelia retusa, Murraya koenigii, Embilica officinalis* were studied as corrosion inhibitor for mild steel in H_2SO_4 and HCl solutions respectively [178, 186, 198]. Sharma et al. have also studied mature leaves extract of *Azadirachta indica* as corrosion inhibitor for mild steel in 2N HNO_3 solution at 30^0C and 60^0C respectively and extract followed Frumkin adsorption isotherm [209].

Fruit extract of Shahjan (*Moringa olifera*) was investigated as a good corrosion inhibitor for mild steel corrosion in HCl solution using weight loss, EIS, linear polarization and potentiodynamic polarization techniques (Tafel). Inhibitor extract obeyed Langmuir adsorption isotherm [217].

The essential oils extracted from aerial parts of *Mentha spicata L.* and *Lavandula multifida L.* were observed as corrosion inhibitor for steel in 1M HCl and 0.5M H_2SO_4 solutions using weight loss method and electrochemical polarization measurements studies by Znini et al. In studies they found that these natural oils act as mixed type of inhibitors and followed Langmuir adsorption isotherm [255, 256].

Rajendran has revealed that flower extract of *Nerium oleander* contains anticorrosive property for mild steel and aluminium in 2M HCl at

$30^{o} \pm 1^{\circ}C$ and observed that inhibition percentage increases with increase in extract concentration [193].

Corrosion inhibition property of aqueous extract of water hyacinth leaves extract-Zn^{+2} system with and without TSC (Tri Sodium Citrate) was studied by Kavitha and Manjula [110] and Kavitha et al. [109] respectively in aqueous environment containing 60 ppm Cl^{-} ion for mild steel. Shanab et al. studied *Eichhornia crassipes* as corrosion inhibitor for Magnesium alloy (AZ31E) in 3.5% NaCl solution [207] while Ulaeto et al. reported leaves and roots extract of *Eichhornia crassipes* as corrosion inhibitor for mild steel in hydrochloric acid medium using gasometric technique [230] and Oloruntoba Daniel Toyin investigated corrosion inhibitive property of leaves extract of water hyacinth for 1014 steel in chloride environment [175].

Sudesh Kumar and Suraj Prakash Mathur had investigated ethanolic extract of leaves, latex and fruit of *Calotropis procera* as corrosion inhibitor for aluminium in sulphuric acid medium [121] while Bharthi et al. reported leaves extract of *Calotropis procera* as corrosion inhibitor for aluminium in 1 M HCl solution [43]. Sudesh kumar et al. also studied corrosion controlling property of alcoholic extracts of leaves, latex and fruit extract of *Calotropis procera* and *Calotropis gigentea* for mild steel in basic solution by mass loss method and thermometric method [122]. Raja and Sethuraman have also reported corrosion inhibitive property of *Calotropis procera* for mild steel in sulphuric acid medium [189].

Sharma et al. studied ethanolic extract of leaves, stem bark and fruit of *Lantana camara* was studied as corrosion inhibitor for aluminium in different concentrations of sulphuric acid solution [208], Petchiammal and Selvaraj have reported anticorrosive effect of fruit peel extract of *Lantana camara* in 1M HCl for mild steel and found maximum 85% inhibition efficiency [179]. Besides these Nkiko et al. also reported *Lantana camara* leaves extract as corrosion inhibitor for Zinc alloy in H_3PO_4 solution [157]

Although large amount of research studies have been done on corrosion inhibition of mild steel in aggressive media by various natural substances, but still there is thirst to search newer and better green corrosion inhibitors which are very less or not studied. To keep this in view, the present work has been undertaken which enlightens, “Studies on potential green corrosion inhibitors for mild steel in different media”, for which no reference could be found in literature reviewed so far.

CHAPTER – 2

MATERIALS, METHODS AND METHODOLOGY

Materials:

Selection of plants as corrosion inhibitors:

Aqueous extract of *Lantana camara* leaves (AELCL), *Nerium oleander* leaves (AENOL), *Calotropis procera* leaves (AECPL) and Water hyacinth (*Eichhornia crassipes)* (AEWHL), 1M HCl solution ,1M H_2SO_4 solution and mild steel cylindrical specimens of, borosil beaker (250 ml),volumetric flasks, measuring cylinders, different emery papers (Marks 80 to 120 grades), distilled water , electronic balance (citizens model CY204), thermostat (12 holes double walled), electronic oven (14') and desiccators (210 ml).

The detailed descriptions of the selected plants for corrosion studies of mild steel are explained below.

1. Lantana camara:

Plant classification

Kingdom : Plantae

Division : Magnoliophyta

Class : Magnoliopsida

Order : Lamilales

Family : Verbenaceae

Genus : Lantana

Species : Lantana camara L.

Lantana camara also known as wild-sage, big-sage (Malaysia), red-sage (carribean) and tick-berry (South Africa). It is a flowering palnt of Verbena family Verbenaceae native to tropical and subtropical America but few taxa are indegenious to tropical Asia and Africa [105]. It is a low erect shrub of 2-4 meters in height. Leaves are ovate, bright green in color with rough and hairy surface and give pungent smell when crushed. It has flowers of various colours like white,

yellow, cream, orange, pink, purple, red. The fruit of *Lnatana camara L.* is greenish blue-black colour, round shining with 5-7 mm in diameter.

Boiled leaves of *Lantana camara* reduce swellings and pain of the body. Lotion prepared from its astringent bark is used in cutiginous eruptions and leprous ulcers. Alkaloids obtained from its leaves reduce blood pressure, accelerate deep respiration and stimulate intestinal movements in experimental animals.

Lantana camara is an invasive species and a nutritious weed and well often out-compete other desirable species, leading to a reduction in bio-diversity. It excretes chemicals (allelopathy) which retards the growth of surrounding plants by inhibiting germination and root elongation [15]. It is toxic to livestock and form thickets, which greatly reduce productivity of agriculture land. The active substance which causes toxicity in grazing animals is pentacyclic triterpenoids which causes liver damage and photosensitivity [34].

The plant has been used to treat variety of disorders. In Asian countries, leaves were used to treat cuts, rheumatism and ulcers [200]. Traditionally it is used as tonic, in abdominal pains, as anthelmintic and insecticide [247].The plant is reported to contain various compounds like triterpenoids [200, 35], flavonoids [200, 239], amino acids [247],saponins , steroids [200] etc.

2. Nerium Oleander:

Plant classification

Kingdom : Plantae

Division : Magnoliophyta

Class : Magnoliopsida

Order : Gentianales

Family : Apocynaceae

Genus : Nerium

Species : Nerium oleander L.

Its common name is Oleander or Kaner. It is an evergreen shrub, belongs to Apocynaceae family. It is also cultivated as ornamental plant. It is found in Mediterranean region, and in Southeast Asia and Southern Europe. It has long narrow dark green leaves with different colored flowers like white, pink, red, light yellow.

Nerium is one of the most poisonous plant and contain many toxic compounds which have been reported lethal to people and to infant or a child. The most significant of these toxins are Oleandrin and nerin, which are cardiac glycosides [36], which can cause numbness by blocking the receptors in skin. Its toxicity remains even after drying of Oleander. The leaves and flower have cardio tonic, diaphoretic, anticancer, diuretic, antifungal [244]. Oil from the root bar is used in skin diseases and leprosy. Seeds are poisonous and used in dropsy and rheumatism. The whole plant is said to have anticancer properties [5]. The most well known effect of oleander is due to two glycosides, nerin and an alkaloid olendrin, which have cardio stimulatory action [253] and to the glycosides, gentiobiosyl-olendrin, gentiobiosyn-nerigoside and gentiobiosyl-beaumontoside extracted from its leaves [144]. Its lymph is rich in minerals [30] and α-tocopherol, an important antioxidant [98]. Olender flowers in fresh and dried condition shows antinociceptive activity [252].

3. <u>Calotropis procera</u>:

<u>Plant classification</u>

Kingdom : Plantae

Division : Magnoliophyta

Class : Magnoliopsida

Order : Gentianales

Family : Asclepiadaceae

Genus : Calotropis

Species : Calotropis procera

Calotropis procera belongs to the Asclepiadaceae family. It has many common names like swallow wort in English, Madar in Hindi, Alarka in Sanskrit. Besides it, it is also known as Apple of Sodom, rubber bush etc. It grows in warm dry climate in sandy and salty soil. It can grow as weed in cultivated areas. It also grows in rubbish heap, waste land, in sand dunes and along roadside. Calotropis procera is found in Pakistan , Nepal, India, Afghanistan, Algeria, Iran, Iraq, Isreal, Kenya, Saudi Arabia, Nigeria , Oman , Vietnam , Kuwait, Yemen , United Zimbabwe and Arab Emirates .

Calotropis procera is erect, tall, large perennial shrub of height approximately 4-5 m and secretes milky latex when cut. Leaves are broadly ovate-oblong, opposite thick, green covered with fine pubescent hair on young. It has purple flowers. Phytochemical studies show that it contains several compounds. Its leaves and stock contains calotropin and calotropagenin. White flowers contain calotrophenyl acetate.

Chemical investigation shows that plant conatins cardiac glycosides catotropogenin , calotropin , uscharin , calotoxin and calactin [14]. It also has been investigated for cardenolides [204] and anthocyanins [16].

Calotropis procera shows medicinal properties. It shows anticancer and insecticidal activity. The flowers show hepatoprotective activity [206], anti-inflammatory, antipyretic, antimicrobial effects and larvicidal activity [146]. The latex is reported to show analgesic and wound healing activity [63], anti-inflammatory and anti-microbial activity [203] while roots show anti-fertility property [107].

4. Water Hyacinth:

Plant classification

Kingdom : Plantae

Division **:** Magnoliophyta

Class **:** Liliopsida

Order **:** Liliales

Family **:** Potenderiaceae

Genus : Eichhornia Kunth

Species : Eichhornia crassipes

Water hyacinth (*Eichhornia crassipes*) is a perennial aquatic herb belongs to Potenderiaceae family. It is free floating water plant. It has glossy green leathery leaves, inflated petioles and hairy roots. It has funnel shaped flowers having six petals of light bluish purple flower with yellow center.

It is native to South America and a worst and noxious aquatic weed. It grows rapidly and forms impenetrable mats which cover the whole waterways. It is an aggressive invader and forms impenetrable mats on the entire pond surface, block water transport, increase water evaporation and transpiration, block irrigation canals, decrease the oxygen and sunlight to the aquatic plants and aquatic animals and thus creates difficulties in survival of aquatic plants and animals and reduce the aquatic biodiversity. So water hyacinth is challenging the ecological stability of fresh water bodies [116] out competing all other species growing in the vicinity, posing a threat to aquatic biodiversity [177]. Its mats prevent the transfer of oxygen from air to water surface or decrease oxygen production by other plants and algae [242]. Low level of oxygen results in the release of phosphorus from sediments which accelerate eutrophication and lead to increase in water hyacinth or algal bloom [45]. Death and decay of water hyacinth vegetation deteriorates water quality and quantity of potable water and increases treatment costs of drinking water [149, 155,177].

Water hyacinth can uptake heavy metals like Cr, Co, Ni, Pb and Hg from industrial waste water [9, 142, 220, 235] and used for bio cleaning of water. It is highly tolerant to these. Beside this it can remove toxins like cyanides, which is

beneficial in gold mining operations [66]. Phytochemical studies showed presence of alkaloids [156], compounds of nutritional values like phenolic flavonoids, glutathione [143] and other metabolites.

Acids selected as different media:

1. Hydrochloric Acid (HCl)

Hydrochloric acid is a pungent smelling colourless solution of HCl gas in water. It is monoprotic acid which gives one H^+ ion in solution. It is highly corrosive acid. The name "Hydrochloric Acid" was coined by Joseph Louis Gay-Lussac, the French chemist in 1814. Hydrochloric acid is a binary mixture (two-component) of HCl and H_2O has a constant boiling azeotrope at 20.2% HCl and 108.6°C (227°F). It is prepared in solutions up to 38% HCl (concentrated grade). Higher concentrations just over 40% has high evaporation rate and thus storage and handling is difficult. 38% HCl has 1.189 kg/L density, BP 48°C and viscosity 2.10 mPa.S. these above data are at 20°C and 1 atm pressure. Hydrochloric acid is used in pickling of steel , removing rust from iron , production of organic and inorganic compounds such as vinyl chloride , bisphenol A and numerous pharmaceutical products, iron (III) chloride, polyaluminium chloride (PAC) (both used as flocculation and coagulation agents in sewage treatment) , calcium chloride salt , nickel (II) chloride , zinc chloride etc.

2. Sulphuric acid (H_2SO_4):

Sulphuric acid is highly corrosive, diprotic acid. It is a mineral acid, having formula H_2SO_4 and molecular weight 98.079 g/mol. It is colourless or slightly yellow viscous liquid and soluble in water. It is also known as oil of vitriol. 98%sulphuric acid has 1.83 kg/L density and 18 mol/L concentration. Sulphuric acid when reacted with SO_3 forms oleum ($H_2S_2O_7$). 98%sulphuric acid has < 1mm Hg vapor pressure at 40°C. Anhydrous H_2SO_4 is very polar liquid having a dielectric constant around 100 and shows high electrical conductivity due to autoprotolysis. It has wide range of applications like domestic acidic drain cleaner, as electrolyte in lead acid batteries, fertilizers production , oil refining ,

mineral processing, waste water processing, as dehydrating agent, production of dyes, detergents, insecticides, antifreeze, in pharmaceutical industries etc.

Methods:

The leaves of *Lantana camara*, *Calotropis procera*, *Nerium oleander* and Water hyacinth (*Eichhornia crassipes*) were collected from local areas and pond of Kota city Rajasthan (India), city. These were washed and air-dried in shed for 6-7 days, crushed and grounded mechanically and converted into fine powdered form.

Preparation of AELCL

For preparation of AELCL (aqueous extract of the *Lantana camara* leaves): 20 g of dried and grounded *Lantana camara L.* leaves were heated between 70°C-80°C in 500 ml of distilled water for one hour in round bottom flask. The extract was left overnight and then filtered and made up to 500 ml with distilled water.

Preparation of AECPL:

Stock solution of AECPL (aqueous solution of *Calotropis procera* leaves): 20 grams of dried grounded leaves powder of *Calotropis procera L.* was heated between 70°C-80°C in 250 ml of distilled water for one hour in round bottom flask. The extract was left overnight and then filtered and made up to 250 ml with distilled water.

Preparation of AENOL:

For preparation of the stock solution of AENOL (aqueous extract of *Nerium oleander* leaves): 20g of dried grounded leaves powder of *Nerium olender L.* was heated between 70°C-80°C in 200 ml of distilled water for one hour in 250 ml round bottom flask with air condenser The extract was left overnight and then filtered and made up to 200 ml with distilled water.

Preparation of AEWHL:

For preparation of the stock solution of AEWHL (aqueous extract of water hyacinth (*Eichhoria crassipes*) leaves): 20g of dried grounded leaves powder of

Eichhoria crassipes was heated between 70°C-80°C in 500 mL of distilled water for one hour in round bottom flask. The extract was left overnight and then filtered and made up to 500 ml with distilled water.

Preparation of different acidic media:

Acidic media for corrosion studies of mild steel were prepared by AR grade HCl (Merck Ltd), and H_2SO_4 (Merck Ltd). 1M standard solution of each acid was prepared using de-ionized distilled water.

Determination of weight loss:

For corrosion studies of mild steel specimens gravimetric technique for weight loss described by Mattson [112] was used. For weight loss cylindrical mild steel specimens of various dimensions (5 cm in length and 0.80 cm in diameter),(4.7 cm in length and 0.50 cm diameter), (4.9 cm in length and 0.70 cm in diameter), (4.8 cm in length and 0.60 cm in diameter) were taken. The above specimens were abraded with different emery papers, degreased in acetone and washed with distilled water dried and the constant weight (W_1) was recorded by electronic balance.

Cylindrical mild steel specimens were hanged by plastic thread and glass rod in 100 ml of different acidic media in 250 ml borosil glass beaker, containing specific amount of aqueous extracts of leaves of four different plants.

After one hour of immersion time the specimens were removed from acidic media, washed with distilled water ,dried and again abraded with emery paper to remove the upper material and weighed accurately (W_2) by electronic balance. Weight loss (ΔW) is calculated by (W_1-W_2). The different employed concentrations range of the aqueous extracts of leaves of the 4 plants were 2%-6%(v/v) for AELCL,1%-8%(v/v) for AECPL, 1%-10%(v/v) for AENOL and 1%-5%(v/v) for AEWHL extract. The corrosion inhibition experiments were performed at four different temperature ranges (30°C, 40°C, 50°C, 60°C).

Determination of Corrosion Rates:

In 1M HCl and 1M H_2S0_4 values of Corrosion Rates (CR) for mild steel specimens in various concentrations of inhibitors at four different studied temperatures were calculated by following equation (1) [159].

$$C R = \left(\frac{\Delta W}{A t} \right) \quad (1)$$

Where ΔW is the weight loss calculated by the difference of initial weight (W_1) and final weight (W_2) of mild steel specimen after treating with different acidic media containing different concentrations of inhibitor solutions. A is the surface area of different specimen and t is immersion time in minute.

Determination of Inhibition Efficiency (IE %):

From the above calculated corrosion rate values (CR) the inhibition efficiencies for the mild steel specimens in 1M HCl and 1M H_2S0_4 solutions containing different amount of inhibitor solutions at various temperatures are calculated by the following equation (2) [159,246].

$$IE\ \% = \left(\frac{CR_{blank} - CR_{inh}}{CR_{blank}} \right) \times 100 \quad (2)$$

Where CR_{blank} and CR_{inh} are the corrosion rates in the absence and presence of the different inhibitors at various concentrations.

Determination of Kinetic Parameters:

Kinetic parameters K (rate constant) and B (reaction constant) are calculated by the straight lines obtained in the graph between the log of inhibitor concentrations and the log of corrosion rate values at different temperatures. The following equation (3) is used to determine the kinetic parameters [114,160].

$$\log CR = \log K + B \log C_{inh} \quad (3)$$

where K is the rate constant and equals to CR when the inhibitor concentration is unity. B is the reaction constant which is the measure of inhibitor effectiveness and CR_{inh} is the concentration in (v/v %) (ml/ 100ml) of four different inhibitors.

Determination of the thermodynamic and activation parameters:

The thermodynamic and activation parameters like the Activation Energy (E_{act}), enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) were calculated for mild steel dissolution process,

Activation energy (E_{act}):

Activation energy was calculated using the following Arrhenius equation (4) [232,246].

$$\log CR = \log A - \left(\frac{E_{act}}{2.303\ R\ T}\right) \quad (4)$$

Where A is the Arrhenius pre exponential factor, CR is corrosion rate, T is absolute temperature in Kelvin and R is the universal gas constant. The slope of graph plotted between log CR and 1/T gives the value of activation energy at various studied temperatures.

Enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*):

The value of enthalpy of activation (ΔH^*) entropy of activation (ΔS^*) can be calculated by the following transition state equation (5) [232,246].

$$\log\left(\frac{CR}{T}\right) = \left[\left(\log\left(\frac{R}{Nh}\right)\right) + \left(\left(\frac{\Delta S^*}{2.303\ R}\right)\right] - \left[\left(\frac{\Delta H^*}{2.303\ RT}\right)\right] \quad (5)$$

Where, CR is corrosion rate, N is Avogadro`s number, T is absolute temperature and R is the universal gas constant, h is Planck`s constant.

A plot between log (CR/T) and (1/T) gives a straight line with slope of $\left(\frac{\Delta H^*}{2.303\ RT}\right)$ and intercept of $\left[\left(\log\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S^*}{2.303\ R}\right)\right)\right]$ from which the values of enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) are calculated.

Absorption Isotherms:

Adsorption has significant role in corrosion inhibition processes. Inhibitors generally physically or chemically adsorbed on metal surface and slow down the metal dissolution process. To understand the nature of adsorption, the obtained

surface coverageϴ were fitted in different adsorption isotherms like Langmuir adsorption isotherm, Temkin adsorption isotherm, Freudlich adsorption isotherm.

Many researchers have use the Langmuir adsorption isotherm to study the adsorption process. The mathematical expression for Langmuir adsorption isotherm is according to equation (6) [38, 83, 161, 185, 237]

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (6)$$

Rearranging the above equation (6)

$$\frac{\theta}{1-\theta} = K_{ads}\, C_{inh} \quad (7)$$

$$\text{Or} \quad \log\left(\frac{\theta}{1-\theta}\right) = \log(K_{ads}) + \log(C_{inh}) \quad (8)$$

where C_{inh} is the inhibitor concentration in (ml/L) and K_{ads} ($ml^{-1}L$) is the equilibrium constant of adsorption , θ is the degree of surface coverage and is equal to IE% / 100. A straight line is obtained between (C_{inh}/θ) and C_{inh} or between log (C_{inh}/θ) and log C_{inh} values, if the adsorption process follows Langmuir adsorption isotherm.

Freundlich adsorption isotherm is given by the following equation (9) and (10)[117].

$$\theta = K_{ads} \cdot C_{inh} \quad (9)$$

$$\log\theta = \log(K_{ads}) + n \log C_{inh} \quad (10)$$

Where θ<n<1, θ is the degree of surface coverage and C_{inh} is the concentration of the inhibitor, K_{ads} is the equilibrium constant in the adsorption process. A straight line is obtained between the logarithm of degree of surface coverage (θ) and logarithm of inhibitor concentration C_{inh} in Freundlich isotherm.

Temkin adsorption is given by the following equation (11) [152, 172]

$$-2a\,\theta = \ln(K_{ads}) + \ln(C_{inh}) \quad (11)$$

Where a is the molecular interaction factor in adsorbed layer, K_{ads} is equilibrium constant and C_{inh} is the inhibitor concentration and θ is the degree of surface coverage.

Determination of Adsorption Parameters:

Gibbs Energy ΔG_{ads}:

The values of K_{ads} obtained from adsorption isotherms is related to Gibbs energy by the following equation (12) [115,159].

$$K_{ads} = \frac{1}{C_{H_2O}} \exp(-\Delta G_{ads} / RT) \quad (12)$$

It can also be written as

$$\Delta G_{ads} = -2.303RT \log (K_{ads} . C_{H_2O}) \quad (13)$$

Where. C_{H_2O} is the concentration of water in (ml/L) in metal solution surface, R is Universal gas constant and T is the absolute temperature.

Determination of Enthalpy of Adsorption(ΔH_{ads}) and Entropy of Adsorption (ΔS_{ads}) :

Enthalpy of adsorption (ΔH_{ads}) and entropy of adsorption (ΔS_{ads}) are calculated by the following basic equation (14) [72,159].

$$\Delta G_{ads} = \Delta H_{ads} - T \Delta S_{ads} \quad (14)$$

The intercept of the graph between the ΔG_{ads} and absolute temperature T, gives the values of ΔH_{ads}. Values of ΔS_{ads} were obtained by putting the values of $\Delta H_{ads.}$ in equation (14) at different temperatures.

Methodology

For investigating the effective natural eco-friendly, cost effective natural corrosion inhibitors for mild steel 4 different plant species as *Lantana camara*, *Calotropis procera*, *Nerium oleander* and *Eichhoria crassipes* (water hyacinth) were selected. The plant leaves of these plants were collected from local land area and

ponds of Kota city, washed, air dried in shed for 6-7 days, crushed mechanically into fine powder and their aqueous extracts were prepared by heating (as specified above mentioned quantity of leaves powder)in distilled water using round bottom flask between 70°C-80°C for one hour. The extracts were left overnight and then filtered and made up to the mark by adding required quantity of distilled water. Analytical grade (Merck Ltd) hydrochloric acid and sulphuric acid were taken to prepare acidic media. 1M solution of each acid was prepared in distilled water for experimental studies. The weight loss method, described by Mattson [112] was used to calculate the corrosion rates. For this cylindrical mild steel specimen of different dimensions were taken for different plant species. The length and diameter of these specimens were (5cm and 0.80cm), (4.9cm and 0.70cm), (4.8cm and 0.60 cm), (4.7cm and 0.50cm). These cylindrical specimens were abraded with series of emery papers degreased with acetone and washed thoroughly with distilled water and finally dried in hot air till constant initial weight (W_1) is recorded from electronic balance(citizen model CY 204). These specimens were hanged with plastic thread and glass rod in 100 ml acidic solution for 1 hour in 250 ml borosil beaker in presence and absence of different concentrations (v/v %) of aqueous extracts of inhibitors at different temperatures. After one hour specimens were removed, washed with distill water, dried and again abraded with emery paper and weighed finally with electronic balance (W_2). Thus weight loss (W_1-W_2) is obtained in grams. The employed concentration range of different plant extracts were different for four different plant species and were expressed in (v/v %). These were 2%-6% (v/v) for AELCL, 1%-8% (v/v) for AECPL, 1%-10% (v/v) for AENOL, 1%-5% (v/v) for AEWHL. The experiments were repeated at 30°C, 40°C, 50°C, 60°C temperatures.

From the above obtained weight loss data, corrosion rates (CR) were calculated by using equation (1). Similarly inhibition efficiencies were calculated using equation (2), Kinetic parameters were calculated by using equation (3), thermodynamic and activation parameters were calculated using equations (4) and (5). The different adsorption isotherms were plotted by using the equations (8), (10) and (11). Gibbs energy of adsorption, enthalpy of adsorption and entropy of adsorption were calculated by equations (13) and (14).

CHAPTER – 3

OBSERVATIONS AND RESULTS

The results obtained from gravimetric (weight loss) method, are used for calculating Corrosion rates, Inhibition efficiencies, Kinetic parameters, Apparent activation energy (E_{act}), Enthalpy of activationΔH^{*}, Entropy of activation (ΔS^{*}) and Gibbs Energy (ΔG_{ads}), Enthalpy of Adsorption (ΔH_{ads}) and Entropy of Adsorption (ΔS_{ads}). These data are summarized in tabular (Table 1 to 40) and graphical (Figure 1 to 62) form under well defined headings for four different plant extracts i.e. AECPL, AELCL, AENOL, AEWHL in two different selected acids. Concentrations of extracts prepared are expressed in % (v/v). Langmuir, Freundlich and Temkin adsorption isotherms are drawn for different plant materials.

Table 1. Mild steel corrosion rates in 1 M HCl solution in absence and presence of different concentrations of AECPL at different temperatures

C_{inh} in (v/v)%	CR x 10^{-3} (g cm^{-2} min^{-1})			
	30°C	40°C	50°C	60°C
0.0	0.69	1.37	2.33	3.07
1.0	0.59	1.21	2.17	2.88
2.0	0.41	1.08	1.94	2.81
3.0	0.38	0.99	1.93	2.74
5.0	0.33	0.86	1.86	2.64
8.0	0.27	0.72	1.57	2.56

Table 2. Inhibition efficiencies of AECPL at different concentrations and temperatures in 1 M HCl solution

C_{inh} in (v/v)%	I E (%)			
	30°C	40°C	50°C	60°C
1.0	14.49	11.67	06.86	06.18
2.0	40.57	21.16	16.73	08.46
3.0	44.92	27.73	17.16	10.74
5.0	52.17	37.22	20.17	14.00
8.0	60.86	47.44	32.61	16.61

Table 3. Kinetic parameters for mild steel corrosion in 1 M HCl solution with AECPL

Temperature (°C)	Kinetic Parameters	
	B	K x 10^{-3} (g cm^{-2} min^{-1})
30°C	-0.3584	0.5736
40°C	-0.2514	1.2755
50°C	-0.1363	2.2024
60°C	-0.0538	2.9080

Table 4. Activation and thermodynamic parameters for mild steel corrosion in 1M HCl solution with AECPL

C_{inh} in (v/v)%	E_{act} (kJ/mol)	ΔH^* (kJ/mol)	ΔS^* (J/mol/K)
0.0	**41.26**	**38.83**	**-177.64**
1.0	**43.20**	**41.39**	**-170.56**
2.0	**52.93**	**50.41**	**-143.63**
3.0	**54.91**	**52.48**	**-137.55**
5.0	**57.86**	**54.99**	**-130.48**
8.0	**60.92**	**59.20**	**-118.53**

Table5. Adsorption parameters for mild steel corrosion in 1M HCl solution with AECPL

Temperature (°C)	ΔG_{ads} (kJ/mol)	ΔH_{ads} (kJ/mol)	ΔS_{ads} (J/mol/K)
30°C	-13.76	-35.95	-73.23
40°C	-12.84		-73.83
50°C	-11.99		-74.17
60°C	-11.59		-73.15

Table 6. Mild steel corrosion rates in 1M H_2SO_4 solution in absence and presence of different concentrations of AECPL at different temperatures

C_{inh} in (v/v)%	CR x 10^{-3} (g cm^{-2} min^{-1})			
	30°C	40°C	50°C	60°C
0.0	0.64	1.55	1.73	2.88
1.0	0.57	1.48	1.63	2.66
2.0	0.51	1.41	1.55	2.59
3.0	0.46	1.32	1.44	2.51
5.0	0.40	1.22	1.37	2.43
8.0	0.31	1.15	1.29	2.30

Table7. Inhibition efficiencies of AECPL at different concentrations and temperatures in 1M H_2SO_4 solution

C_{inh} in (v/v)%	I E (%)			
	30°C	40°C	50°C	60°C
1.0	10.93	04.51	05.78	07.63
2.0	20.31	09.03	10.40	10.06
3.0	28.12	14.83	16.76	12.84
5.0	37.50	21.29	20.80	15.62
8.0	51.56	25.80	25.43	20.13

Table 8. Kinetic parameters for mild steel corrosion in 1M H_2SO_4 solution with AECPL

Temperature (°C)	Kinetic Parameters	
	B	K x 10^{-3} (gcm^{-2} min^{-1})
30°C	-0.2776	0.6055
40°C	-0.1264	1.5282
50°C	-0.1167	1.6730
60°C	-0.0671	2.7158

Table 9. Activation and thermodynamic parameters for mild steel corrosion in 1M H_2SO_4 solution with AECPL

C_{inh} in (v/v)%	E_{act} (kJ/mol)	ΔH^* (kJ/mol)	ΔS^* (J/mol/K)
0.0	**40.77**	**38.96**	**-177.95**
1.0	**42.40**	**39.88**	**-175.59**
2.0	**44.92**	**42.49**	**-167.92**
3.0	**46.08**	**43.56**	**-165.22**
5.0	**49.21**	**46.78**	**-155.72**
8.0	**55.58**	**53.27**	**-136.40**

Table10. Adsorption parameters for mild steel corrosion in 1M H_2SO_4 solution with AECPL

Temperature (°C)	ΔG_{ads} (kJ/mol)	ΔH_{ads} (kJ/mol)	ΔS_{ads} (J/mol/K)
30°C	-12.15	-69.11	-187.99
40°C	-10.27	-69.11, 19.13	-187.99, 93.93
50°C	-11.28	19.13	94.15
60°C	-12.15	19.13	93.93

Table11. Mild steel corrosion rates in 1M HCl solution in absence and presence of different concentrations of AELCL at different temperatures

C_{inh} in (v/v)%	CR x 10^{-3} (g cm^{-2} min^{-1})			
	30°C	40°C	50°C	60°C
0.0	1.00	1.50	2.16	2.70
2.0	0.61	1.10	2.00	2.60
3.0	0.50	0.83	1.90	2.57
4.0	0.33	0.66	1.80	2.54
6.0	0.11	0.50	1.70	2.40

Table12. Inhibition efficiencies of AELCL at different concentrations and temperatures in 1M HCl solution

C_{inh} in (v/v)%	I E (%)			
	30°C	40°C	50°C	60°C
2.0	40.00	26.66	07.40	03.70
3.0	50.00	44.66	12.03	04.81
4.0	70.00	56.00	16.66	05.92
6.0	90.00	66.66	21.29	11.11

Table 13. Kinetic parameters for mild steel corrosion in 1M HCl solution with AELCL

Temperature (°C)	Kinetic Parameters	
	B	K x 10^{-3} (g cm^{-2} min^{-1})
30°C	-1.5439	2.2289
40°C	-0.7379	1.8647
50°C	-0.1476	2.2496
60°C	-0.0836	2.8029

Table 14. Activation and thermodynamic parameters for mild steel corrosion in 1M HCl solution with AELCL

C_{inh} in (v/v)%	E_{act} (kJ/mol)	ΔH^* (kJ/mol)	ΔS^* (J/mol/K)
0.0	**27.48**	**24.47**	**-221.99**
2.0	**39.80**	**37.86**	**-182.12**
3.0	**44.12**	**41.60**	**-171.58**
4.0	**55.20**	**52.68**	**-138.46**
6.0	**86.12**	**84.18**	**-43.23**

Table15. Adsorption parameters for mild steel corrosion in 1 M HCl solution with AELCL

Temperature (°C)	ΔG_{ads} (kJ/mol)	ΔH_{ads} (kJ/mol)	ΔS_{ads} (J/mol/K)
30°C	-11.60	23.85	116.99
40°C	-12.77	23.85 , -89.62	116.99 , -245.53
50°C	-09.89	-89.62	-246.84
60°C	-07.85	-89.62	-245.56

Table16. Mild steel corrosion rates in 1 M H_2SO_4 solution in absence and presence of different concentrations of AELCL at different temperatures

C_{inh} in (v/v)%	CR x 10^{-3} (g cm^{-2} min^{-1})			
	30°C	40°C	50°C	60°C
0.0	0.98	1.59	2.42	2.94
2.0	0.92	1.32	2.27	2.70
3.0	0.79	1.09	2.19	2.22
4.0	0.35	0.82	1.40	1.95
6.0	0.34	0.81	1.37	1.84

Tables17. Inhibition efficiencies of AELCL at different concentrations and temperatures in 1 M H_2SO_4 solution

C_{inh} in (v/v)%	I E (%)			
	30°C	40°C	50°C	60°C
2.0	06.12	16.98	06.19	08.16
3.0	19.39	31.44	09.50	24.48
4.0	64.28	48.42	42.14	33.67
6.0	65.30	49.05	43.38	37.41

Table18. Kinetic parameters for mild steel corrosion in 1 M H_2SO_4 solution with AELCL

Temperature (°C)	Kinetic Parameters	
	B	K x 10^{-3} (g cm^{-2} min^{-1})
30°C	-1.0232	1.9592
40°C	-0.4931	1.8454
50°C	-0.5291	3.4119
60°C	-0.3591	3.4182

Table19. Activation and thermodynamic parameters for mild steel corrosion in 1M H_2SO_4 solution with AELCL

C_{inh} in (v/v)%	E_{act} (kJ/mol)	ΔH^* (kJ/mol)	ΔS^* (J/mol/K)
0.0	**29.86**	**28.05**	**-210.30**
2.0	**29.41**	**26.41**	**-216.24**
3.0	**28.90**	**25.99**	**-218.79**
4.0	**47.67**	**44.67**	**-231.28**
6.0	**46.69**	**44.18**	**-229.52**

Table20. Adsorption parameters for mild steel corrosion in 1 M H_2SO_4 solution with AELCL

Temperature (°C)	ΔG_{ads} (kJ/mol)	ΔH_{ads} (kJ/mol)	ΔS_{ads} (J/mol/K)
30°C	-05.18	20.28	84.03
40°C	-11.60		101.85
50°C	-06.42		82.66
60°C	-09.90		90.63

Table21. Mild steel corrosion rates in 1M HCl solution in absence and presence of different concentrations of AENOL at different temperatures

C_{inh} in (v/v)%	CR x 10^{-3} (g cm^{-2} min^{-1})			
	30°C	40°C	50°C	60°C
0.0	1.17	1.75	3.72	3.85
1.0	0.83	1.41	3.08	3.19
2.0	0.79	1.32	2.84	3.14
3.0	0.44	0.89	2.27	2.97
5.0	0.34	0.79	1.73	2.74
10.0	0.19	0.45	1.00	1.77

Table 22. Inhibition efficiencies of AENOL at different concentrations and temperatures in 1M HCl solution

C_{inh} in (v/v)%	I E (%)			
	30°C	40°C	50°C	60°C
1.0	29.05	19.42	17.20	17.14
2.0	32.47	24.57	23.65	18.44
3.0	62.39	49.14	38.97	22.85
5.0	70.94	54.85	53.49	28.83
10.0	83.76	74.28	73.11	54.02

Table 23. Kinetic parameters for mild steel corrosion in 1M HCl solution with AENOL

Temperature (°C)	Kinetic Parameters	
	B	K x 10^{-3} (g cm^{-2} min^{-1})
30°C	-0.6753	0.9831
40°C	-0.5013	1.6084
50°C	-0.5002	3.6132
60°C	-0.2466	3.6157

Table24. Activation and thermodynamic parameters for mild steel corrosion in 1M HCl solution with AENOL

C_{inh} in (v/v)%	E_{act} (kJ/mol)	ΔH^* (kJ/mol)	ΔS^* (J/mol/K)
0.0	**33.58**	**30.93**	**-199.27**
1.0	**38.22**	**35.79**	**-186.02**
2.0	**38.58**	**36.06**	**-185.61**
3.0	**52.37**	**49.94**	**-144.85**
5.0	**56.19**	**53.76**	**-134.45**
10.0	**60.05**	**57.66**	**-126.74**

Table 25. Adsorption parameters for mild steel corrosion in 1M HCl solution with AENOL

Temperature (°C)	ΔG_{ads} (kJ/mol)	ΔH_{ads} (kJ/mol)	ΔS_{ads} (J/mol/K)
30°C	-14.73	-27.04	-40.63
40°C	-13.97	-27.04	-41.76
50°C	-13.91	-27.04, -09.07	-40.65, 14.98
60°C	-14.06	-09.07	14.98

Table 26. Mild steel corrosion rates in 1M H_2SO_4 solution in absence and presence of different concentrations of AENOL at different temperatures

C_{inh} in (v/v)%	CR x 10^{-3} (g cm^{-2} min^{-1})			
	30°C	40°C	50°C	60°C
0.0	0.75	1.54	2.51	3.69
1.0	0.62	1.39	2.36	3.60
2.0	0.45	0.94	2.27	3.54
3.0	0.39	0.79	2.14	3.45
5.0	0.32	0.69	2.08	3.39
10.0	0.21	0.54	1.97	3.32

Table 27. Inhibition efficiencies of AENOL at different concentrations and temperatures in 1 M H_2SO_4 solution

C_{inh} in (v/v)%	I E (%)			
	30°C	40°C	50°C	60°C
1.0	17.33	09.74	05.98	02.44
2.0	40.00	38.96	09.56	04.07
3.0	48.00	48.70	14.74	06.50
5.0	57.33	55.19	17.13	08.13
10.0	72.00	64.94	21.51	10.03

Table 28. Kinetic parameters for mild steel corrosion in 1 M H_2SO_4 solution with AENOL

Temperature (°C)	Kinetic Parameters	
	B	K x 10^{-3} (g cm^{-2} min^{-1})
30°C	-0.4542	0.6266
40°C	-0.3977	1.2972
50°C	-0.0826	2.3708
60°C	-0.0414	3.6350

Table 29. Activation and thermodynamic parameters for mild steel corrosion in 1M H_2SO_4 solution with AENOL

C_{inh} in (v/v)%	E_{act} (kJ/mol)	ΔH^* (kJ/mol)	ΔS^* (J/mol/K)
0.0	43.17	40.32	-172.49
1.0	48.21	44.75	-159.45
2.0	55.97	48.03	-152.55
3.0	58.71	50.21	-146.74
5.0	63.21	54.59	-134.21
10.0	74.78	64.55	-105.03

Table 30. Adsorption parameters for mild steel corrosion in 1 M H_2SO_4 solution with AENOL

Temperature (°C)	ΔG_{ads} (kJ/mol)	ΔH_{ads} (kJ/mol)	ΔS_{ads} (J/mol/K)
30°C	-13.99	-64.62	-167.10
40°C	-13.55		-163.16
50°C	-11.38		-164.83
60°C	-09.20		-166.43

Table 31. Mild steel corrosion rates in 1M HCl solution in absence and presence of different concentrations of AEWHL at different temperatures

C_{inh} in (v/v)%	CR x 10^{-3} (g cm^{-2} min^{-1})			
	30°C	40°C	50°C	60°C
0.0	0.88	1.56	2.25	2.96
1.0	0.67	1.35	2.17	2.81
2.0	0.62	1.21	2.08	2.74
3.0	0.52	1.14	1.99	2.69
4.0	0.42	1.04	1.91	2.60
5.0	0.28	0.80	1.73	2.51

Table 32. Inhibition efficiencies of AEWHL at different concentrations and temperatures in 1M HCl solution

C_{inh} in (v/v)%	I E (%)			
	30°C	40°C	50°C	60°C
1.0	23.86	13.46	03.55	05.06
2.0	29.54	22.43	07.55	07.43
3.0	40.90	26.92	11.55	09.12
4.0	52.27	33.33	15.11	12.16
5.0	68.18	48.71	23.11	15.20

Table 33. Kinetic parameters for mild steel corrosion in 1M HCl solution with AEWHL

Temperature (°C)	Kinetic Parameters	
	B	K x 10^{-3} (g cm^{-2} min^{-1})
30°C	-0.4885	0.7675
40°C	-0.2762	1.4217
50°C	-0.1301	2.2387
60°C	-0.0651	2.8510

Table 34. Activation and thermodynamic parameters for mild steel corrosion in 1M HCl solution with AEWHL

C_{inh} in (v/v)%	E_{act} (kJ/mol)	ΔH^* (kJ/mol)	ΔS^* (J /K/mol)
0.0	**33.69**	**31.01**	**-200.82**
1.0	**39.92**	**38.01**	**-179.88**
2.0	**42.17**	**39.50**	**-175.67**
3.0	**45.69**	**43.78**	**-162.88**
4.0	**51.33**	**48.27**	**-149.57**
5.0	**61.51**	**58.84**	**-117.92**

Table 35. Adsorption parameters for mild steel corrosion in 1M HCl solution with AEWHL

Temperature (°C)	**ΔG_{ads} (kJ/mol)**	**ΔH_{ads} (kJ/mol)**	**ΔS_{ads} (J/K /mol)**
30°C	**-13.91**	**-79.90**	**-217.79**
40°C	**-12.92**	**-79.90**	**-213.99**
50°C	**-09.58**	**-79.90 , 31.76**	**-217.71 , 127.99**
60°C	**-10.86**	**31.76**	**127.99**

Table 36. Mild steel corrosion rates in 1M H_2SO_4 solution in absence and presence of different concentrations of AEWHL at different temperatures

C_{inh} in (v/v)%	CR x 10^{-3} (g cm^{-2} min^{-1})			
	30°C	40°C	50°C	60°C
0.0	0.71	1.43	2.14	2.77
1.0	0.62	1.29	1.87	2.25
2.0	0.58	1.19	1.73	2.21
3.0	0.41	1.03	1.64	2.09
4.0	0.34	0.79	1.47	1.90
5.0	0.25	0.62	1.36	1.73

Table 37. Inhibition efficiencies of AEWHL at different concentrations and temperatures in 1M H_2SO_4 solution

C_{inh} in (v/v)%	I E (%)			
	30°C	40°C	50°C	60°C
1.0	12.67	09.79	12.61	18.77
2.0	18.30	16.78	19.15	20.21
3.0	42.25	27.97	23.36	24.54
4.0	52.11	44.75	31.30	31.40
5.0	64.78	56.64	36.44	37.54

Table 38. Kinetic parameters for mild steel corrosion in 1M H_2SO_4 solution with AEWHL

Temperature (°C)	Kinetic Parameters	
	B	K x 10^{-3} (g cm^{-2} min^{-1})
30°C	-0.5555	0.7194
40°C	-0.4369	1.4645
50°C	-0.1943	1.9534
60°C	-0.1627	2.3966

Table 39. Activation and thermodynamic parameters for mild steel corrosion in 1M H_2SO_4 solution with AEWHL

C_{inh} in (v/v)%	E_{act} (kJ/mol)	ΔH^* (kJ/mol)	ΔS^* (J/mol/K)
0.0	**37.63**	**34.95**	**-189.31**
1.0	**35.62**	**32.35**	**-198.63**
2.0	**36.69**	**34.22**	**-193.32**
3.0	**45.08**	**42.61**	**-168.13**
4.0	**48.06**	**46.15**	**-158.40**
5.0	**55.22**	**52.51**	**-139.87**

Table40. Adsorption parameters for mild steel corrosion in 1 M H_2SO_4 solution with AEWHL

Temperature (°C)	ΔG_{ads} (kJ/mol)	ΔH_{ads} (kJ/mol)	ΔS_{ads} (J/mol/K)
30°C	-12.00	-13.52	-05.02
40°C	-11.95	-13.52, 31.44	-05.02, 138.63
50°C	-13.22	31.44	138.27
60°C	-14.72	31.44	138.62

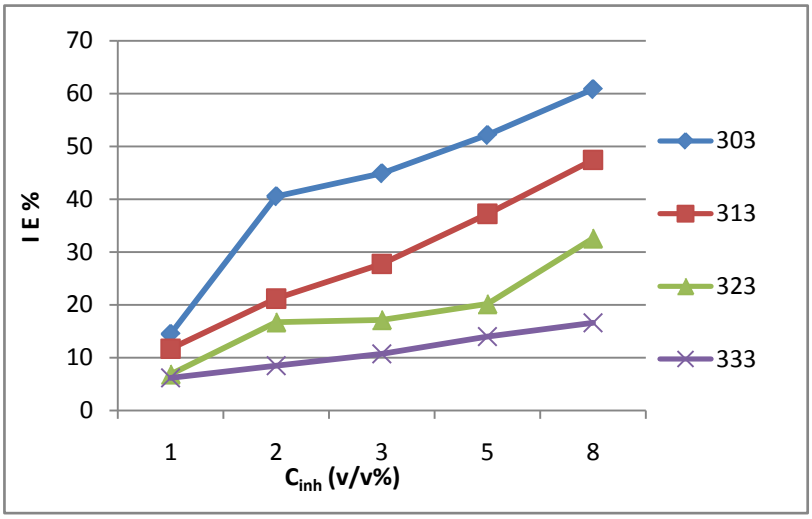

Figure 1. Variation in IE % for mild steel corrosion in 1M HCl at different concentrations of AECPL at different studied temperatures

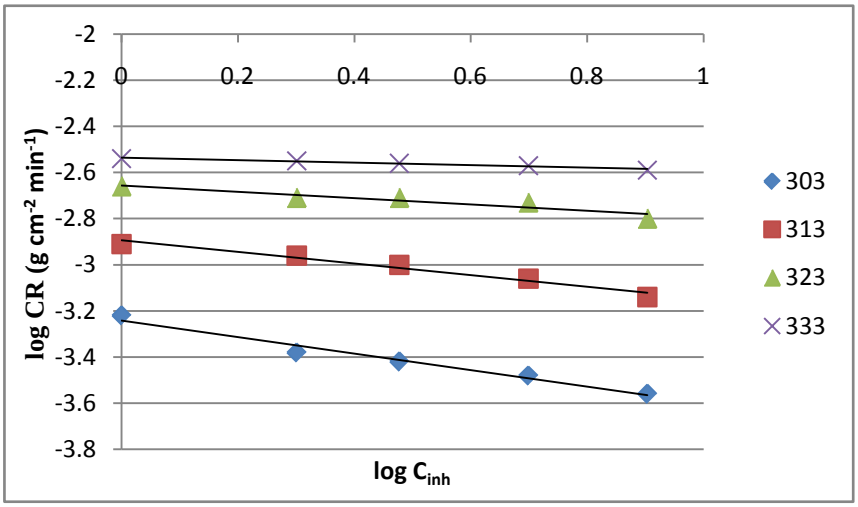

Figure 2. Variation of log CR with log C_{inh} for mild steel corrosion in 1M HCl in presence of different concentrations of AECPL at various studied temperatures

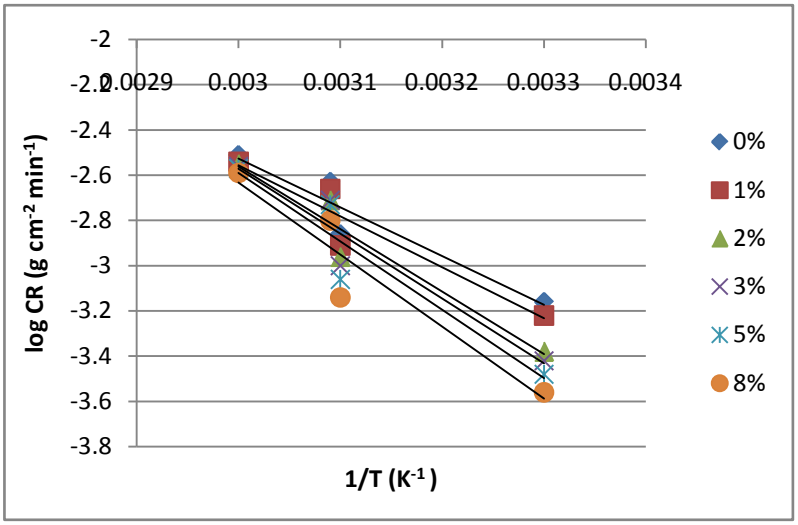

Figure 3. Arrhenius plots for mild steel corrosion in 1M HCl in absence and presence of various concentrations of AECPL

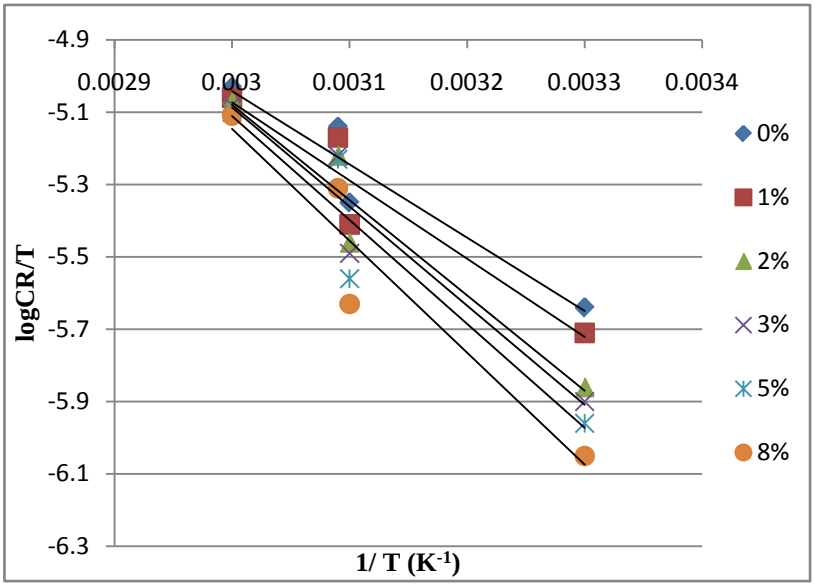

Figure 4. Transition-state plots for mild steel corrosion in 1M HCl in absence and presence of various concentrations of AECPL

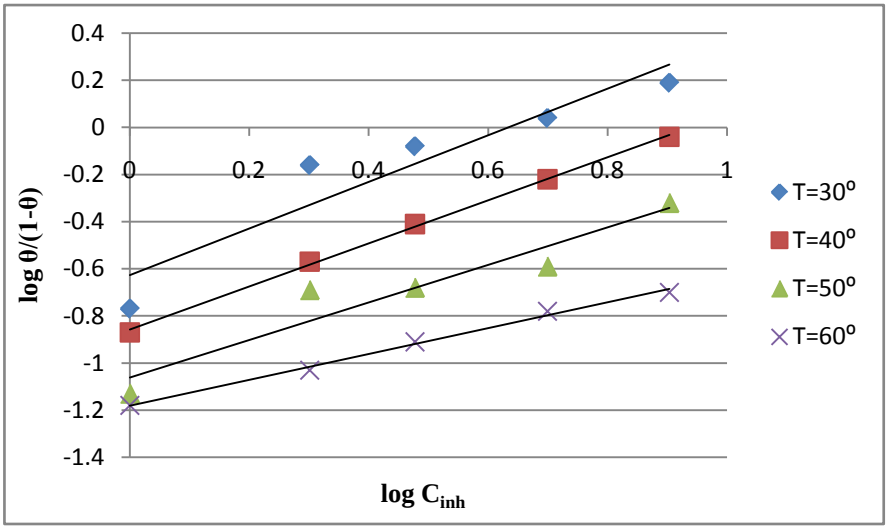

Figure 5. Langmuir adsorption isotherms of AECPL on mild steel surface in 1M HCl at different studied temperatures

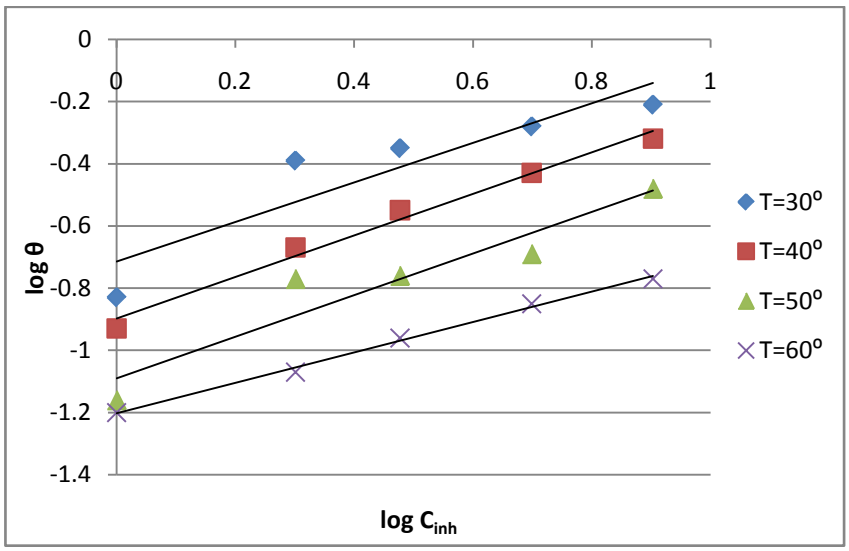

Figure 6. Freundlich adsorption isotherms of AECPL on mild steel surface in 1M HCl at different studied temperatures

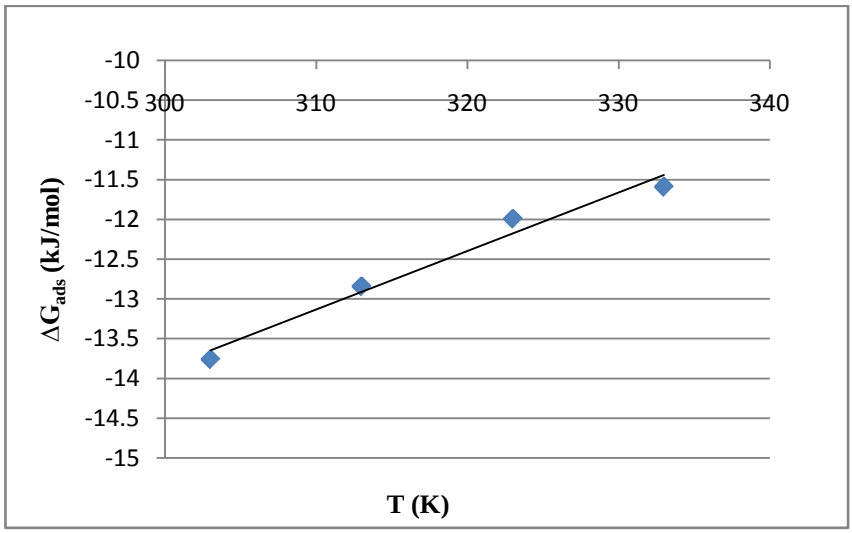

Figure 7. The variation of ΔG_{ads} (kJ/mol) with T (K) for mild steel corrosion in 1M HCl solution with AECPL

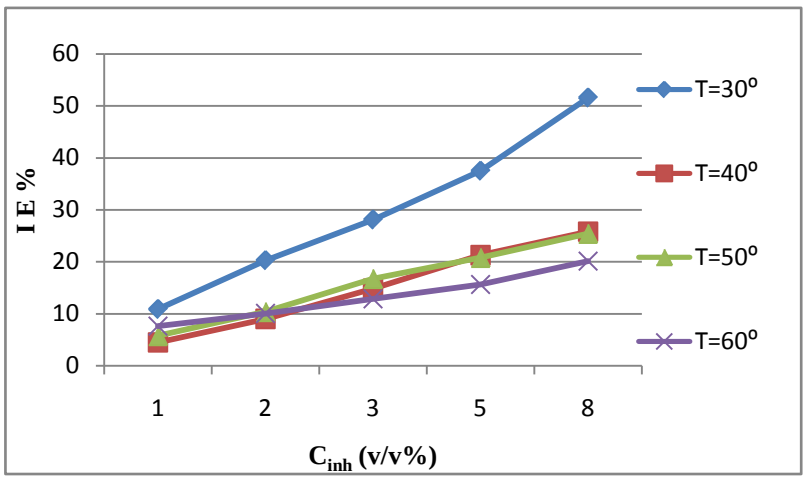

Figure 8. Variation in IE % for mild steel corrosion in 1M H_2SO_4 at different concentrations of AECPL at different studied temperatures

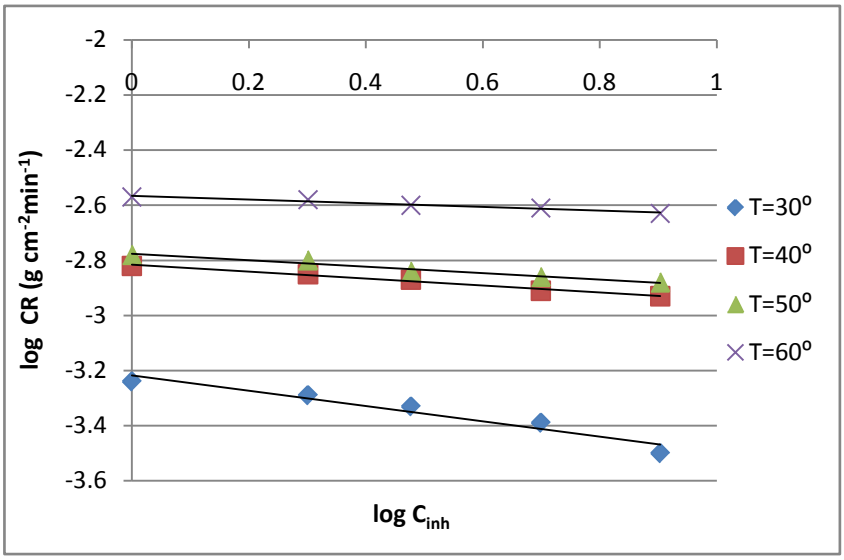

Figure 9. Variation of logCR with $logC_{inh}$ for mild steel corrosion in 1M H_2SO_4 in presence of different concentrations of AECPL at various studied temperatures

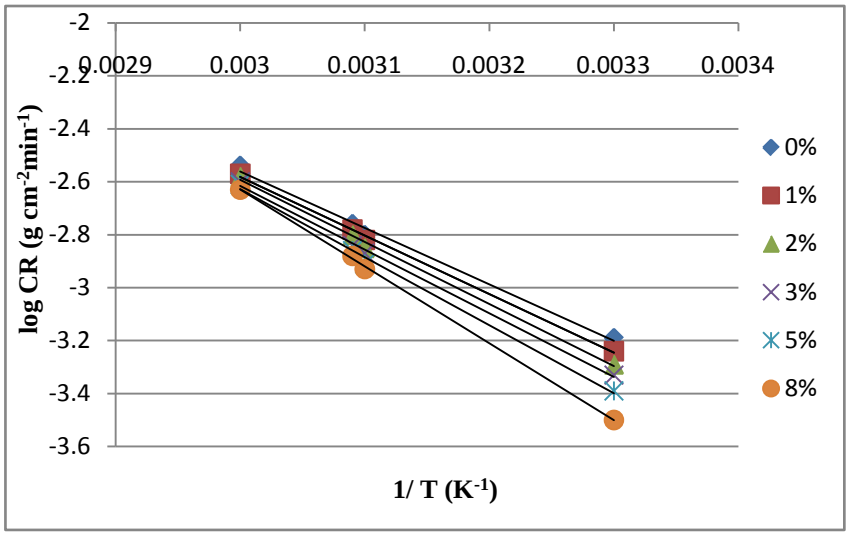

Figure10. Arrhenius plots for mild steel corrosion in 1M H_2SO_4 in absence and presence of various concentrations of AECPL

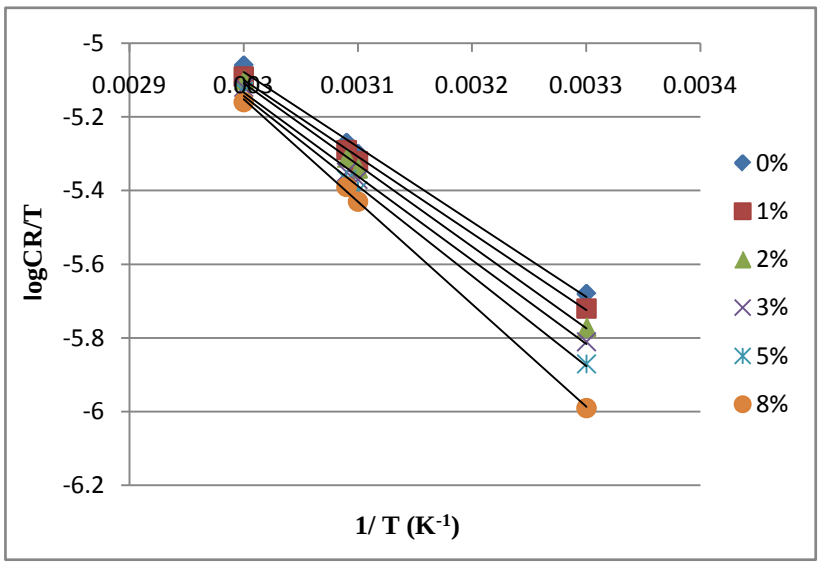

Figure 11. Transition-state plots for mild steel corrosion in 1M H_2SO_4 in absence and presence of various concentrations of AECPL

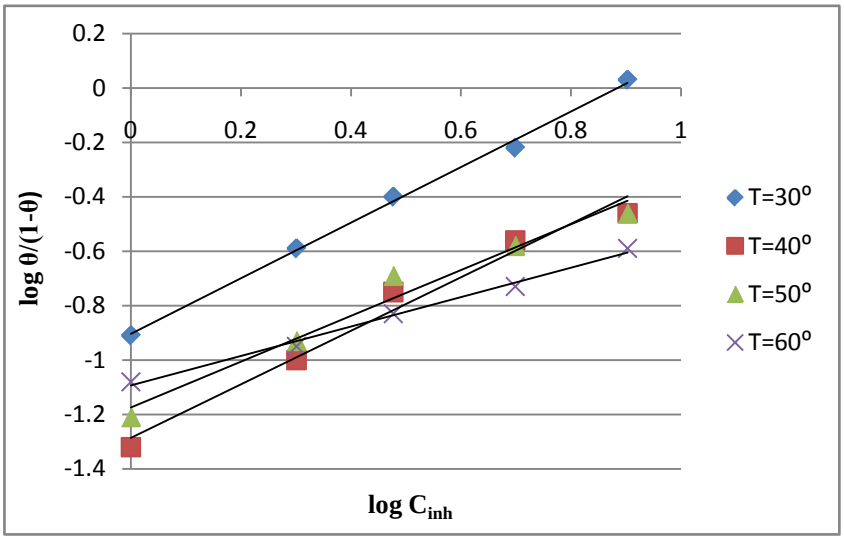

Figure 12. Langmuir adsorption isotherms of AECPL on mild steel surface in 1M H_2SO_4 at different studied temperatures

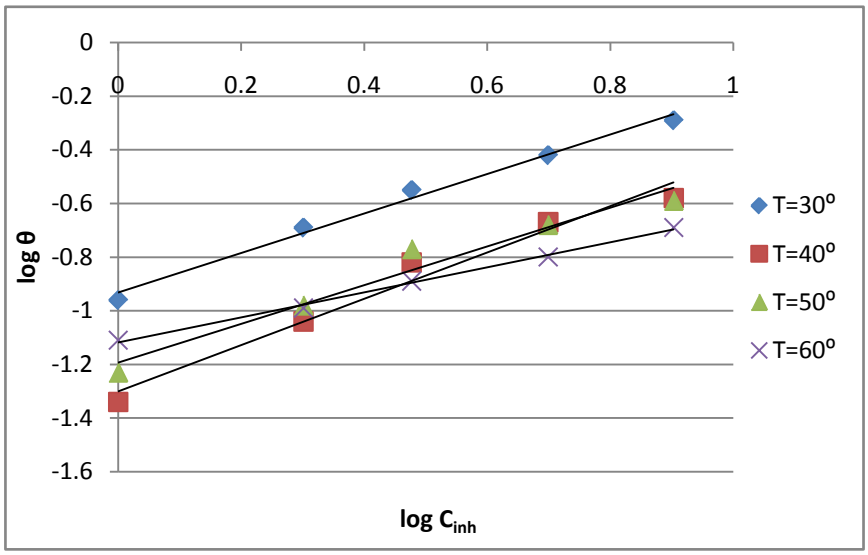

Figure 13. Freundlich adsorption isotherms of AECPL on mild steel surface in 1M H_2SO_4 at different studied temperature

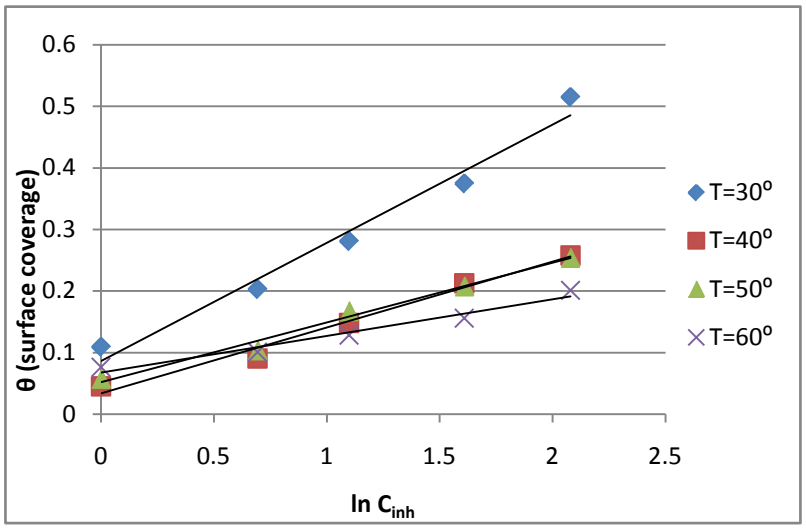

Figure 14. Temkin adsorption isotherms of AECPL on mild steel surface in 1M H_2SO_4 at different studied temperatures

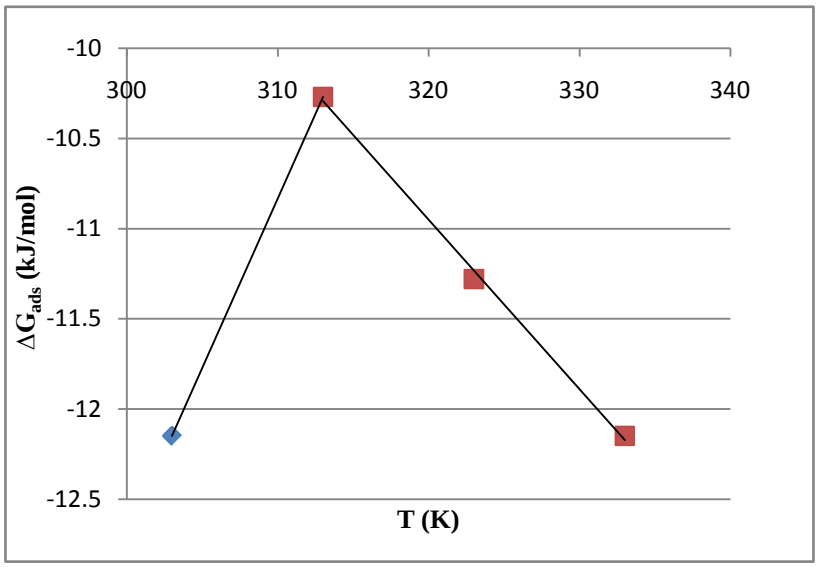

Figure 15. The variation of ΔG_{ads} (kJ/mol) with T (K) for mild steel corrosion in 1M H_2SO_4 solution with AECPL

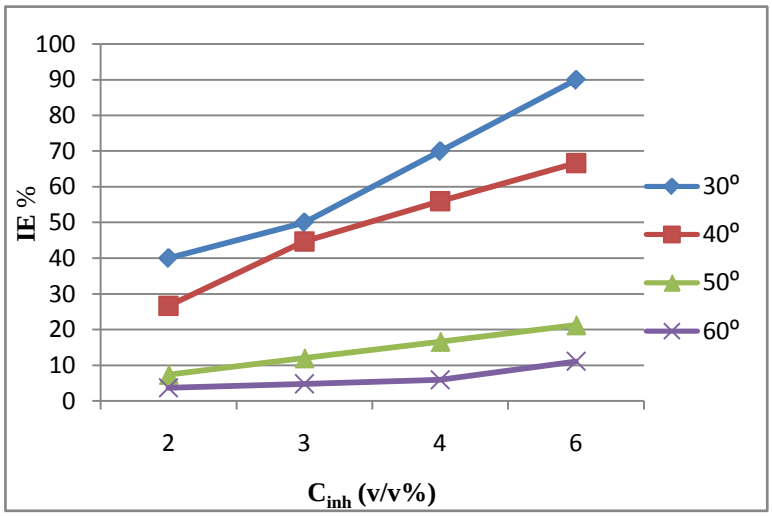

Figure 16. Variation in IE % for mild steel corrosion in 1M HCl at different concentrations of AELCL at different studied temperatures

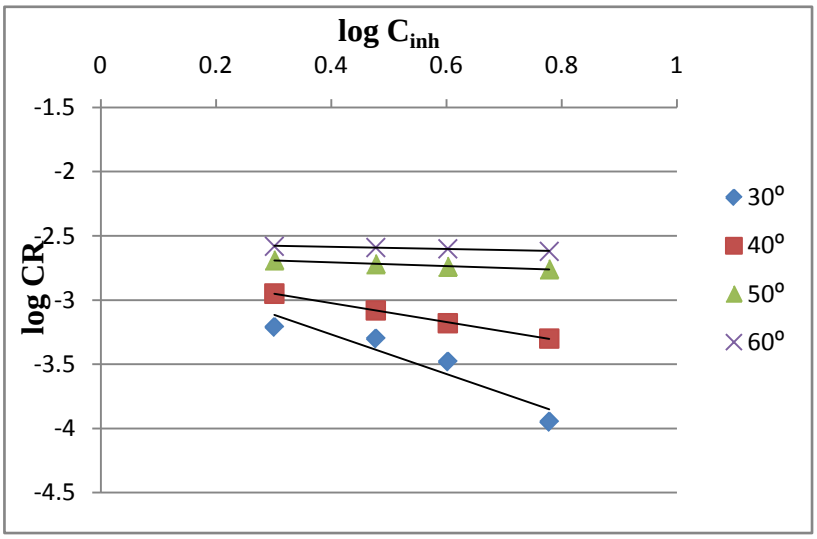

Figure 17. Variation of logCR with log C_{inh} for mild steel corrosion in 1 M HCl in presence of different concentrations of AELCL at various studied temperatures

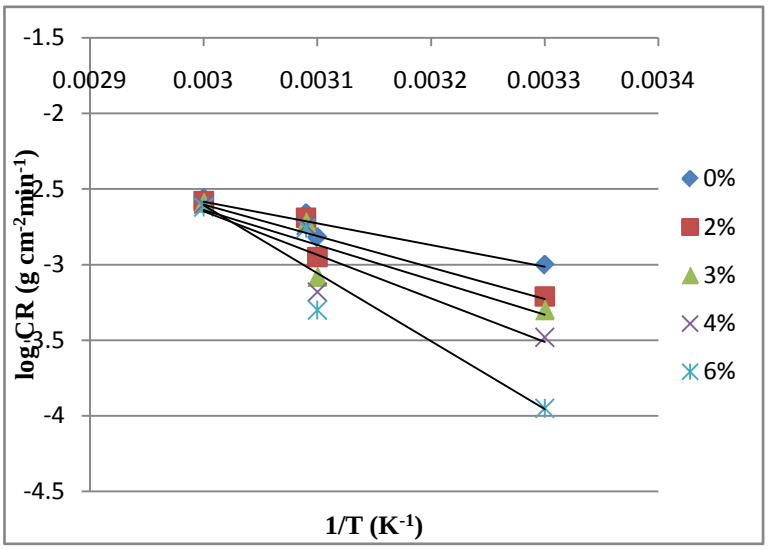

Figure 18. Arrhenius plots for mild steel corrosion in 1M HCl in absence and presence of various concentrations of AELCL

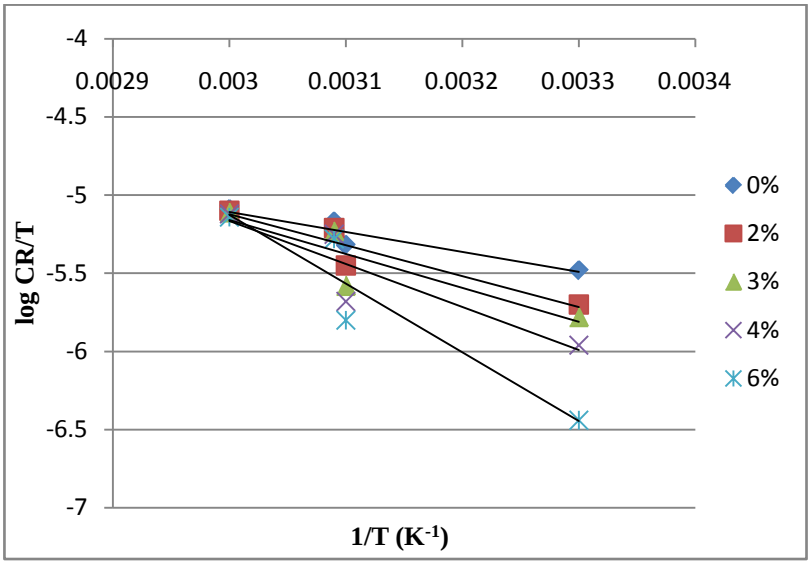

Figure 19. Transition-state plots for mild steel corrosion in 1M HCl in absence and presence of various concentrations of AELCL

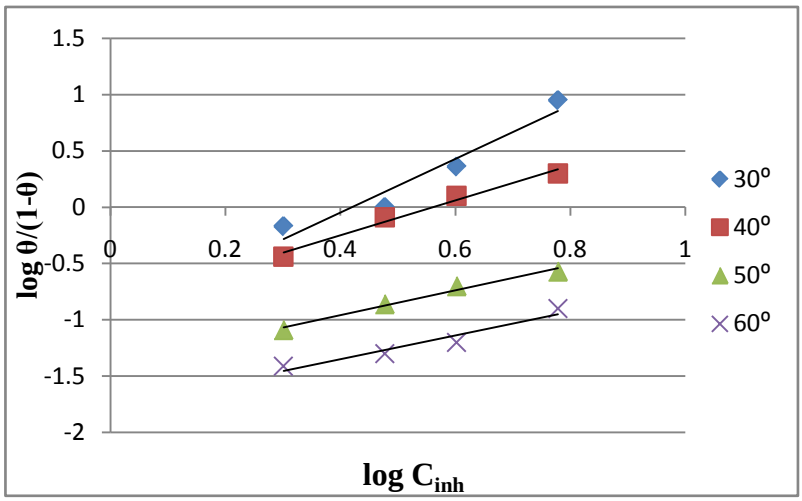

Figure 20. Langmuir adsorption isotherms of AELCL on mild steel surface in 1M HCl at different studied temperatures

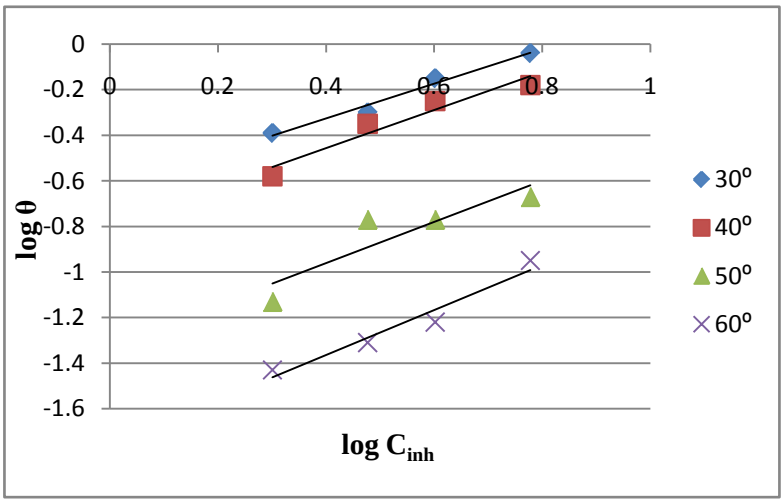

Figure 21. Freundlich adsorption isotherms of AELCL on mild steel surface in 1M HCl at different studied temperatures

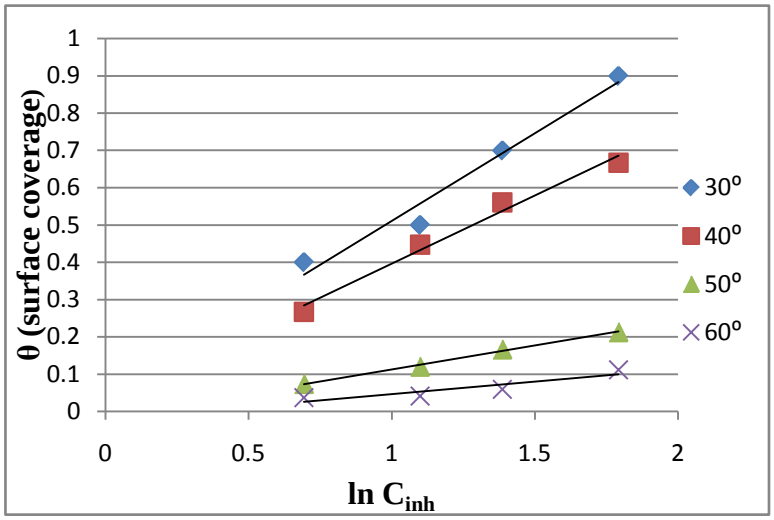

Figure 22. Temkin adsorption isotherms of AELCL on mild steel surface in 1M HCl at different studied temperatures

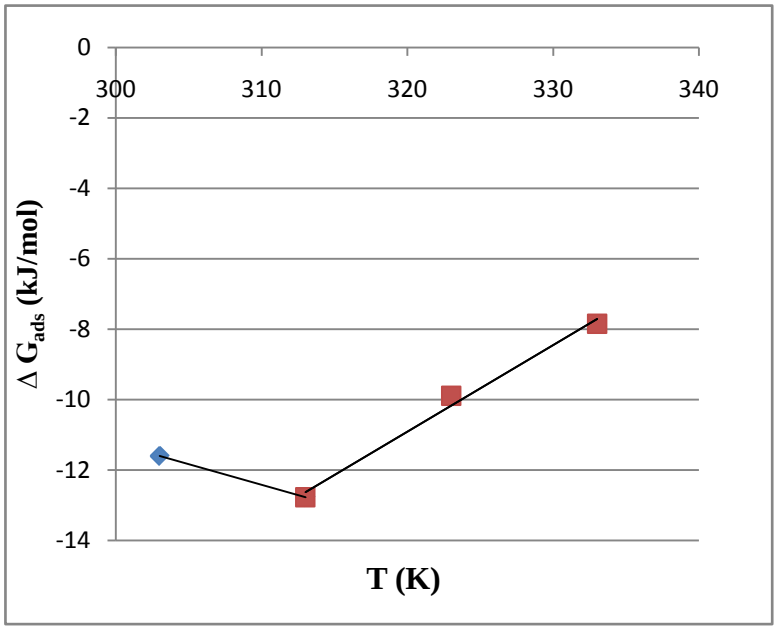

Figure 23. The variation of ΔG_{ads} (kJ/mol) with T (K) for mild steel corrosion in 1M HCl solution with AELCL

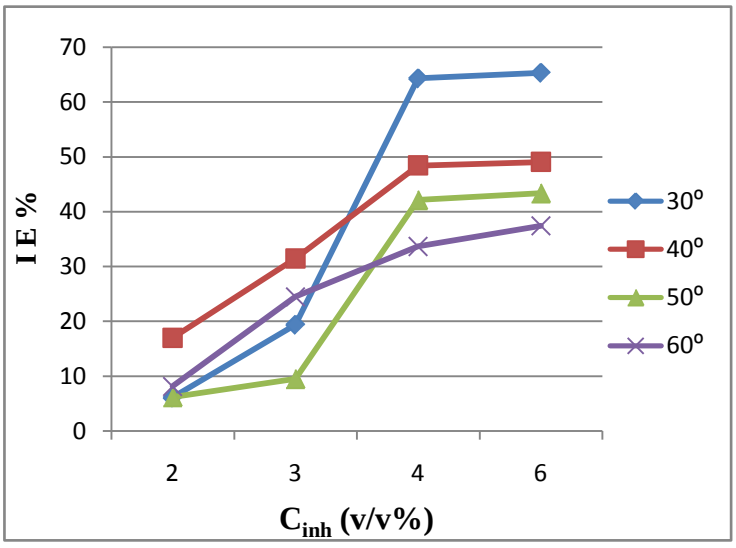

Figure 24. Variation in IE % for mild steel corrosion in 1M H_2SO_4 at different concentrations of AELCL at different studied temperatures

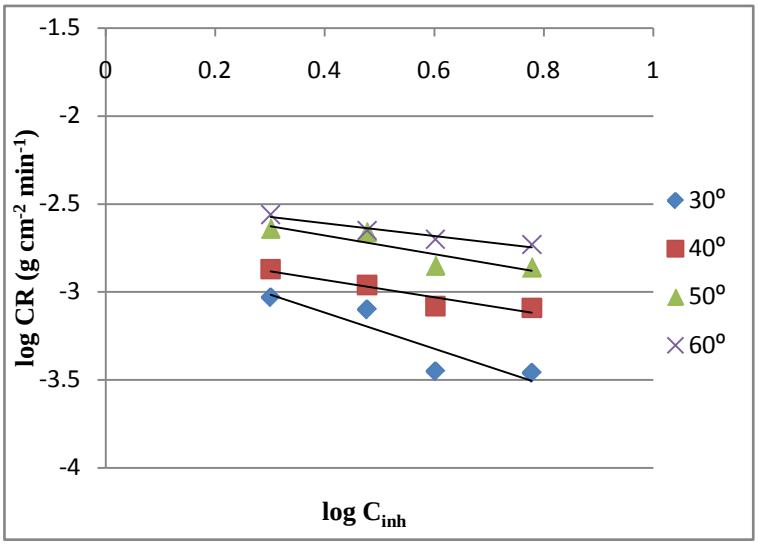

Figure 25. Variation of logCR with $logC_{inh}$ for mild steel corrosion in 1M H_2SO_4 in presence of different concentrations of AELCL at various studied temperatures

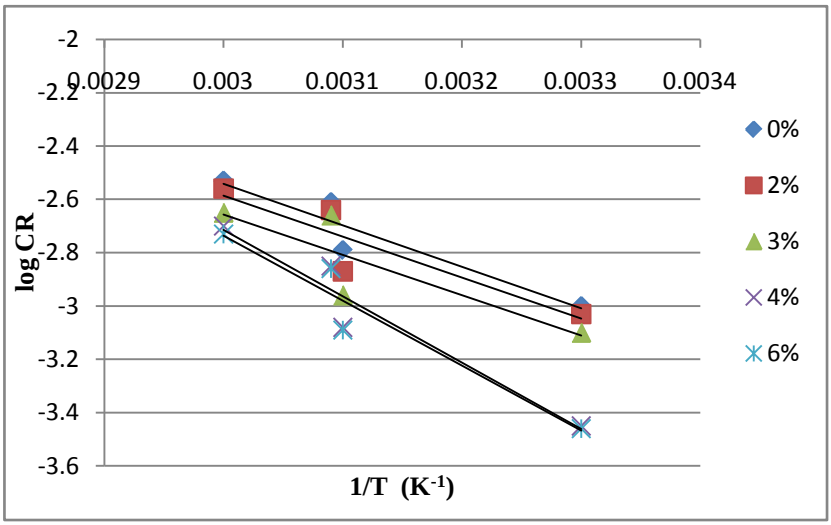

Figure 26. Arrhenius plots for mild steel corrosion in 1M H_2SO_4 in absence and presence of various concentrations of AELCL

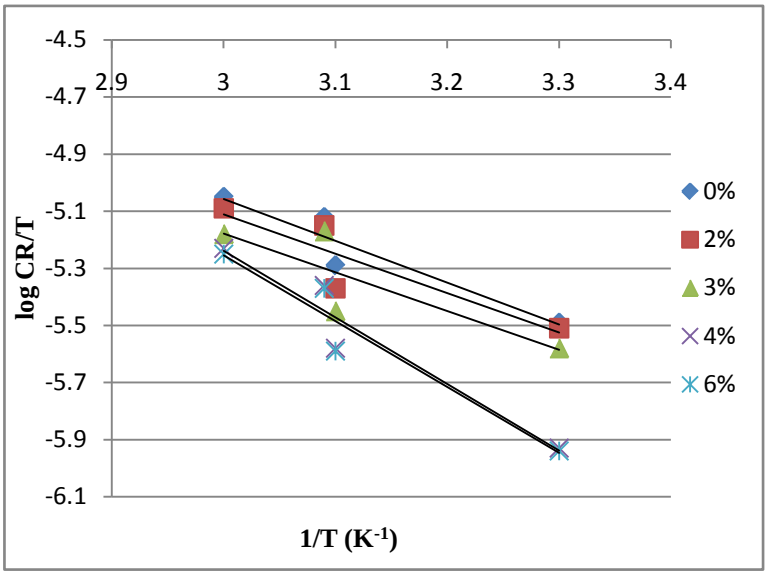

Figure 27. Transition-state plots for mild steel corrosion in 1M H_2SO_4 in absence and presence of various concentrations of AELCL

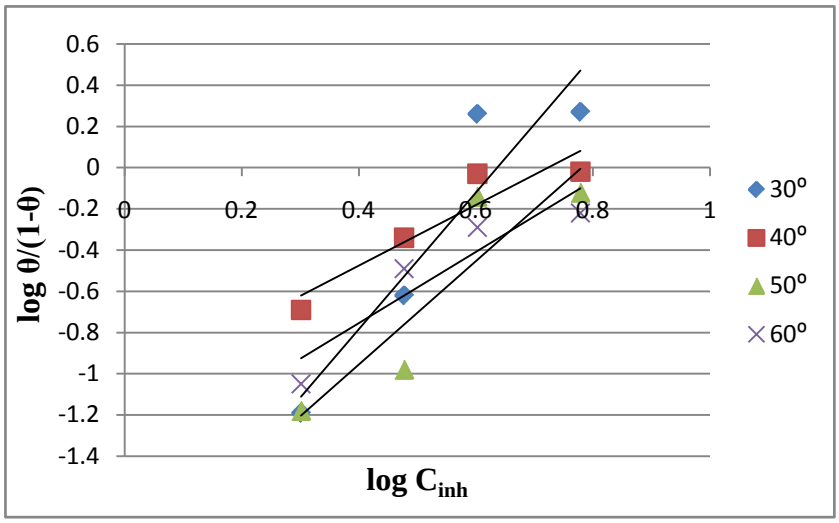

Figure 28. Langmuir adsorption isotherms of AELCL on mild steel surface in 1M H_2SO_4 at different studied temperatures

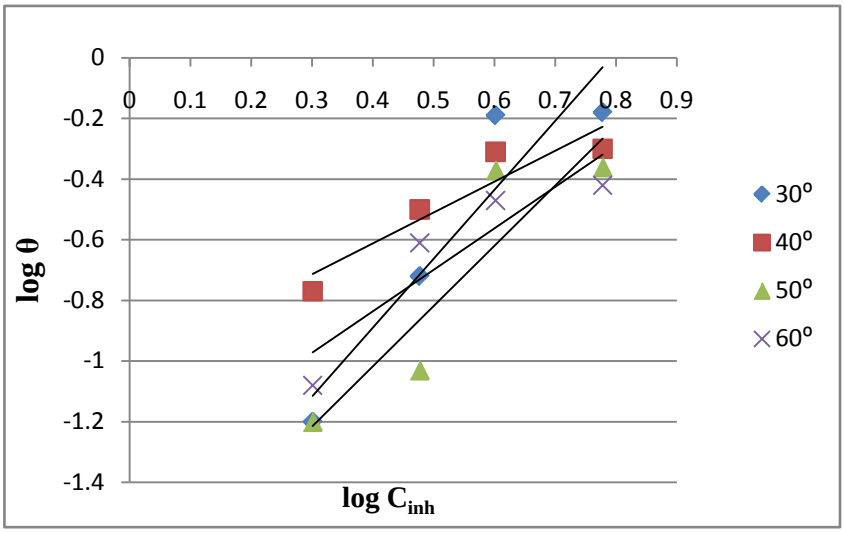

Figure 29. Freundlich adsorption isotherms of AELCL on mild steel surface in 1M H_2SO_4 at different studied temperatures

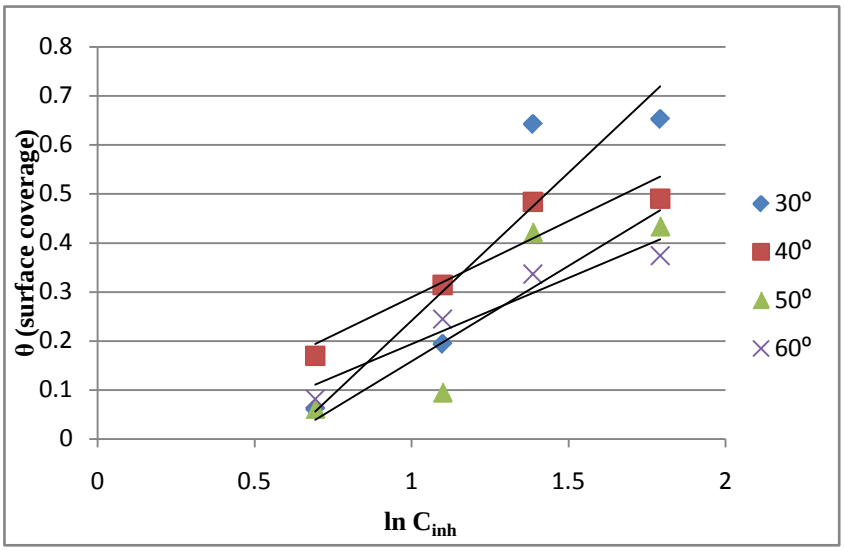

Figure 30. Temkin adsorption isotherms of AELCL on mild steel surface in 1M H_2SO_4 at different studied temperatures

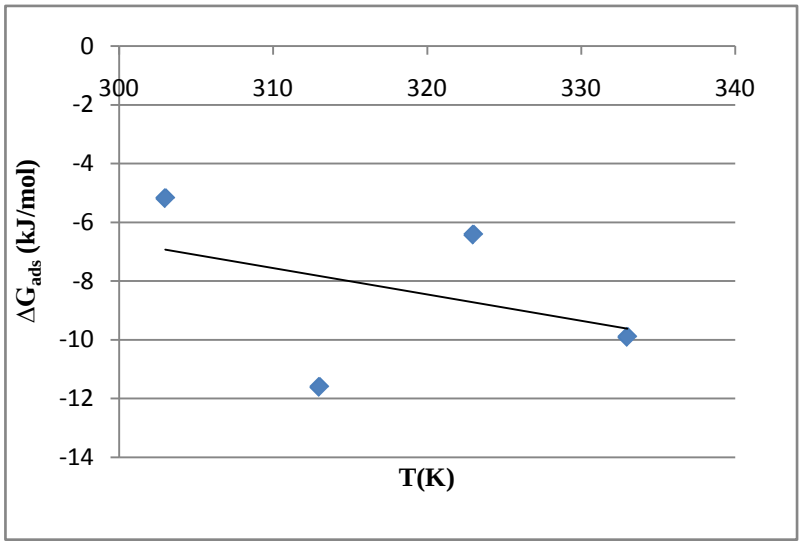

Figure 31. The variation of ΔG_{ads} (kJ/mol) with T (K) for mild steel corrosion in 1M H_2SO_4 solution with AELCL

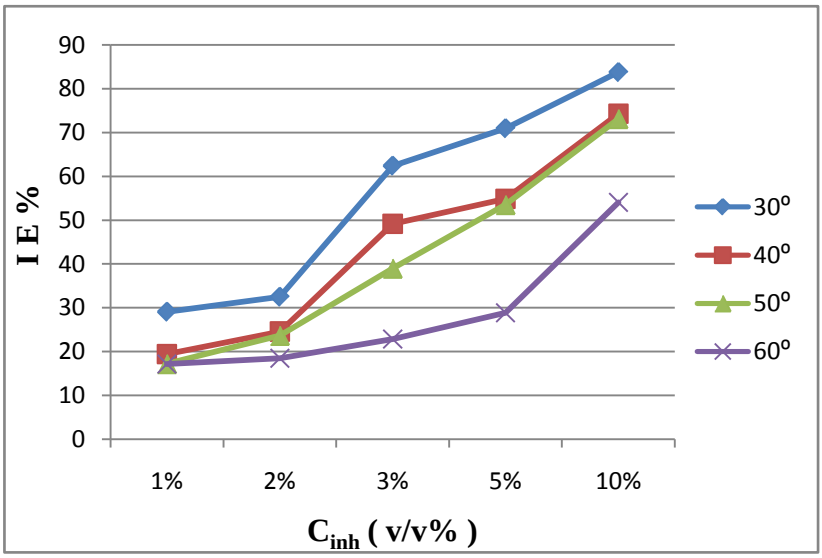

Figure32. Variation in IE % for mild steel corrosion in 1M HCl at different concentrations of AENOL at different studied temperatures

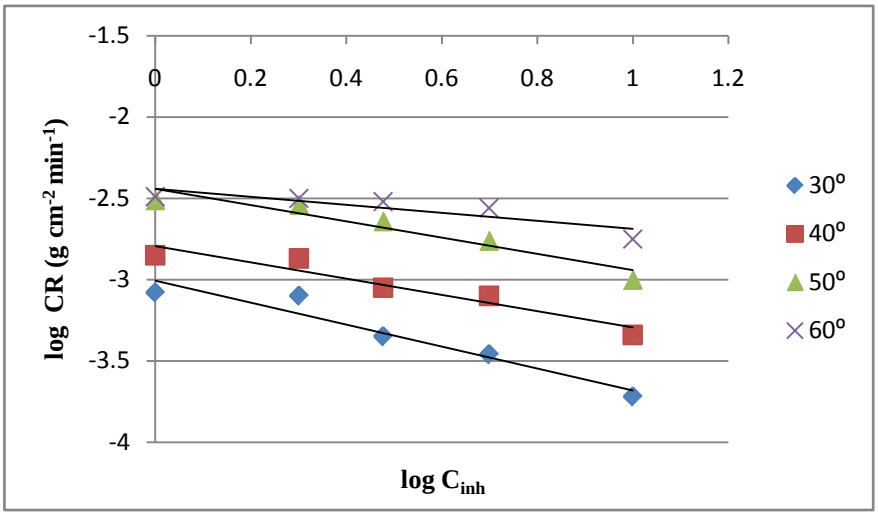

Figure 33. Variation of logCR with $logC_{inh}$ for mild steel corrosion in 1M HCl in presence of different concentrations of AENOL at various studied temperatures

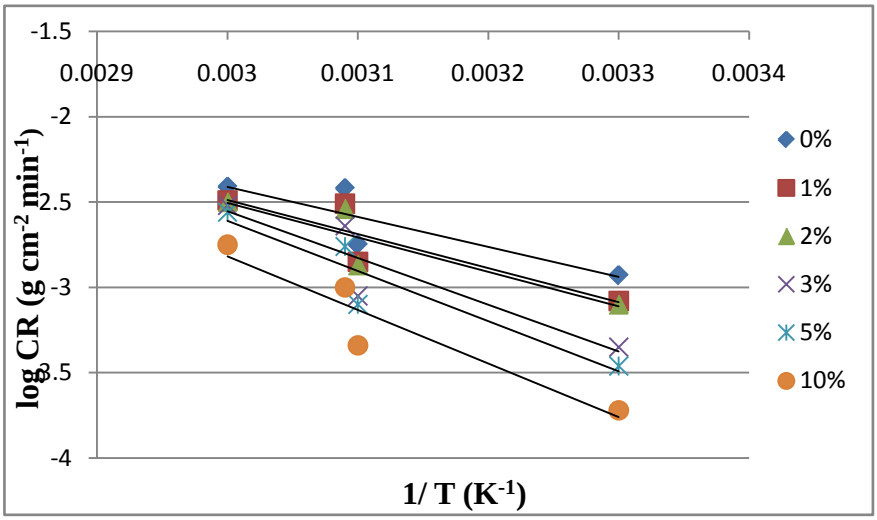

Figure 34. Arrhenius plots for mild steel corrosion in 1M HCl in absence and presence of various concentrations of AENOL

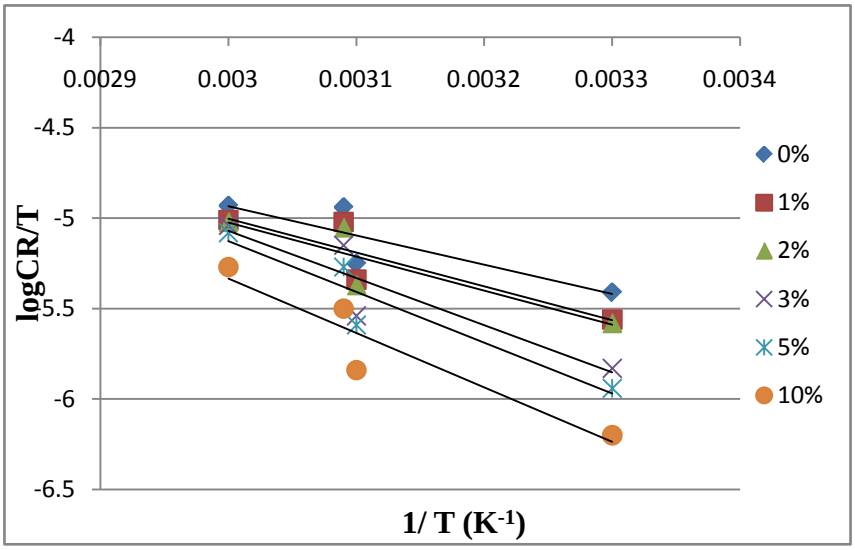

Figure 35. Transition-state plots for mild steel corrosion in 1M HCl in absence and presence of various concentrations of AENOL

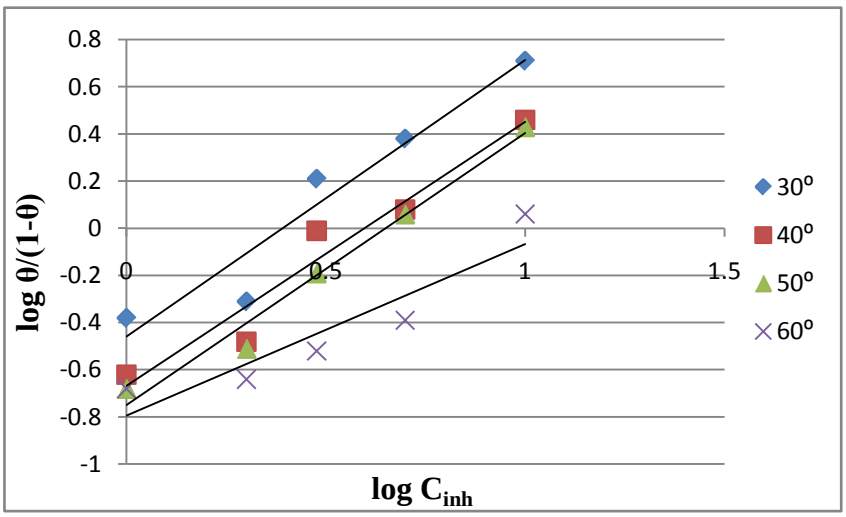

Figure 36. Langmuir adsorption isotherms of AENOL on mild steel surface in 1M HCl at different studied temperatures

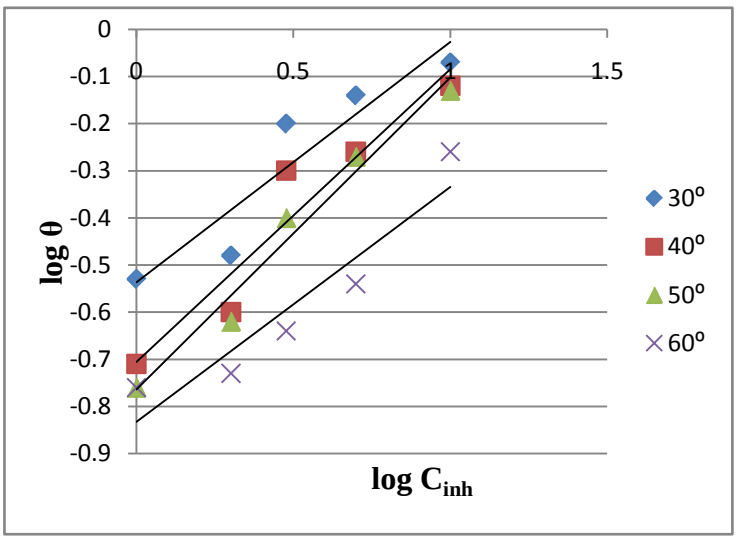

Figure37. Freundlich adsorption isotherms of AENOL on mild steel surface in 1M HCl at different studied temperatures

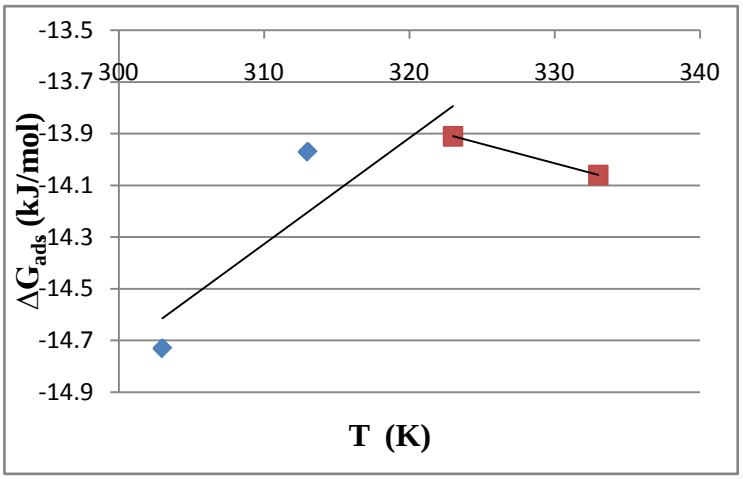

Figure 38. The variation of ΔG_{ads} (kJ/mol) with T (K) for mild steel corrosion in 1M HCl solution with AENOL

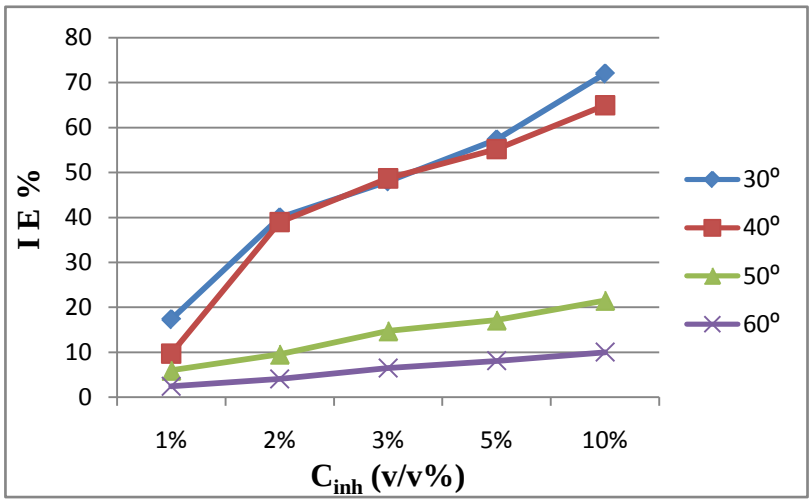

Figure 39. Variation in IE% for mild steel corrosion in 1M H_2SO_4 at different concentrations of AENOL at different studied temperatures

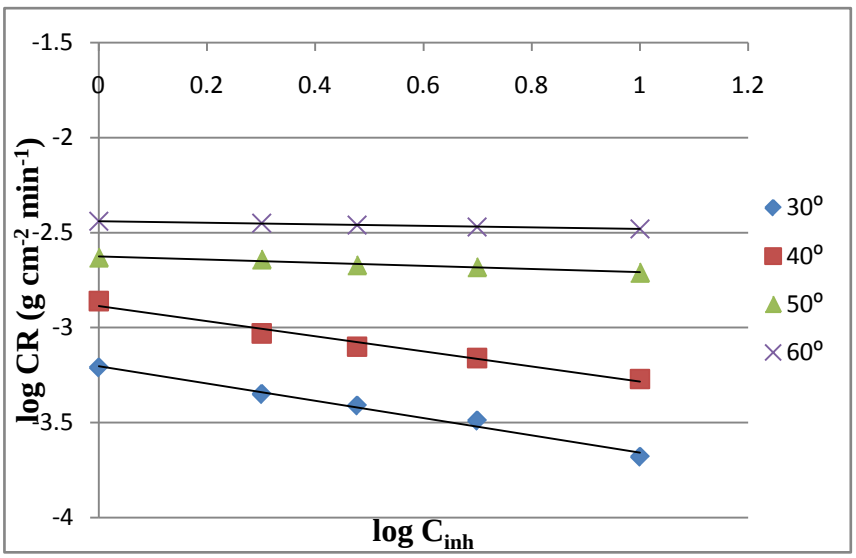

Figure 40. Variation of logCR with logC_{inh} for mild steel corrosion in 1M H_2SO_4 in presence of different concentrations of AENOL at various studied temperatures

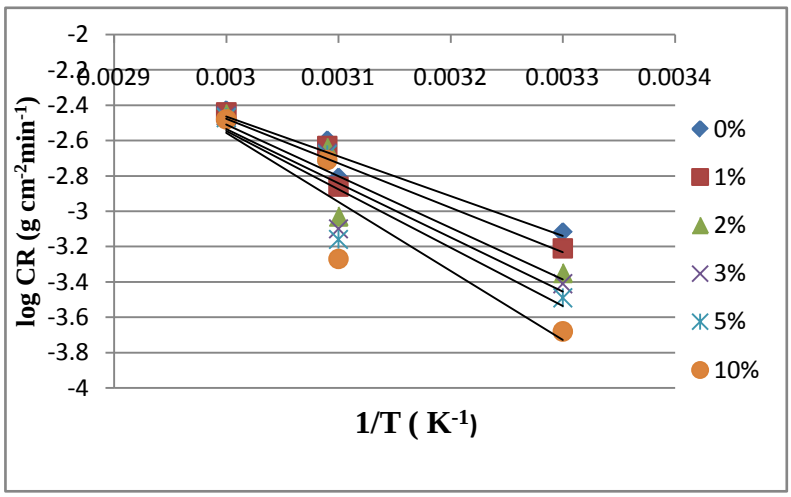

Figure 41. Arrhenius plots for mild steel corrosion in 1M H_2SO_4 in absence and presence of various concentrations of AENOL

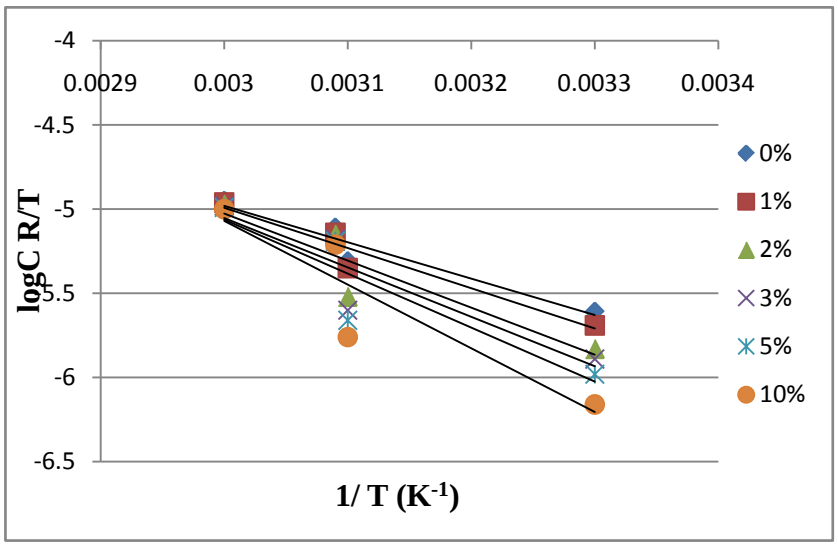

Figure 42. Transition-state plots for mild steel corrosion in 1M H_2SO_4 in absence and presence of various concentrations of AENOL

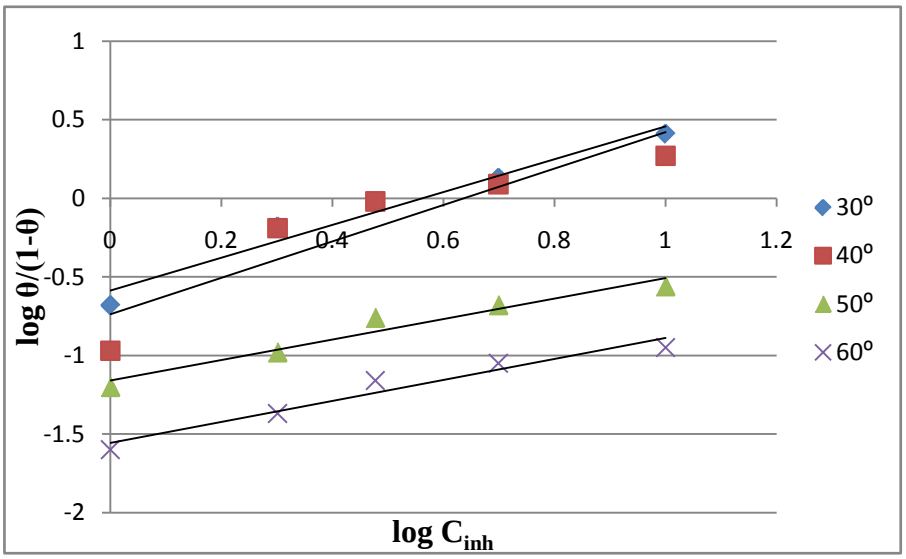

Figure 43. Langmuir adsorption isotherms of AENOL on mild steel surface in 1M H_2SO_4 at different studied temperatures

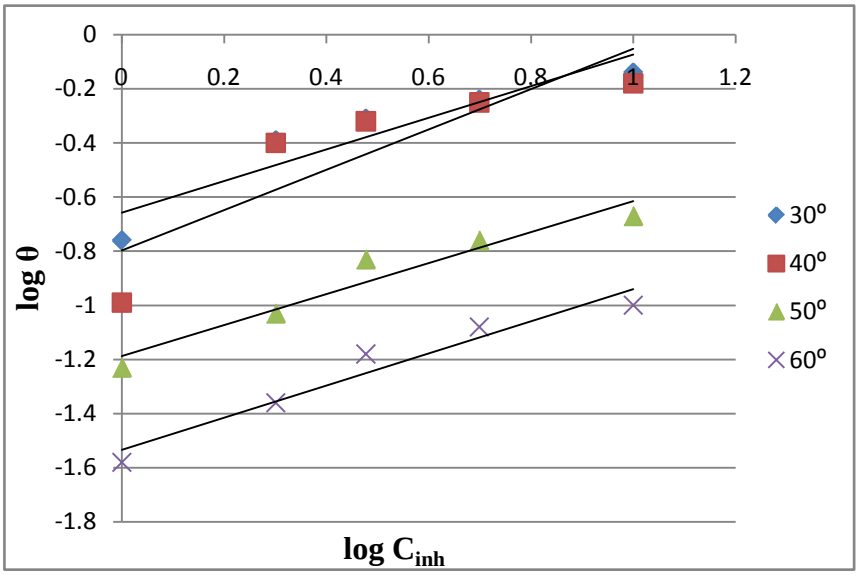

Figure 44. Freundlich adsorption isotherms of AENOL on mild steel surface in 1M H_2SO_4 at different studied temperatures

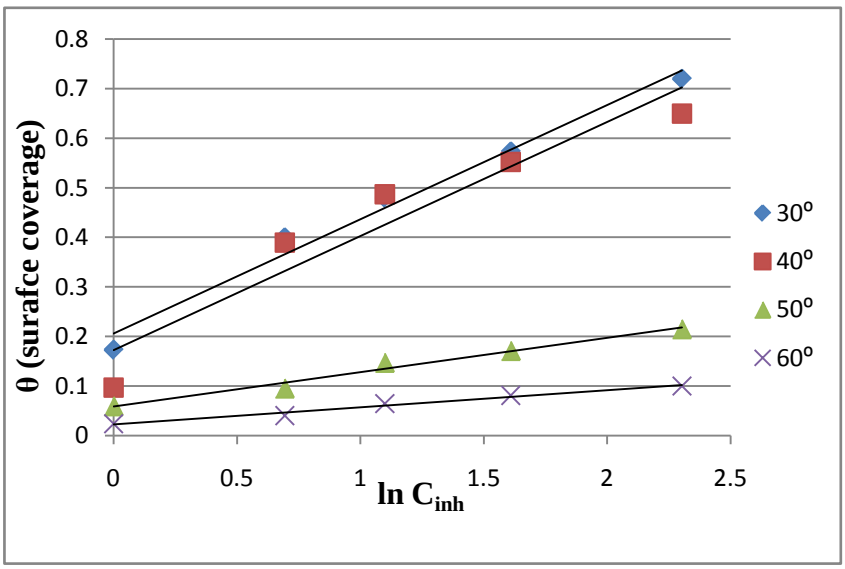

Figure 45. Temkin adsorption isotherms of AENOL on mild steel surface in 1M H_2SO_4 at different studied temperatures

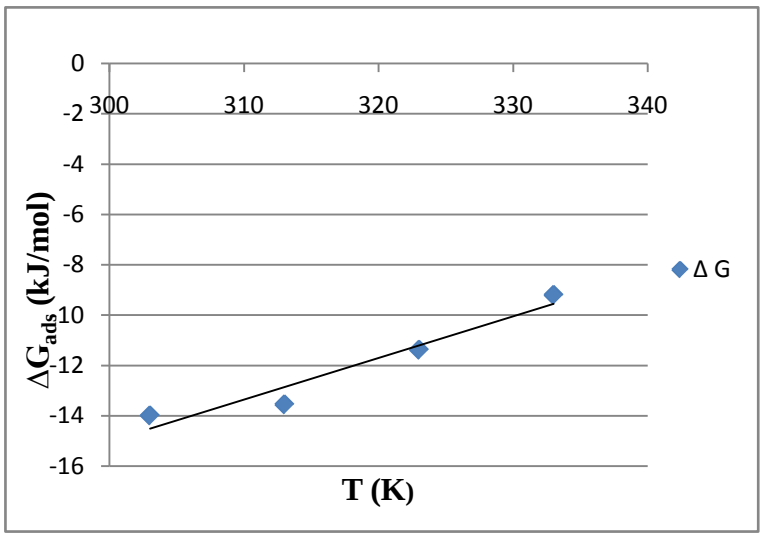

Figure 46. The variation of ΔG_{ads} (kJ/mol) with T (K) for mild steel corrosion in 1M H_2SO_4 solution with AENOL

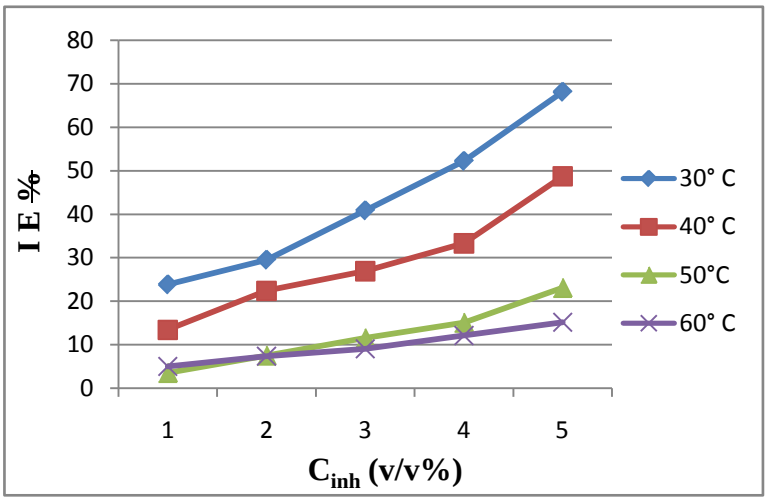

Figure 47.Variation in IE% for mild steel corrosion in 1M HCl at different concentrations of AEWHL at different studied temperatures

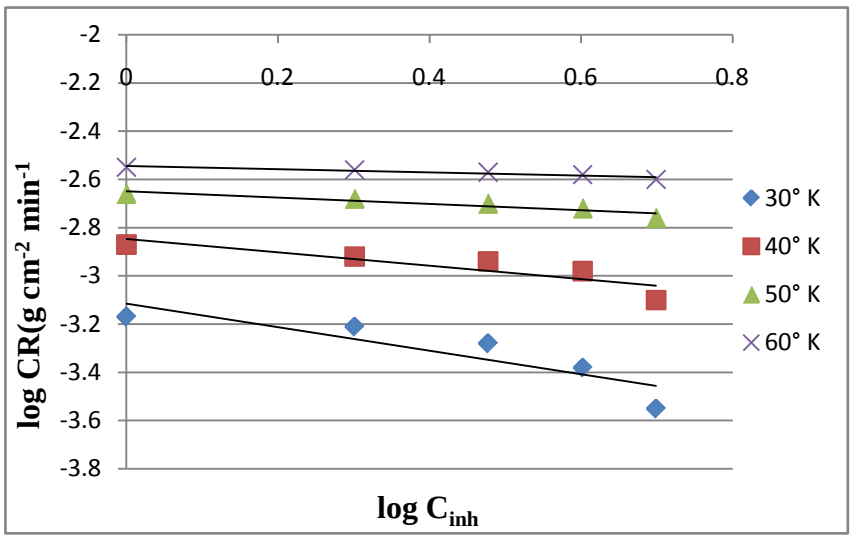

Figure 48. Variation of logCR with $logC_{inh}$ for mild steel corrosion in 1M HCl in presence of different concentrations of AEWHL at various studied temperatures

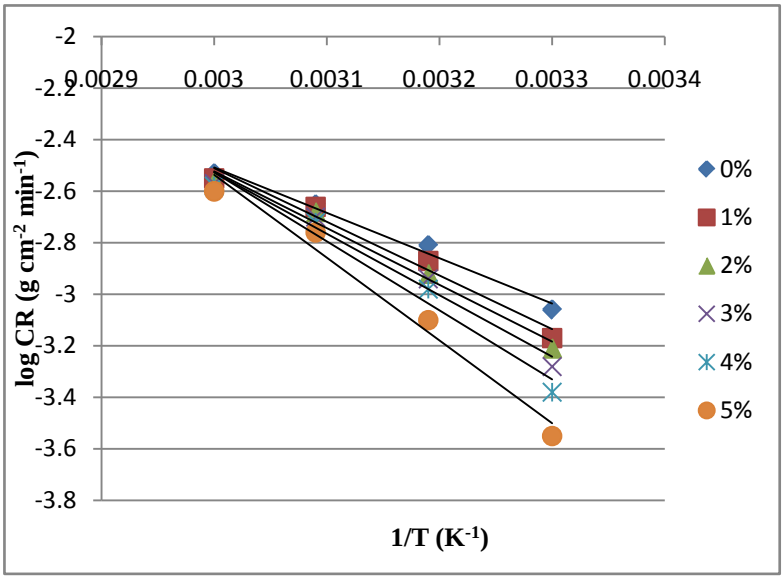

Figure 49. Arrhenius plots for mild steel corrosion in 1M HCl in absence and presence of various concentrations of AEWHL

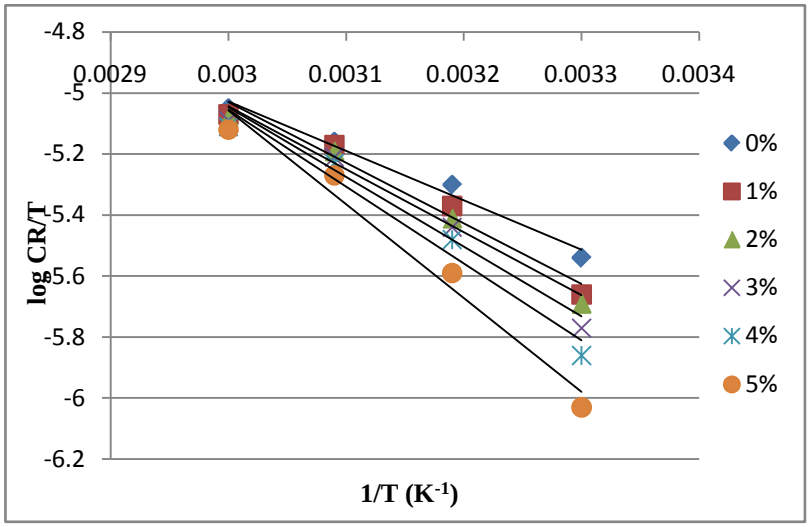

Figure 50. Transition-state plots for mild steel corrosion in 1M HCl in absence and presence of various concentrations of AEWHL

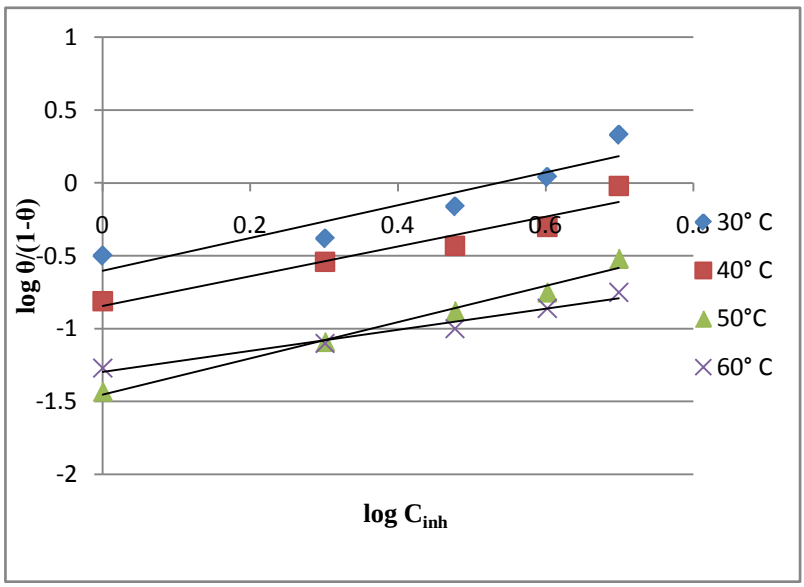

Figure 51. Langmuir adsorption isotherms of AEWHL on mild steel surface in 1M HCl at different studied temperatures

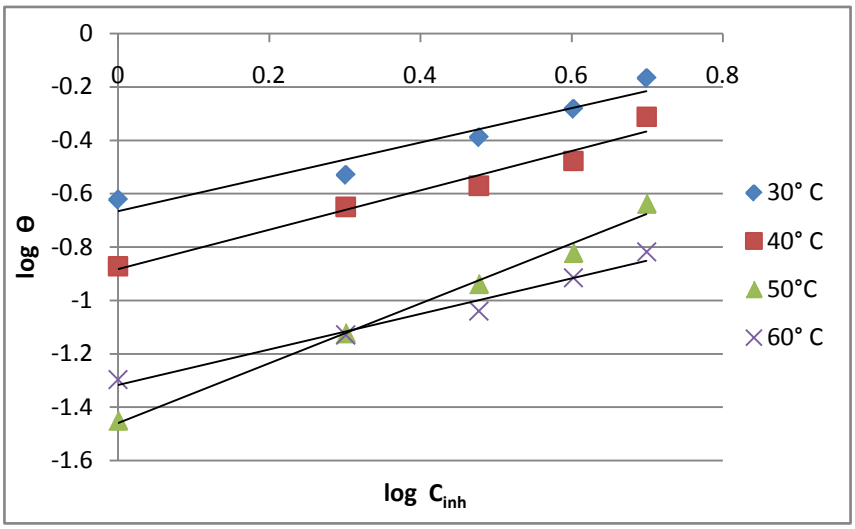

Figure 52. Freundlich adsorption isotherms of AEWHL on mild steel surface in 1M HCl at different studied temperatures

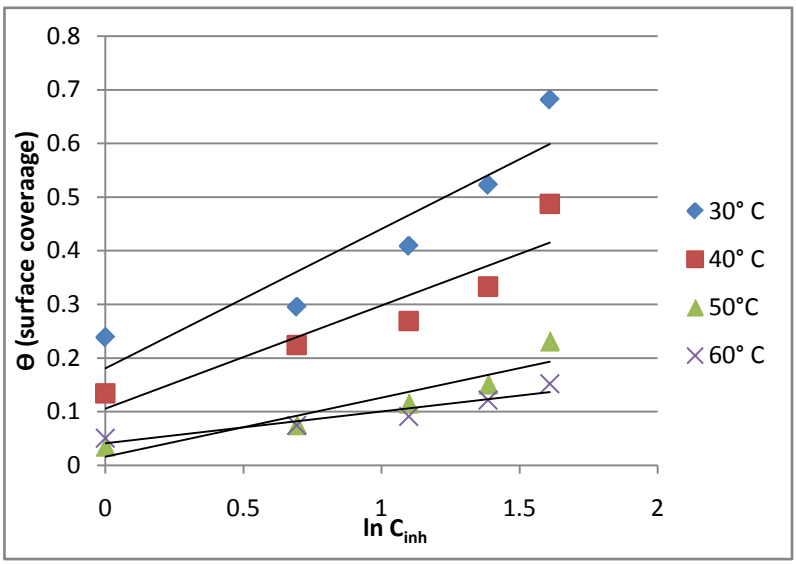

Figure 53. Temkin adsorption isotherms of AEWHL on mild steel surface in 1M HCl at different studied temperatures

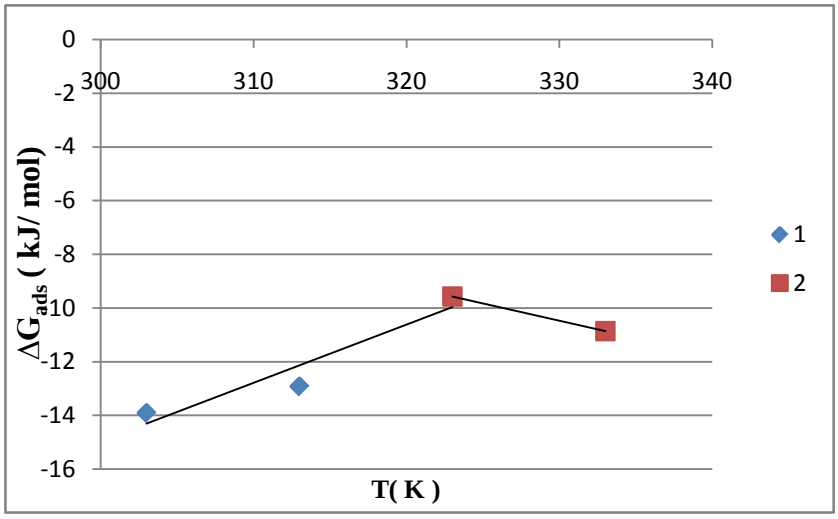

Figure 54. The variation of ΔG_{ads} (kJ/mol) with T (K) for mild steel corrosion in 1M HCl solution with AEWHL

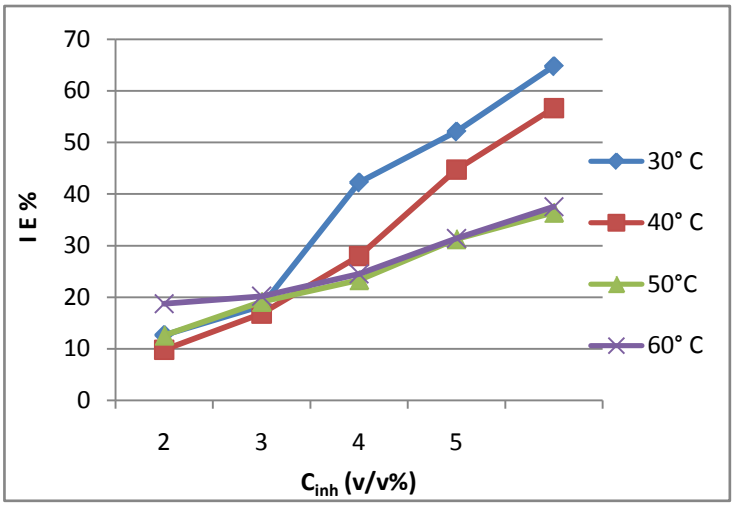

Figure 55.Variation in IE% for mild steel corrosion in 1M H_2SO_4 at different concentrations of AEWHL at different studied temperatures

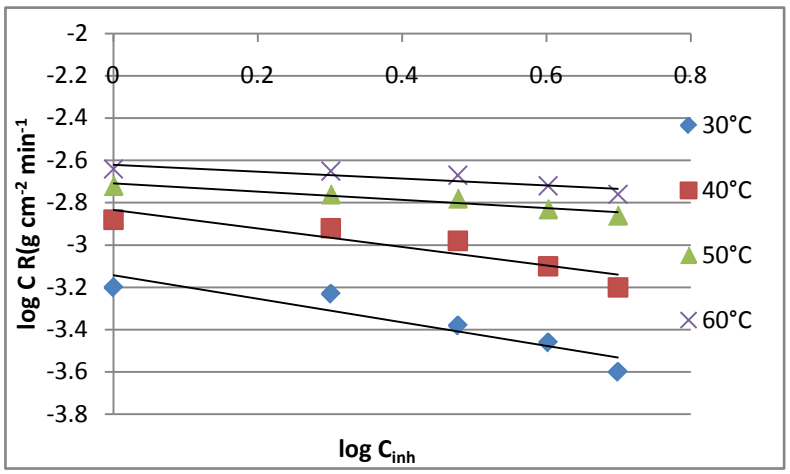

Figure 56. Variation of logCR with $logC_{inh}$ for mild steel corrosion in 1M H_2SO_4 in presence of different concentrations of AEWHL at different studied temperatures

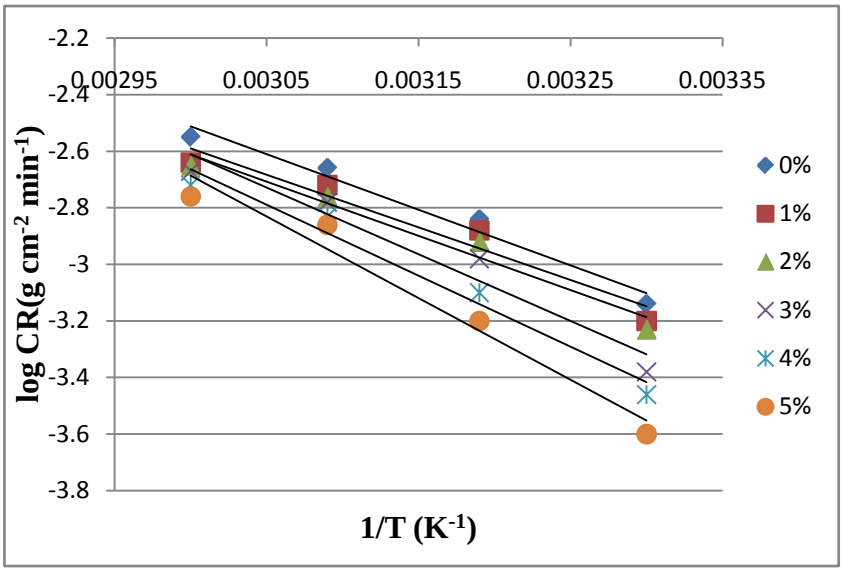

Figure 57. Arrhenius plots for mild steel corrosion in 1M H_2SO_4 in absence and presence of various concentrations of AEWHL

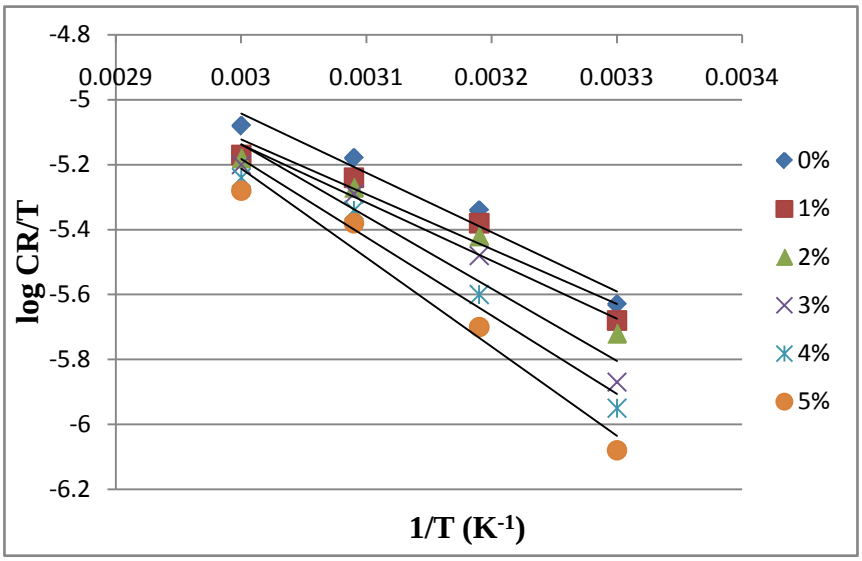

Figure 58. Transition-state plots for mild steel corrosion in 1M H_2SO_4 in absence and presence of various concentrations of AEWHL

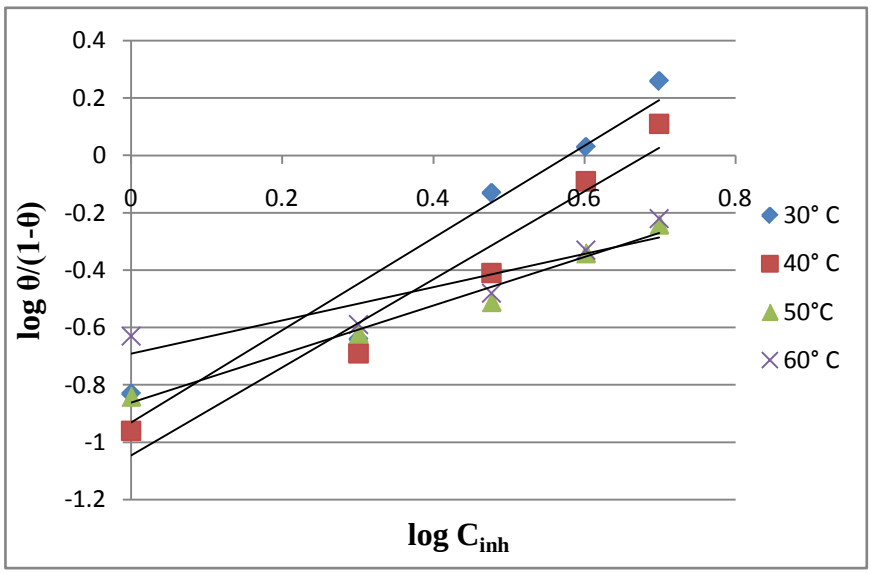

Figure 59. Langmuir adsorption isotherms of AEWHL on mild steel surface in 1M H_2SO_4 at different studied temperatures

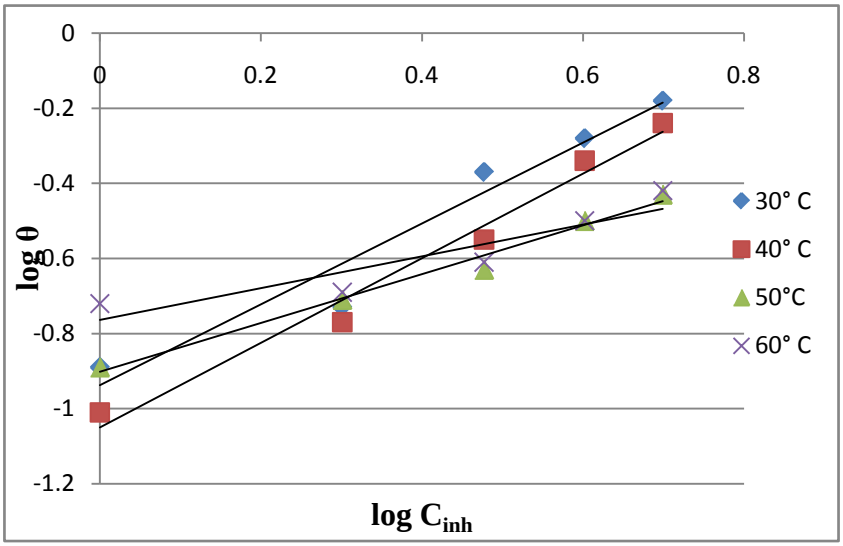

Figure 60. Freundlich adsorption isotherms of AEWHL on mild steel surface in 1M H_2SO_4 at different studied temperatures

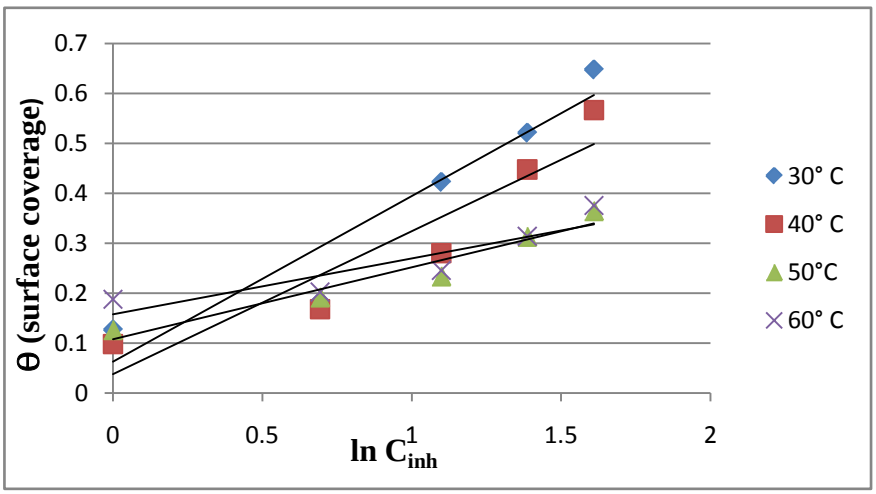

Figure 61. Temkin adsorption isotherms of AEWHL on mild steel surface in 1M H_2SO_4 at different studied temperatures

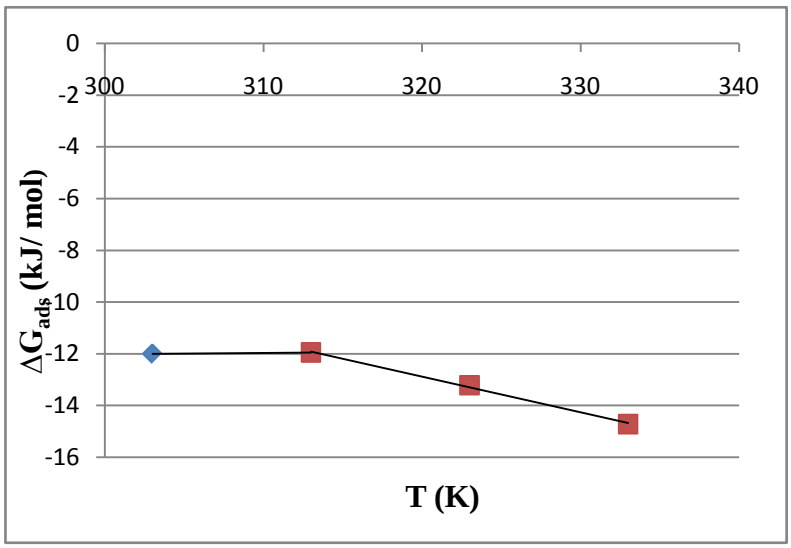

Figure 62. The variation of ΔG_{ads} (kJ/mol) with T (K) for mild steel corrosion in 1M H_2SO_4 solution with AEWHL

CHAPTER – 4

DISCUSSION ON FINDINGS AND CONCLUSIONS

Discussion on findings of present study for corrosion inhibition at mild steel surfaces is done and conclusions are drawn under eight main headings (4.1 to 4.8) according to different plant materials used viz: AECPL, AELCL, AENOL, AEWHL in two different aggressive media chosen. These discussions are enlisted below:

4.1 AQUEOUS EXTRACT OF CALOTROPIS PROCERA LEAVES IN 1M HCl

4.2 AQUEOUS EXTRACT OF CALOTROPIS PROCERA LEAVES IN 1M H_2SO_4

4.3 AQUEOUS EXTRACT OF LANTANA CAMARA LEAVES IN 1M HCl

4.4 AQUEOUS EXTRACT OF LANTANA CAMARA LEAVES IN 1M H_2SO_4

4.5 AQUEOUS EXTRACT OF NERIUM OLEANDER LEAVES IN 1M HCl

4.6 AQUEOUS EXTRACT OF NERIUM OLEANDER LEAVES IN 1M H_2SO_4

4.7 AQUEOUS EXTRACT OF WATER HYACINTH LEAVES IN 1M HCl

4.8 AQUEOUS EXTRACT OF WATER HYCINTH LEAVES IN 1M H_2SO_4

4.1 AQUEOUS EXTRACT OF CALOTROPIS PROCERA LEAVES IN 1M HCl

CORROSION RATES:

Corrosion rates were calculated by Eq.(1) [159]. Table1 shows that corrosion rates of mild steel decrease with increase in concentration of AECPL as inhibitor at all studied temperatures. This could be subjected to the adsorption of the phytoconstituents of inhibitor molecules with increase in concentration of inhibitor. The corrosion rate obeys Arrhenius type reaction, as it increases with rise in temperature [159].

INHIBITION EFFICIENCY:

From the obtained corrosion rates, inhibition efficiencies were calculated by using Eq.(2) [159,246]. Fig.1 represents the variation of IE% with different concentrations of AECPL at various studied temperatures. Data in Table2 show that IE% increase with increase in extract concentration, which is an indication of an increase in number of components of extract adsorbed on mild steel surface, which block the active sites of metal from acid attack and protect the metallic corrosion [162, 168]. Further the decrease in IE% with rise in temperature suggests electrostatic interaction (physical adsorption) of the extract molecules on mild steel surface [168]. This further indicates desorption of adsorbed inhibitor species at higher temperatures and metal dissolution takes place [83]. 60.86% inhibition efficiency is observed at 8% (v/v) concentration of inhibitor at 30°C.

KINETIC PARAMETERS:

Corrosion rates of steel specimens against concentration of inhibitor was calculated using kinetic relationship Eq.(3) [114, 160]. Fig 2 represents plot between log CR and log C_{inh} values at various studied temperatures. B and

were calculated by slope and intercept of straight lines of the graph. The obtained results in Table 3 can be discussed as follows [159].

- Negative values of B indicate that corrosion rate is inversely proportional to concentration of inhibitor. In other words the corrosion rates decrease with increase in concentration of inhibitor species.
- The high negative values of B reflect good inhibitive property of inhibitor. High negative value of B can be observed as steep slope in graph (Fig.2).
- Value of B is high at lower temperatures, indicates that inhibitive species is more effective at comparatively lower temperatures.
- The increase in K values with increase in temperature, indicating the increase in corrosion rates with temperatures.

THRMODYNAMIC AND ACTIVATION PARAMETERS:

Thermodynamic and activation parameters like apparent activation energy E_{act}, enthalpy of activation ΔH^* and entropy of activation ΔS^* were calculated for steel dissolution process. Activation energies E_{act} were calculated from the slopes of Arrhenius plots drawn between log CR and 1/T in Fig.3 in accordance with the Arrhenius Eq.(4) [246,232]. Table4 represents the calculated data of activation energies. The values of activation energies in presence of inhibitor were found higher than in uninhibited solution. This indicates the formation of higher energy barrier in corrosion reaction by inhibitor molecules. The increase in E_{act} for corrosion process further interpreted as physical adsorption of inhibitor species on mild steel surface [136, 166, 181]. Besides this according to Damaskin [58], the value of activation energy lesser than 80kJ/mol and even smaller than 5kJ/mol represents physical adsorption. This assertion supports the experimental results obtained in the present work. The values of enthalpies of activation ΔH^* and entropy of activation ΔS^* were calculated by transition state Eq.(5) [232, 246]. A plot of log (CR/T) versus 1/T gave a straight line with slope of $(-\Delta H^*/2.303R)$ and intercept of $[(\log R/Nh) + (\Delta S^*/2.303\ R)]$ from which the values of ΔH^* and ΔS^* were calculated (Fig.4). These values are tabulated in

Table4. Values of ΔH^* were found positive. Positive values indicate endothermic nature of steel dissolution process [37, 153, 246]. Endothermic process further indicates that mild steel dissolution reduces at lower temperatures and increases with increase in temperatures. Negative values of ΔS^* are indicative of formation of activated complex in rate determining step, which represents association rather than dissociation step, meaning the decrease in disorder takes place on going from reactants to activated complex [37,85,223]. It is also observed from data in Table 4 that E_{act} and ΔH^* vary in the same manner. Values of both E_{act} and ΔH^* increase with increase in concentration of inhibitor, suggesting that energy barrier is increases with increase in inhibitor concentration. This means that corrosion reaction will further be pushed to surface sites that are characterized by progressively higher values of E_{act} as the concentration of inhibitor becomes greater [37, 221, 227]. The values of activation energy were found larger than corresponding values of enthalpy of activation, indicate the involvement of a gaseous reaction, simply hydrogen evolution in corrosion process, associated with a decrease in total reaction volume [159].

ADSORPTION ISOTHERMS:

The nature of adsorption can be explained by understanding the process at metal/electrolyte interface. Further to understand the nature of adsorption, obtained surface coverage (θ) were fitted in different adsorption isotherms. Langmuir adsorption isotherm was drawn by using Eq. (8) [38, 83, 161, 185, 237]. Freundlich adsorption isotherm was also drawn using the Eq.(10) [117] and straight lines were obtained. These isotherms are shown in Fig.5 and Fig.6 respectively.

ADSORPTION PARAMETERS:

[Gibbs Energy of Adsorption[ΔG_{ads}], Enthalpy of Adsorption[ΔH_{ads}] and Entropy of Adsorption [ΔS_{ads}]

Values of K_{ads} were calculated by the intercept of Langmuir isotherm drawn according to the Eq.(8) between log (θ/1- θ) and log C_{inh} and by using this

Gibbs energy was calculated by using Eq. (13) [115, 159]. The values of ΔG_{ads} were tabulated in Table5 ΔG_{ads} values has been found negative at all studied temperatures indicating spontaneous adsorption process of inhibitor molecules and strong interactions between inhibitor molecules and metal surface [1, 37, 49, 67, 213, 225, 226] Increase in ΔG_{ads} values (becomes less negative) with the increase of temperature indicates the occurrence of exothermic process [159]. Table5 shows increase in ΔG_{ads} values with temperature indicates exothermic process of adsorption of inhibitor molecules, which is unfavourable at higher temperature due to desorption of inhibitor from metal surface [159, 225]. Generally values of ΔG_{ads} upto -20 KJ/mol are consistent with electrostatic interactions(physical adsorption) between charged molecules and charged metal surface and values upto -40 KJ/mol or higher involve charge sharing or transfer from inhibitor molecules to metal surface to form coordinate type of bond (chemical adsorption) [37, 49, 90, 132, 163, 165, 233]. The values of ΔG_{ads} were found from -13.76kJ/mol to -11.59 kJ/mol. The obtained values of ΔG_{ads} were found less than -20kJ/mol indicated physical adsorption of inhibitor molecules. Further the value of ΔG_{ads} is more negative at lower temperatures indicating that corrosion inhibition process is more effective at lower temperatures. It has been observed that adsorption of negatively charged species is facilitated due to the positively charged metal. But positively charged species can also be adsorbed and protect the positively charged metal surface acting with a negatively charged intermediate such as acid anions, adsorbed on metal surface [37, 181, 233]. Obtained values of Gibbs energy were plotted against temperature (Fig.7) according to the basic Eq. (14) [72, 159]. Intercept of graph between ΔG_{ads} versus T (Fig.7) gives value of ΔH_{ads} and by putting the value of intercept in Eq.(14) values of ΔS_{ads} were obtained .These obtained adsorption parameters Gibbs free energy of adsorption (ΔG_{ads}), enthalpy of adsorption (ΔH_{ads}), entropy of adsorption (ΔS_{ads}), are listed in Table 5. Values of ΔH_{ads} have been found negative indicating the exothermic adsorption process [85, 134, 136, 162], which further indicates lower IE% at higher temperatures, due to desorption of inhibitor molecules. The exothermic process is attributed to either physical or

chemical adsorption or mixture of both [42]. In exothermic process, values of ΔH_{ads} predict physiorption or chemisorption. For physiorption values of ΔH_{ads} is lower than 40kJ/mol while for chemisorption it approaches to 100 kJ/mol [39, 251]. Values of ΔH_{ads} in Table 5 indicate physiorption. Negative values of ΔS_{ads} indicate decrease in entropy of adsorption process. This behavior can be explained as follows: Before the adsorption of inhibitor molecules onto mild steel surface, inhibitor molecules might freely move in bulk solution (inhibitor molecules were chaotic). But with the process of adsorption, inhibitor molecules were orderly adsorbed onto the steel surface as a result decrease in entropy is observed [132, 133].

A more interesting behavior is observed in Table5 that negative ΔS_{ads} value is accompanied with negative ΔH_{ads} value. This further agrees that when the adsorption is an exothermic process, it must be accompanied by a decrease in the entropy change and vice versa [159, 228].

CONCLUSIONS:

1. Result showed that AECPL is good corrosion inhibitor for mild steel in 1M HCl solution.
2. Corrosion rates increase with increase in temperature and decrease with increase in inhibitor concentration.
3. Inhibition efficiency increases at lower temperature suggests the physiorption process of inhibitor on mild steel surface.
4. Apparent activation energy increases with increase in inhibitor concentrations also suggests pysiorption.
5. Enthalpy of adsorption comes out to be negative and lower than 40 kJ/mol, which shows exothermic and physical adsorption process of inhibitor on mild steel surface.
6. The values of Gibbs free energies calculated were negative shows spontaneity of corrosion inhibition process of mild steel in 1 M HCl in AECPL.

4.2 AQUEOUS EXTRACT OF CALOTROPIS PROCERA LEAVES IN 1M H_2SO_4

CORROSION RATES:

Corrosion rates were calculated by Eq.(1) [159]. Table6 shows that corrosion rates of mild steel decrease with increase in concentration of AECPL as inhibitor at all studied temperatures. This could be subjected to the adsorption of the phyto-constituents of inhibitor molecules with increase in concentration of inhibitor. The corrosion rate obeys Arrhenius type reaction, as it increases with rise in temperature [159].

INHIBITION EFFICIENCY:

From the obtained corrosion rates, inhibition efficiencies were calculated by using Eq.(2) [159,246]. Fig.8 represents the variation of IE% with different concentrations of AECPL at various studied temperatures. Data in Table 7 show that IE% increases or decreases with increasing temperatures at different studied extract concentrations of AECPL. This indicates the comprehensive adsorption (physical and chemical) of inhibitor species on mild steel surface [159]. Such type of observations were found in previous study by Noor [159]. Further it has been observed that IE% were increase with increase in inhibitor concentration. 51.56% inhibition efficiency is observed at 8% (v/v) concentration of inhibitor at 30^{o}C.

KINETIC PARAMETERS:

Corrosion rates of steel specimens against concentration of inhibitor were calculated using kinetic relationship as Eq.(3) [114,160]. Fig 9 represents plot between log CR and log C_{inh} values at various studied temperatures. B and K were calculated by slope and intercept of straight lines of the graph.

The obtained results in Table 8 can be discussed as follows [159]:

- Negative values of B indicate that corrosion rate is inversely proportional to concentration of inhibitor. In other words the corrosion rates decrease with increase in concentration of inhibitor species.
- The high negative values of B reflect good inhibitive property of inhibitor. High negative value of B can be observed as steep slope in graph Fig.(9).
- Value of B is high at lower temperatures, indicates that inhibitive species is more effective at comparatively lower temperatures.
- The increase in K values with increase in temperature, indicating the increase in corrosion rates with temperatures.

THRMODYNAMIC AND ACTIVATION PARAMETERS:

Thermodynamic and activation parameters like apparent activation energy E_{act}, enthalpy of activation ΔH^*entropy of activation ΔS^*were calculated for steel dissolution process. Activation energies E_{act} were calculated from the slopes of Arrhenius plots drawn between log CR and 1/T in Fig.10 in accordance with the Arrhenius Eq. (4) [232, 246]

Table 9 represents the calculated data of activation energies. The values of activation energies in presence of inhibitor were found higher than in uninhibited solution. This indicates the formation of higher energy barrier in corrosion reaction by inhibitor molecules. The increase in E_{act} for corrosion process further interpreted as physical adsorption of inhibitor species on mild steel surface [136,166, 181]. Besides this according to Damaskin [58], the value of activation energy lesser than 80 kJ /mol and even smaller than 5 kJ/mol represents physical adsorption. This assertion supports the experimental results obtained in the present work. The values of enthalpy of activation ΔH^* and entropy of activation ΔS^* were calculated by transition state Eq.(5) [232, 246]. A plot of log (CR/T) vs 1/T gave a straight line with slope of (-ΔH*/2.303R) and intercept of [(log R/Nh) + (ΔS^*/2.303 R)] from which the values of ΔH^* and ΔS^* were calculated (Fig.11). These values are tabulated in Table 9 Values of ΔH^*were found positive. Positive values indicate endothermic nature of steel dissolution process [37, 153, 246]. Endothermic process further indicates that mild steel dissolution reduces at lower

temperatures and increases with increase in temperatures. Negative values of ΔS^* are indicative of formation of activated complex in rate determining step, which represents association rather than dissociation step, meaning the decrease in disorder takes place on going from reactants to activated complex [37, 85, 223].

It is also observed from data in Table 9 that E_{act} and ΔH^* vary in the same manner. Values of both E_{act} and ΔH^* increase with increase in concentration of inhibitor, suggesting that energy barrier is increases with increase in inhibitor concentration. This means that corrosion reaction will further be pushed to surface sites that are characterized by progressively higher values of E_{act} as the concentration of inhibitor becomes greater [37, 221, 227]. The values of activation energy were found larger than corresponding values of enthalpy of activation, indicate the involvement of a gaseous reaction, simply hydrogen evolution in corrosion process, associated with a decrease in total reaction volume [159].

ADSORPTION ISOTHERMS:

The nature of adsorption can be explained by understanding the process at metal/electrolyte interface. Further to understand the nature of adsorption, obtained surface coverage (θ) were fitted in different adsorption isotherms. Langmuir adsorption isotherm was plotted using Eq. (8) [38, 83, 161, 185, 237]. Freundlich and Temkin isotherm were also plotted using following Eq.(10) [117] & Eq.(11) [152, 172] and straight lines were observed. These isotherms are shown in Fig.12, Fig.13 and Fig.14 respectively.

ADSORPTION PARAMETERS:

[Gibbs Energy of Adsorption[ΔG_{ads}], Enthalpy of Adsorption[ΔH_{ads}] and Entropy of Adsorption [ΔS_{ads}] :

Values of K_{ads} were calculated by the intercept of Langmuir isotherm drawn according to the Eq.(8) between log (θ/1-θ) and logC_{inh} and using this Gibbs energy was calculated by using Eq.(13) [115, 159]. The values of ΔG_{ads} were tabulated in Table10 ΔG_{ads} values has been found negative at all studied temperatures indicating spontaneous adsorption process of inhibitor molecules on

metal surface and strong interactions between inhibitor molecules and metal surface [1, 37, 49, 67, 213, 225, 226]. Generally values of ΔG_{ads} upto -20 kJ/mol are consistent with electrostatic interactions (physical adsorption) between charged molecules and charged metal surface and values upto -40 kJ/mol or higher involve charge sharing or transfer from inhibitor molecules to metal surface to form coordinate type of bond (chemical adsorption) [37, 49, 90, 132, 163, 165, 233]. The values of ΔG_{ads} were found from-10.27 kJ/mol to-12.15 kJ/mol. The obtained values of ΔG_{ads} were found less than -20kJ/mol indicated physical adsorption of inhibitor molecules. It has been observed that adsorption of negatively charged species is facilitated due to the positively charged metal. But positively charged species can also be adsorbed and protect the positively charged metal surface acting with a negatively charged intermediate such as acid anions, adsorbed on metal surface [37, 181,233]. Obtained values of Gibbs energy were plotted against temperature in accordance with the following basic Eq.(14) [72, 159]. Fig.15 shows the graph between ΔG_{ads} and T (K). Intercept of graph between ΔG_{ads} vs T give value of ΔH_{ads} and by putting the value of intercept in Eq.(14) values of ΔS_{ads} were obtained .These obtained adsorption parameters Gibbs free energy of adsorption (ΔG_{ads}), enthalpy of adsorption (ΔH_{ads}) and entropy of adsorption (ΔS_{ads}) are listed in Table10. A segmented line of two opposite slopes was obtained in Fig.15 indicating two sets of adsorption sites having different ΔH_{ads} values. Similar type of results have been found in previous study between ΔG_{ads} and T(K) by E.A. Noor [159]. The calculated ΔH_{ads} values have been found negative and positive indicating both exothermic adsorption process [85, 134, 136, 162] and endothermic adsorption process [94,237] respectively, depend upon the specific temperature range. Such type of comprehensive adsorption processes were obtained in previous study [159]. The exothermic process is attributed to either physical or chemical adsorption or mixture of both [42], while the endothermic process is attributed to chemisorption [65]. In exothermic process, values of ΔH_{ads} predict physiorption or chemisorption. For physiorption values of ΔH_{ads} is lower than 40kJ/mol while for chemisorption it approaches to 100kJ/mol [39, 251]. Negative values of ΔH_{ads} in Table10 indicate chemisorption as it is greater than 40kJ/mol.

Negative values of ΔS_{ads} indicate decrease in entropy of adsorption process. This behaviour can be explained as follows: Before the adsorption of inhibitor molecules onto mild steel surface, inhibitor molecules might freely move in bulk solution (inhibitor molecules were chaotic). But with the process of adsorption, inhibitor molecules were orderly adsorbed onto the steel surface as a result decrease in entropy is observed [132, 133]. The obtained positive values of ΔS_{ads} are the algebraic sum of the entropies of adsorption of organic molecules and the desorption of water molecules [78, 137] .Therefore the positive values of entropy of adsorption is the result of the substitution process, which can be attributed to the increase in the solvent entropy and more positive water desorption entropy [29, 151].

A more interesting behaviour is observed in Table10 that negative ΔS_{ads} value is accompanied with negative ΔH_{ads} value. This further agrees that when the adsorption is an exothermic process, it must be accompanied by a decrease in the entropy change and vice versa [159, 228].

CONCLUSIONS:

1. Result showed that AECPL is good corrosion inhibitor for mild steel in 1M H_2SO_4 solution.
2. Corrosion rates increase with increase in temperature and decrease with increase in inhibitor concentration.
3. Inhibition efficiency increases or decreases with increase in temperatures at given concentrations of inhibitor suggests comprehensive adsorption process.
4. Apparent activation energy increases with increase in inhibitor concentrations also suggests pysiorption.
5. Enthalpy of adsorption comes out to be negative and positive suggests exothermic and endothermic adsorption process.
6. The values of Gibbs free energies calculated were negative show spontaneity of corrosion inhibition process of mild steel in 1M H_2SO_4 in AECPL.

4.3 AQUEOUS EXTRACT OF LANTANA CAMARA LEAVES IN 1M HCl

CORROSION RATES:

Corrosion rates were calculated by Eq.(1)[159]. Table 11 shows that corrosion rates of mild steel decrease with increase in concentration of AELCL as inhibitor at all studied temperatures. This could be subjected to the adsorption of the phytoconstituents of inhibitor molecules with increase in concentration of inhibitor. The corrosion rate obeys Arrhenius type reaction, as it increases with rise in temperature [159].

INHIBITION EFFICIENCY:

From the obtained corrosion rates, inhibition efficiencies were calculated using Eq.(2)[159,246]. Fig.16 represents the variation of IE% with different concentrations of AELCL at various studied temperatures. Data in Table 12 show that IE% increases with increase in extract concentration, which is an indication of an increase in number of components of extract adsorbed on mild steel surface, which block the active sites of metal from acid attack and protect the metallic corrosion [162,168]. Further the decrease in IE% with rise in temperature suggests electrostatic interaction (physical adsorption) of the extract molecules on mild steel surface. This further indicates desorption of adsorbed inhibitor species at higher temperatures and metal dissolution takes place [83]. 90% inhibition efficiency is observed at 30^{o}C at 6% (v/v) concentration of inhibitor.

KINETIC PARAMETERS:

Corrosion rates of steel specimens against concentration of inhibitor were calculated using kinetic relationship Eq.(3)[114,160]. Fig.17 represents plot between log CR and log C_{inh} values at various studied temperatures. B and K

were calculated by slope and intercept of straight lines of the graph. The obtained results in Table13 can be discussed as follows [159].

- Negative values of B indicate that corrosion rate is inversely proportional to concentration of inhibitor. In other words the corrosion rates decrease with increase in concentration of inhibitor species.
- The high negative values of B reflect good inhibitive property of inhibitor. High negative value of B can be observed as steep slope in graph [Fig.17].
- Value of B is high at lower temperatures, indicates that inhibitive species is more effective at comparatively lower temperatures.
- The increase in K values with increase in temperature, indicating the increase in corrosion rates with temperatures.

THRMODYNAMIC AND ACTIVATION PARAMETERS:

Thermodynamic and activation parameters like apparent activation energy E_{act}, enthalpy of activation ΔH^* and entropy of activation ΔS^* were calculated for steel dissolution process. Activation energies E_{act} were calculated from the slopes of Arrhenius plots drawn between log CR and 1/T in Fig.18 in accordance with the Arrhenius Eq.(4)[232,246]. Table14 represents the calculated data of activation energies. The values of activation energies in presence of inhibitor were found higher than in uninhibited solution. This indicates the formation of higher energy barrier in corrosion reaction by inhibitor molecules. The increase in E_{act} for corrosion process further interpreted as physical adsorption of inhibitor species on mild steel surface [136, 166, 181]. Besides this according to Damaskin [58], the value of activation energy lesser than 80kJ/mol and even smaller than 5kJ/mol represents physical adsorption. This assertion supports the experimental results obtained in the present work upto the 4% (v/v) concentration of inhibitor. But at concentration 6% (v/v) of inhibitor 86.12 kJ/mol activation energy is observed, indicating chemical adsorption. The values of enthalpy of activation ΔH^* and entropy of activation ΔS^* were calculated by transition state Eq.(5). A plot of log (CR/T) versus 1/T in Fig.19 gave a straight line with slope of $(-\Delta H^*/2.303R)$ and intercept of $[(\log R/Nh) + (\Delta S^*/2.303R)]$ from which the values of ΔH^* and ΔS^*

were calculated. These values are tabulated in Table 14. Values of ΔH^* were found positive. Positive values indicate endothermic nature of steel dissolution process [37, 153, 246]. Endothermic process further indicates that mild steel dissolution reduces at lower temperatures and increases with increase in temperatures. Negative values of ΔS^* are indicative of formation of activated complex in rate determining step, which represents association rather than dissociation step, meaning the decrease in disorder takes place on going from reactants to activated complex [37, 85, 223]. It is also observed from data in Table 14 that E_{act} and ΔH^* vary in the same manner. Values of both E_{act} and ΔH^* increase with increase in concentration of inhibitor, suggesting that energy barrier is increases with increase in inhibitor concentration. This means that corrosion reaction will further be pushed to surface sites that are characterized by progressively higher values of E_{act} as the concentration of inhibitor becomes greater [37, 221, 227]. The values of activation energy were found larger than corresponding values of enthalpy of activation, indicate the involvement of a gaseous reaction, simply hydrogen evolution in corrosion process, associated with a decrease in total reaction volume [159].

ADSORPTION ISOTHERMS:

The nature of adsorption can be explained by understanding the process at metal/electrolyte interface. Further to understand the nature of adsorption, obtained surface coverage (θ) were fitted in different adsorption isotherms. Langmuir adsorption isotherm was drawn by using Eq.(8) [38,83,161,185,237]. Freundlich and Temkin adsorption isotherms were also drawn according to Eq.(10) [117] and Eq.(11) [152,172] and straight lines were obtained. These isotherms are shown in Fig.20, Fig.21 and Fig.22 respectively.

ADSORPTION PARAMETERS:

Gibbs Energy of Adsorption[ΔG_{ads}], Enthalpy of Adsorption[ΔH_{ads}] and Entropy of Adsorption [ΔS_{ads}

Values of K_{ads} were calculated by the intercept of Langmuir isotherm drawn according to the Eq.(8) between log (θ/1- θ) and log C_{inh} and by using this Gibbs energy was calculated by using Eq.(13) [115,159]. The values of ΔG_{ads} were tabulated in Table15. ΔG_{ads} values has been found negative at all studied temperatures indicating spontaneous adsorption process of inhibitor molecules on metal surface and strong interactions between inhibitor molecules and metal surface [1, 37, 49, 67, 213, 225, 226]. Increase in ΔG_{ads} values (becomes less negative) with the increase of temperature indicates the occurrence of exothermic process [159]. Data in Table15 shows increase in ΔG_{ads} values with temperature indicates exothermic process of adsorption of inhibitor molecules, which is unfavourable at higher temperature due to desorption of inhibitor from metal surface [159, 225]. Generally values of ΔG_{ads} upto -20 kJ/mol are consistent with electrostatic interactions (physical adsorption) between charged molecules and charged metal surface and values upto -40 kJ/mol or higher involve charge sharing or transfer from inhibitor molecules to metal surface to form coordinate type of bond (chemical adsorption) [37, 49, 90, 132, 163, 165, 233]. The values of ΔG_{ads} were found from -11.60 kJ/mol to -7.85 kJ/mol. The obtained values of ΔG_{ads} were found less than -20 kJ/mol indicated physical adsorption of inhibitor molecules. Further the value of ΔG_{ads} is more negative at lower temperatures indicating that corrosion inhibition process is more effective at lower temperatures. Obtained values of Gibbs energy were plotted against temperature in Fig.23 according to the basic Eq.(14)[72,159]. Intercept of graph between ΔG_{ads} versus T in Fig.23 gives value of ΔH_{ads} and by putting the value of intercept in Eq.(14) values of ΔS_{ads} were obtained. These obtained adsorption parameters Gibbs free energy of adsorption (ΔG_{ads}), enthalpy of adsorption (ΔH_{ads}) and entropy of adsorption (ΔS_{ads}) are listed in Table15. A segmented line of two opposite slopes was obtained in Fig.23 indicating two sets of adsorption sites having different ΔH_{ads} values. Similar type of results have been found in previous study between ΔG_{ads} and T(K) by E.A. Noor [159]. The calculated ΔH_{ads} values have been found negative and positive indicating both exothermic adsorption process [85, 134, 136, 162] and endothermic adsorption process [94, 237] respectively, depend upon the specific temperature range. Similar type of

comprehensive adsorption processes were obtained in previous study [159]. Exothermic process is attributed to either physical or chemical adsorption or mixture of both [42], while the endothermic process is attributed to chemisorption [65]. In exothermic process, values of ΔH_{ads} predict physiorption or chemisorption. For physiorption values of ΔH_{ads} is lower than 40 kJ/mol while for chemisorption it approaches to 100 kJ/mol [39, 251]. Values of ΔH_{ads} in Table 15 indicate both physiorption and chemisorption process. Negative values of ΔS_{ads} indicate decrease in entropy of adsorption process. This behavior can be explained as follows: Before the adsorption of inhibitor molecules onto mild steel surface, inhibitor molecules might freely move in bulk solution (inhibitor molecules were chaotic). But with the process of adsorption, inhibitor molecules were orderly adsorbed onto the steel surface as a result decrease in entropy is observed [132, 133]. The obtained positive values of ΔS_{ads} are the algebraic sum of the entropies of adsorption of organic molecules and desorption of water molecules [78, 137]. Therefore the positive values of entropy of adsorption is the result of the substitution process, which can be attributed to the increase in the solvent entropy and more positive water desorption entropy [29, 151].

A more interesting behavior is observed in Table15 that negative ΔS_{ads} value is accompanied with negative ΔH_{ads} value and positive ΔS_{ads} value is accompanied with positive ΔH_{ads} value. This further agrees that when the adsorption is an exothermic process, it must be accompanied by a decrease in the entropy change and vies versa [159, 228]. It has been observed that adsorption of negatively charged species is adsorbed due to the positively charged metal. But positively charged species can also be adsorbed and protect the positively charged metal surface acting with a negatively charged intermediate such as acid anions, adsorbed on metal surface [37, 181, 233].

CONCLUSIONS:

1. Result showed that AELCL is good corrosion inhibitor for mild steel in 1M HCl solution.
2. Corrosion rates increase with increase in temperature and decrease with increase in inhibitor concentration.

3. Inhibition efficiencies increases at lower temperature suggest the physiorption process of inhibitor on mild steel surface.
4. Apparent activation energy increases with increase in inhibitor concentrations also suggests pysiorption but chemisorptions is observed at 6 % (v/v) concentration.
5. Enthalpy of adsorption comes out to be positive and negative both at specific temperatures and its values indicate both chemisorption and physiorption process.
6. The values of Gibbs free energies calculated were negative shows spontaneity of corrosion inhibition process of mild steel in 1M HCl in AELCL.

4.4 AQUEOUS EXTRACT OF LANTANA CAMARA LEAVES IN 1M H_2SO_4

CORROSION RATES:

Corrosion rates were calculated by using Eq.(1)[159]. Table16 shows that corrosion rates of mild steel decrease with increase in concentration of AELCL as inhibitor at all studied temperatures. This could be subjected to the adsorption of the phyto-constituents of inhibitor molecules with increase in concentration of inhibitor. The corrosion rate obeys Arrhenius type reaction, as it increases with rise in temperature [159].

INHIBITION EFFICIENCY:

From the obtained corrosion rates, inhibition efficiencies were calculated by using Eq.(2)[159,246]. Fig.24 represents the variation of IE% with different concentrations of AELCL at various studied temperatures. Data in Table 17 show that IE% increases or decreases with increasing temperatures at different studied extract concentrations of AELCL. This indicates the comprehensive adsorption (physical and chemical adsorption) of inhibitor species on mild steel surface [159]. Such type of observations were found in previous study by E.A. Noor [159]. Further it has been observed that IE% were increase with increase in inhibitor concentration. 65.30% inhibition efficiency is observed at 30°C at 6% (v/v) concentration of inhibitor.

KINETIC PARAMETERS:

Corrosion rates of mild steel specimens were calculated by using the kinetic relationship according to Eq.(3)[114,160]. Fig 25 represents plot between log CR and log C_{inh} values at various studied temperatures. B and K were calculated by slope and intercept of straight lines of the graph. The obtained results in Table 18 can be discussed as follows [159].

- Negative values of B indicate that corrosion rate is inversely proportional to concentration of inhibitor. In other words the corrosion rates decrease with increase in concentration of inhibitor species.
- The high negative values of B reflect good inhibitive property of inhibitor. High negative value of B can be observed as steep slope in graph [Fig.25].
- Value of B is high at lower temperatures, indicates that inhibitive species is more effective at comparatively lower temperatures.
- The increase in K values with increase in temperature, indicating the increase in corrosion rates with temperatures.

THRMODYNAMIC AND ACTIVATION PARAMETERS:

The thermodynamic and activation parameters like apparent activation energy E_{act}, enthalpy of activation ΔH^*entropy of activation ΔS^* were calculated for steel dissolution process. Activation energies E_{act} were calculated from the slopes of Arrhenius plots drawn between logCR and 1/T in Fig.26 in accordance with the Arrhenius Eq.(4)[232,246]. Table19 represents the calculated data of activation energies. The values of activation energies in presence of inhibitor were found higher than in uninhibited solution. This indicates the formation of higher energy barrier in corrosion reaction by inhibitor molecules. The increase in E_{act} for corrosion process further interpreted as physical adsorption of inhibitor species on mild steel surface [136, 166, 181]. Besides this According to Damaskin [58], the value of activation energy lesser than 80kJ /mol and even smaller than 5kJ/mol represents physical adsorption. This assertion supports the experimental results obtained in the present work. The values of enthalpy of activation ΔH^* and entropy of activation ΔS^* were calculated by using transition state Eq.(5)[232,246]. A plot of log (CR/T) vs 1/T gave a straight line with slope of ($-\Delta H^*/2.303R$) and intercept of [(log R/Nh) + ($\Delta S^*/2.303R$)] from which the values of ΔH^* and ΔS^* were calculated (Fig.27). These values are tabulated in Table19. Values of ΔH^*were found positive. Positive values indicate endothermic nature of steel dissolution process [37, 153, 246]. Endothermic process further indicates that mild steel dissolution reduces at lower

temperatures and increases with increase in temperatures. Negative values of ΔS^* are indicative of formation of activated complex in rate determining step, which represents association rather than dissociation step, meaning that the decrease in disorder takes place on going from reactants to activated complex [37, 85, 223].

It is also observed from data in Table 19 that E_{act} and ΔH^* vary in the same manner. Values of both E_{act} and ΔH^* increase with increase in concentration of inhibitor, suggesting that energy barrier is increases with increase in inhibitor concentration. This means that corrosion reaction will further be pushed to surface sites that are characterized by progressively higher values of E_{act} as the concentration of inhibitor becomes greater [37,221,227]. The values of activation energy were found larger than corresponding values of enthalpy of activation, indicate the involvement of a gaseous reaction, simply hydrogen evolution in corrosion process, associated with a decrease in total reaction volume [159].

ADSORPTION ISOTHERMS:

The nature of adsorption can be explained by understanding the process at metal/electrolyte interface. Further to understand the nature of adsorption, obtained surface coverage (θ) were fitted in different adsorption isotherms. The mathematical expressions for Langmuir adsorption isotherm can be expressed by the Eq.(8) [38,83,161,185,237]. Freundlich and Temkin adsorption isotherms were also drawn according to Eq.(10)[117] and Eq.(11)[152,172] and straight lines were obtained in Fig.28, Fig. 29 and Fig.30 respectively.

ADSORPTION PARAMETERS:

Gibbs Energy of Adsorption [ΔG_{ads}], Enthalpy of Adsorption[ΔH_{ads}] and Entropy of Adsorption [ΔS_{ads}] :

Values of K_{ads} were calculated by the intercept of Langmuir isotherm drawn according to the Eq.(8) between log (θ/1-θ) and log C_{inh} and by using this

Gibbs energy of adsorption was calculated by using Eq.(13)[115,159]. The values of ΔG_{ads} were tabulated in Table20. ΔG_{ads} values has been found negative at all studied temperatures indicating spontaneous adsorption process of inhibitor molecules on metal surface and strong interactions between inhibitor molecules and metal surface [1, 37, 49, 67, 213, 225, 226]. Generally values of ΔG_{ads} upto -20 kJ/mol are consistent with electrostatic interactions (physical adsorption) between charged molecules and charged metal surface and values upto -40kJ/mol or higher involve charge sharing or transfer from inhibitor molecules to metal surface to form coordinate type of bond (chemical adsorption) [37, 49, 90, 132, 163, 165, 233]. The values of ΔG_{ads} were found from -5.18kJ/mol to -11.60 kJ/mol. The obtained values of ΔG_{ads} were found less than -20kJ/mol indicated physical adsorption of inhibitor molecules. Obtained values of Gibbs energy were plotted against temperature in Fig.31 accordance with the following basic Eq.(14)[72,159]. Intercept of graph between ΔG_{ads} vs T gives value of ΔH_{ads} and by putting the value of intercept in Eq.(14) values of ΔS_{ads} were obtained . These obtained adsorption parameters Gibbs free energy of adsorption (ΔG_{ads}), enthalpy of adsorption (ΔH_{ads}) and entropy of adsorption (ΔS_{ads}) are listed in Table20. The calculated ΔH_{ads} values have been found positive indicating endothermic adsorption process [94, 237] at given temperature range. The endothermic process is attributed to chemisorption [65]. Positive values of ΔH_{ads} in Table20 indicate chemisorption. The obtained positive values of ΔS_{ads} are the algebraic sum of the entropies of adsorption of organic molecules and desorption of water molecules [78, 137]. Therefore the positive values of entropy of adsorption are the result of the substitution process, which can be attributed to the increase in the solvent entropy and more positive water desorption entropy [29, 151].

A more interesting behaviour is observed in Table 20 that positive ΔS_{ads} value is accompanied with positive ΔH_{ads} value. This further agrees that when the adsorption is an exothermic process, it must be accompanied by a decrease in the entropy change and vies versa [159, 228]. It has been observed that adsorption of negatively charged species is facilitated due to the positively charged metal. But positively charged species can also be adsorbed and

protect the positively charged metal surface acting with a negatively charged intermediate such as acid anions, adsorbed on metal surface [37, 181, 233].

CONCLUSIONS:

1. Result showed that AELCL is good corrosion inhibitor for mild steel in 1M H_2SO_4 solution.
2. Corrosion rates increase with increase in temperature and decrease with increase in inhibitor concentration.
3. Inhibition efficiency increases or decreases with increase in temperatures at given concentrations of inhibitor suggesting comprehensive adsorption process.
4. Apparent activation energy increases with increase in inhibitor concentrations also suggests pysiorption.
5. Enthalpy of adsorption comes out to be negative and positive suggests exothermic and endothermic adsorption process which further suggests chemisorption.
6. The values of Gibbs free energies calculated were negative show spontaneity of corrosion inhibition process of mild steel in 1M H_2SO_4 in AELCL.

4.5 AQUEOUS EXTRACT OF NERIUM OLEANDER LEAVES IN 1M HCl

CORROSION RATES:

Corrosion rates were calculated by applying Eq.(1)[159]. Table 21 shows that corrosion rates of mild steel decrease with increase in concentration of AENOL as inhibitor at all studied temperatures. This could be subjected to the adsorption of the phyto-constituents inhibitor molecules with increase in concentration of inhibitor. The corrosion rate obeys Arrhenius type reaction, as it increases with rise in temperature [159].

INHIBITION EFFICIENCY:

From the obtained corrosion rates, inhibition efficiencies were calculated by using Eq.(2)[159,246]. Fig.32 represents the variation of IE% with different concentrations of AENOL at various studied temperatures. Data in Table 22 shows that IE% increase with increase in extract concentration, which is an indication of an increase in number of components of extract adsorbed on mild steel surface, which block the active sites of metal from acid attack and protect the metallic corrosion [162,168]. Further the decrease in IE% with rise in temperature suggests electrostatic interaction (physical adsorption) of the extract molecules on mild steel surface. This further indicates desorption of adsorbed inhibitor species at higher temperatures and metal dissolution takes place [83]. It can be observed that 83.76% inhibition efficiency is obtained at 30°C temperature at 10% (v/v) concentration of AENOL.

KINETIC PARAMETERS:

Corrosion rates of mild steel specimens were calculated by using the kinetic relationship as Eq.(3)[114,160]. Fig33 represents plot between logCR and $\log C_{inh}$ values at various studied temperatures. B and K were calculated by slope and intercept of straight lines of the graph. The obtained results in Table 23 can be discussed as follows [159].

- Negative values of B indicate that corrosion rate is inversely proportional to concentration of inhibitor. In other words the corrosion rates decrease with increase in concentration of inhibitor species.
- The high negative values of B reflect good inhibitive property of inhibitor. High negative value of B can be observed as steep slope in graph (Fig.33).
- Value of B is high at lower temperatures, indicates that inhibitive species is more effective at comparatively lower temperatures.
- The increase in K values with increase in temperature, indicating the increase in corrosion rates with temperatures.

THRMODYNAMIC AND ACTIVATION PARAMETERS:

The thermodynamic and activation parameters like apparent activation energy E_{act}, enthalpy of activation ΔH^* and entropy of activation ΔS^* were calculated for mild steel dissolution process. Activation energy E_{act} were calculated from the slopes of Arrhenius plots drawn between logCR and 1/T in Fig.34 in accordance with the by applying Arrhenius Eq.(4)[246,232]. Table 24 represents the calculated data of activation energies. The values of activation energies in presence of inhibitor were found higher than in uninhibited solution. This indicates the formation of higher energy barrier in corrosion reaction by inhibitor molecules. The increase in E_{act} for corrosion process further interpreted as physical adsorption of inhibitor species on mild steel surface [136,166,181]. Besides this According to Damaskin [58], the value of activation energy lesser than 80kJ/mol and even smaller than 5kJ/mol represents physical adsorption. This assertion supports the experimental results obtained in the present work. The values of enthalpy of activation ΔH^* and entropy of activation ΔS^* were calculated by using the transition state Eq.(5)[232,246]. A plot of log (CR/T) versus 1/T gave a straight line with slope of ($-\Delta H^*/2.303R$) and intercept of [(log R/Nh) + ($\Delta S^*/2.303$ R)] from which the values of ΔH^* and ΔS^* were calculated (Fig.35). These values are tabulated in Table 24. Values of ΔH^*were found positive. Positive values indicate endothermic nature of steel dissolution process [37,153,246]. Endothermic process further indicates that mild steel dissolution reduces at

lower temperatures and increases with increase in temperatures. Negative values of ΔS^* are indicative of formation of activated complex in rate determining step, which represents association rather than dissociation step, meaning the decrease in disorder takes place on going from reactants to activated complex [37, 85, 223]. It is also observed from data in Table 24 that E_{act} and ΔH^* vary in the same manner. Values of both E_{act} and ΔH^* increase with increase in concentration of inhibitor, suggesting that energy barrier is increases with increase in inhibitor concentration. This means that corrosion reaction will further be pushed to surface sites that are characterized by progressively higher values of E_{act} as the concentration of inhibitor becomes greater [37,221,227]. The values of activation energy were found larger than corresponding values of enthalpy of activation, indicate the involvement of a gaseous reaction, simply hydrogen evolution in corrosion process, associated with a decrease in total reaction volume [159].

ADSORPTION ISOTHERMS:

The nature of adsorption can be explained by understanding the process at metal/electrolyte interface. Further to understand the nature of adsorption, obtained surface coverage (θ) were fitted in different adsorption isotherms. Langmuir adsorption isotherm was drawn by using the Eq.(8)[38,83,161,185,237]. Freundlich adsorption isotherm was also drawn according to Eq.(10)[117] and straight lines were obtained. These isotherms are shown in Fig.36 and Fig.37 respectively.

ADSORPTION PARAMETERS:

[Gibbs Energy of Adsorption[ΔG_{ads}], Enthalpy of Adsorption[ΔH_{ads}] and Entropy of Adsorption [ΔS_{ads}] :

Values of K_{ads} were calculated by the intercept of straight lines of Langmuir isotherm drawn according to the Eq.(8) between log (θ /1- θ) and log C_{inh} and by using this Gibbs energy of adsorption was calculated by using the Eq.(13) [115, 159]. The values of ΔG_{ads} are tabulated in Table25. ΔG_{ads} values has

been found negative at all studied temperatures indicating spontaneous adsorption process of inhibitor molecules on metal surface and strong interactions between inhibitor molecules and metal surface [1, 37, 49, 67, 213, 225, 226]. Generally values of ΔG_{ads} upto -20 kJ/mol are consistent with electrostatic interactions (physical adsorption) between charged molecules and charged metal surface and values upto -40 kJ/mol or higher involve charge sharing or transfer from inhibitor molecules to metal surface to form coordinate type of bond (chemical adsorption) [37, 49, 90, 132, 163, 165, 233]. The values of ΔG_{ads} were found from -13.91kJ/mol to -14.73 kJ/mol. The obtained values of ΔG_{ads} were less than -20 kJ/mol indicated physical adsorption of inhibitor molecules. It has been observed that adsorption of negatively charged species is facilitated due to the positively charged metal. But positively charged species can also be adsorbed and protect the positively charged metal surface acting with a negatively charged intermediate such as acid anions, adsorbed on metal surface [37, 181, 233]. Obtained values of Gibbs energy were plotted against temperature in Fig.38 in accordance with the Eq. (14) [72, 159]. Intercept of graph between ΔG_{ads} vs T give value of ΔH_{ads} and by putting the value of intercept in Eq.(14) values of ΔS_{ads} were obtained .These obtained adsorption parameters Gibbs free energy of adsorption (ΔG_{ads}), enthalpy of adsorption (ΔH_{ads}) and entropy of adsorption (ΔS_{ads}) are listed in Table25. A segmented line of two opposite slopes was obtained in Fig. 38 indicating two sets of adsorption sites having different ΔH_{ads} values. Similar type of segmented lined graph has been formed in previous study between ΔG_{ads} and T (K) by E.A. Noor [159]. Values of ΔH_{ads} has been found negative indicating the exothermic adsorption process [85, 134, 136, 162], which further indicates lower IE% at higher temperatures, due to desorption of inhibitor molecules. The exothermic process is attributed to either physical or chemical adsorption or mixture of both [42]. In exothermic process, values of ΔH_{ads} predict physiorption or chemisorption. For physiorption values of ΔH_{ads} is lower than 40kJ/mol while for chemisorption it approaches to 100kJ/mol [39,251]. Values of ΔH_{ads} in Table25 indicate physiorption. Negative values of ΔS_{ads} indicate decrease in entropy of

adsorption process. This behavior can be explained as follows: Before the adsorption of inhibitor molecules onto mild steel surface, inhibitor molecules might freely move in bulk solution (inhibitor molecules were chaotic). But with the process of adsorption, inhibitor molecules were orderly adsorbed onto the steel surface as a result decrease in entropy is observed [132, 133]. A more interesting behaviour is observed in Table 25 that negative ΔS_{ads} value is accompanied with negative ΔH_{ads} value. This further agrees that when the adsorption is an exothermic process, it must be accompanied by a decrease in the entropy change and vies versa [159, 228]. The obtained positive values of ΔS_{ads} are the algebraic sum of the adsorption of organic molecules and the desorption of water molecules [78, 137] .Therefore the positive values of entropy of adsorption is the result of the substitution process, which can be attributed to the increase in the solvent entropy and more positive water desorption entropy [29, 151].

CONCLUSIONS:

1. Result showed that AENOL is good corrosion inhibitor for mild steel in 1M HCl solution.
2. Corrosion rates increase with increase in temperature and decrease with increase in inhibitor concentration.
3. Inhibition efficiencies increases at lower temperature suggest the physiorption process of inhibitor on mild steel surface.
4. Apparent activation energy increases with increase in inhibitor concentrations also suggests pysiorption.
5. Enthalpy of adsorption comes out to be negative and lower than 40 kJ/mol, which shows exothermic and physical adsorption process of inhibitor.
6. The values of Gibbs free energies calculated were negative shows spontaneity of corrosion inhibition process of mild steel in 1M HCl in AENOL.

4.6 AQUEOUS EXTRACT OF NERIUM OLEANDER LEAVES IN 1M H_2SO_4

CORROSION RATES:

Corrosion rates were calculated by applying Eq.(1)[159]. Table 26 shows that corrosion rates of mild steel decrease with increase in concentration of AENOL as inhibitor at all studied temperatures. This could be subjected to the adsorption of the phyto-constituents of inhibitor molecules with increase in concentration of inhibitor. The corrosion rate obeys Arrhenius type reaction, as it increases with rise in temperature [159].

INHIBITION EFFICIENCY:

From the obtained corrosion rates, inhibition efficiencies were calculated by using Eq.(2)[159,246]. Fig.39 represents the variation of IE% with different concentrations of AENOL at various studied temperatures. Data in Table27 show that IE% increase with increase in extract concentration, which is an indication of an increase in number of components of extract adsorbed on mild steel surface, which block the active sites of metal from acid attack and protect the metallic corrosion [162, 168]. Further the decrease in IE% with rise in temperature suggests electrostatic interaction (physical adsorption) of the extract molecules on mild steel surface. This further indicates desorption of adsorbed inhibitor species at higher temperatures and metal dissolution takes place [83]. It can be observed that 72% inhibition efficiency is obtained at 30°C temperature at 10% (v/v) concentration of AENOL.

KINETIC PARAMETERS:

Corrosion rates of mild steel specimens were calculated by using the kinetic relationship as Eq.(3)[114,160]. Fig.40 represents plot between logCR and $\log C_{inh}$ values at various studied temperatures. B and K were calculated by slope and intercept of straight lines of the graph. The obtained results in Table28 can be discussed as follows [159].

- Negative values of B indicate that corrosion rate is inversely proportional to concentration of inhibitor. In other words the corrosion rates decrease with increase in concentration of inhibitor species.
- The high negative values of B reflect good inhibitive property of inhibitor. High negative value of B can be observed as steep slope in graph (Fig.40).
- Value of B is high at lower temperatures, indicates that inhibitive species is more effective at comparatively lower temperatures.
- The increase in K values with increase in temperature, indicating the increase in corrosion rates with temperatures.

THRMODYNAMIC AND ACTIVATION PARAMETERS:

The thermodynamic and activation parameters like apparent activation energy E_{act}, enthalpy of activation ΔH^*entropy of activation ΔS^* were calculated for mild steel dissolution process. Activation energies E_{act} were calculated from the slopes of Arrhenius plots drawn between logCR and 1/T in Fig.41 in accordance with the Arrhenius Eq.(4) [232,246] . The slope of logCR versus 1/T gives the values of activation energies at studied concentrations. Table29 represents the calculated data of activation energies. The values of activation energies in presence of inhibitor were found higher than in uninhibited solution. This indicates the formation of higher energy barrier in corrosion reaction by inhibitor molecules. The increase in E_{act} for corrosion process further interpreted as physical adsorption of inhibitor species on mild steel surface [136, 166, 181]. Besides this according to Damaskin [58], the value of activation energy lesser than 80kJ/mol and even smaller than 5kJ/mol represents physical adsorption. This assertion supports the experimental results obtained in the present work. The values of enthalpy of activation ΔH^* and entropy of activation ΔS^* were calculated by using the transition state Eq.(5) [232, 246]. A plot of log (CR/T) vs 1/T gave a straight line in Fig.42 with slope of ($-\Delta H^*/2.303R$) and intercept of [(log R/Nh) + ($\Delta S^*/2.303$ R)] from which the values of ΔH^* and ΔS^* were calculated. These values are tabulated in Table 29. Values of ΔH^*were found positive. Positive values indicate endothermic nature of steel dissolution process [37, 153, 246].

Endothermic process further indicates that mild steel dissolution reduces at lower temperatures and increases with increase in temperatures. Negative values of ΔS^* are indicative of formation of activated complex in rate determining step, which represents association rather than dissociation step, meaning that the decrease in disorder takes place on going from reactants to activated complex [37, 85, 223].

It is also observed from data in Table 29 that E_{act} and ΔH^* vary in the same manner. Values of both E_{act} and ΔH^* increase with increase in concentration of inhibitor, suggesting that energy barrier increases with increase in inhibitor concentration. This means that corrosion reaction will further be pushed to surface sites that are characterized by progressively higher values of E_{act} as the concentration of inhibitor becomes greater [37,221,227]. The values of activation energy were found larger than corresponding values of enthalpy of activation, indicate the involvement of a gaseous reaction, simply hydrogen evolution in corrosion process, associated with a decrease in total reaction volume [159].

ADSORPTION ISOTHERMS:

The nature of adsorption can be explained by understanding the process at metal/electrolyte interface. Further to understand the nature of adsorption, obtained surface coverage (θ) were fitted in different adsorption isotherms. **Langmuir isotherm** was best fit and drawn by using the Eq.(8) [38,83,161,185,237]. Freundlich and Temkin adsorption isotherms were also drawn according to Eq.(10) [117] & Eq.(11) [152,172] and straight lines were obtained. These isotherms are shown in Fig.43,Fig.44 and Fig.45 respectively.

ADSORPTION PARAMETERS:

[Gibbs Energy of Adsorption[ΔG_{ads}], Enthalpy of Adsorption[ΔH_{ads}] and Entropy of Adsorption [ΔS_{ads}] :

Values of K_{ads} were calculated by the intercept of straight lines of Langmuir isotherm drawn according to the Eq.(8) between log (θ/1- θ) and logC_{inh} and

by using this Gibbs energy of adsorption was calculated by using the Eq. (13) [115, 159]. The values of ΔG_{ads} are tabulated in Table30. ΔG_{ads} values has been found negative at all studied temperatures indicating spontaneous adsorption process of inhibitor molecules on metal surface and strong interactions between inhibitor molecules and metal surface [37, 49, 67, 213, 225, 226]. Generally values of ΔG_{ads} upto -20kJ/mol are consistent with electrostatic interactions (physical adsorption) between charged molecules and charged metal surface and values upto -40kJ/mol or higher involve charge sharing or transfer from inhibitor molecules to metal surface to form coordinate type of bond (chemical adsorption) [37, 49, 90, 132, 163, 165]. The values of ΔG_{ads} were found from -13.99kJ/mol to -9.20kJ/mol. The obtained values of ΔG_{ads} were less than -20kJ/mol indicated physical adsorption of inhibitor molecules. It has been observed that adsorption of negatively charged species is facilitated due to the positively charged metal. But positively charged species can also be adsorbed and protect the positively charged metal surface acting with a negatively charged intermediate such as acid anions, adsorbed on metal surface [37, 181, 233]. Obtained values of Gibbs energy were plotted against temperature in Fig.46 according to the Eq.(14) [72,159]. Intercept of graph between ΔG_{ads} versus T give value of ΔH_{ads} and by putting the value of intercept in Eq.(14) values of ΔS_{ads} were obtained. These obtained adsorption parameters Gibbs free energy of adsorption (ΔG_{ads}), enthalpy of adsorption (ΔH_{ads}), entropy of adsorption (ΔS_{ads}), are listed in Table30. Values of ΔH_{ads} has been found negative indicating the exothermic adsorption process [85, 134, 136, 162], which further indicates lower IE% at higher temperatures, due to desorption of inhibitor molecules. The exothermic process is attributed to either physical or chemical adsorption or mixture of both [42]. In exothermic process, values of ΔH_{ads} predict physiorption or chemisorption. For physiorption values of ΔH_{ads} is lower than 40kJ/mol while for chemisorption it approaches to 100kJ/mol [39,251]. Values of ΔH_{ads} in Table30 indicate chemisorptions as it is larger than 40 kJ/mol. Negative values of ΔS_{ads} indicate decrease in entropy of adsorption process. This behavior can be explained as follows: Before the

adsorption of inhibitor molecules onto mild steel surface, inhibitor molecules might freely move in bulk solution (inhibitor molecules were chaotic). But with the process of adsorption, inhibitor molecules were orderly adsorbed onto the steel surface as a result decrease in entropy is observed [132, 133]. A more interesting behaviour is observed in Table 30 that negative ΔS_{ads} value is accompanied with negative ΔH_{ads} value. This further agrees that when the adsorption is an exothermic process, it must be accompanied by a decrease in the entropy change and vice versa [159, 228].

CONCLUSIONS:

1. Result showed that AENOL is good corrosion inhibitor for mild steel in 1M H_2SO_4 solution.
2. Corrosion rates increase with increase in temperature and decrease with increase in inhibitor concentration.
3. Inhibition efficiencies increases at lower temperature suggest the physiorption process of inhibitor on mild steel surface.
4. Apparent activation energy increases with increase in inhibitor concentrations also suggests pysiorption.
5. Enthalpy of adsorption comes out to be negative and higher than 40 kJ/mol, which shows exothermic and chemical adsorption process of inhibitor.
6. The values of Gibbs free energies calculated were negative shows spontaneity of corrosion inhibition process of mild steel in 1M H_2SO_4 in AENOL.

4.7 AQUEOUS EXTRACT OF WATER HYACINTH LEAVES IN 1M HCl

CORROSION RATES:

Corrosion rates were calculated by using Eq.(1) [159]. Table31 shows that corrosion rates of mild steel decrease with increase in concentration of AEWHL as inhibitor at all studied temperatures. This could be subjected to the adsorption of the phyto-constituents of inhibitor molecules with increase in concentration of inhibitor. The corrosion rate obeys Arrhenius type reaction, as it increases with rise in temperature [159].

INHIBITION EFFICIENCY:

From the obtained corrosion rates, inhibition efficiencies were calculated using Eq.(2) [159,246]. Fig.47 represents the variation of IE% with different concentrations of AEWHL at various studied temperatures. Data in Table 32 show that IE% increase with increase in extract concentration, which is an indication of an increase in number of components of extract adsorbed on mild steel surface, which block the active sites of metal from acid attack and protect the metallic corrosion [162,168]. Further the decrease in IE% with rise in temperature suggests electrostatic interaction (physical adsorption) of the extract molecules on mild steel surface [168]. This further indicates desorption of adsorbed inhibitor species at higher temperatures and metal dissolution takes place [83]. 68.18% inhibition efficiency is observed at 5% (v/v) concentration of inhibitor at 30^{o}C.

KINETIC PARAMETERS:

Assuming that corrosion rates of steel specimens against concentration were calculated by kinetic relationship as Eq.(3) [114,160]. Fig 48 represents plot between logCR and logC_{inh} values at various studied temperatures. B and K were calculated by slope and intercept of straight lines of the graph.

The obtained results in Table33 can be discussed as follows [159]:

- Negative values of B indicate that corrosion rate is inversely proportional to concentration of inhibitor. In other words the corrosion rates decrease with increase in concentration of inhibitor species.
- The high negative values of B reflect good inhibitive property of inhibitor. High negative value of B can be observed as steep slope in graph (Fig.48).
- Value of B is high at lower temperatures, indicates that inhibitive species is more effective at comparatively lower temperatures.
- The increase in K values with increase in temperature, indicating the increase in corrosion rates with temperatures.

THERMODYNAMIC AND ACTIVATION PARAMETERS:

Thermodynamic and activation parameters like apparent activation energy E_{act}, enthalpy of activation ΔH^* and entropy of activation ΔS^* were calculated for steel dissolution process. Activation energies E_{act} were calculated from the slopes of Arrhenius plots drawn between logCR and 1/T in Fig.49 in accordance with the Arrhenius Eq.(4) [232,246]. Table34 represents the calculated data of activation energies. The values of activation energies in presence of inhibitor were found higher than in uninhibited solution. This indicates the formation of higher energy barrier in corrosion reaction by inhibitor molecules. The increase in E_{act} for corrosion process further interpreted as physical adsorption of inhibitor species on mild steel surface [136, 166, 181]. Besides this according to Damaskin [58], the value of activation energy lesser than 80kJ/mol and even smaller than 5kJ/mol represents physical adsorption. This assertion supports the experimental results obtained in the present work.

The values of enthalpy of activation ΔH^* and entropy of activation ΔS^* were calculated by transition state Eq.(5) [232,246]. A plot of log(CR/T) versus 1/T in Fig.50 gave a straight line with slope of $(-\Delta H^*/2.303R)$ and intercept of $[(\log R/Nh) + (\Delta S^*/2.303\ R)]$ from which the values of ΔH^* and ΔS^* were calculated. These values are tabulated in Table34. Values of ΔH^*were found positive. Positive values indicate endothermic nature of steel dissolution process [37,153,246]. Endothermic process further indicates that mild steel dissolution

reduces at lower temperatures and increases with increase in temperatures. Negative values of ΔS^* are indicative of formation of activated complex in rate determining step, which represents association rather than dissociation step, meaning that the decrease in disorder takes place on going from reactants to activated complex [37, 85, 223].

It is also observed from data in Table34 that E_{act} and ΔH^* vary in the same manner. Values of both E_{act} and ΔH^* increase with increase in concentration of inhibitor, suggesting that energy barrier is increases with increase in inhibitor concentration. This means that corrosion reaction will further be pushed to surface sites that are characterized by progressively higher values of E_{act} as the concentration of inhibitor becomes greater [37, 221, 227]. The values of activation energy were found larger than corresponding values of enthalpy of activation, indicate the involvement of a gaseous reaction, simply hydrogen evolution in corrosion process, associated with a decrease in total reaction volume [159].

ADSORPTION ISOTHERMS:

The nature of adsorption can be explained by understanding the process at metal/electrolyte interface. Further to understand the nature of adsorption, obtained surface coverage (θ) were fitted in different adsorption isotherms. Langmuir adsorption isotherm was found best fit and plotted according to the Eq.(8) [38,83,161,185,237]. Freundlich and Temkin adsorption isotherms were also drawn according to Eq.(10) [117] and Eq.(11) [152,172] and straight lines were obtained. These isotherms are shown in Fig.51, Fig.52 and Fig.53 respectively.

ADSORPTION PARAMETERS:

[Gibbs Energy of Adsorption[ΔG_{ads}], Enthalpy of Adsorption[ΔH_{ads}] and Entropy of Adsorption [ΔS_{ads}] :

Values of K_{ads} were calculated by the intercept of Langmuir isotherm drawn according to the Eq.(8) between log (θ/1- θ) and logC_{inh} and by using this Gibbs energy was calculated by the Eq.(13) [115,159]. The values of ΔG_{ads} were

tabulated in Table35. ΔG_{ads} values has been found negative at all studied temperatures indicating spontaneous adsorption process of inhibitor molecules on metal surface and strong interactions between inhibitor molecules and metal surface [1, 37, 49, 67, 213, 225, 226]. Generally values of ΔG_{ads} upto -20 kJ/mol are consistent with electrostatic interactions [physical adsorption] between charged molecules and charged metal surface and values upto -40 kJ/mol or higher involve charge sharing or transfer from inhibitor molecules to metal surface to form coordinate type of bond (chemical adsorption) [37, 49, 90, 132, 163, 165, 233]. The values of ΔG_{ads} were found from -13.91kJ/mol to -9.58kJ/mol. The obtained values of ΔG_{ads} were found less than -20kJ/mol indicated physical adsorption of inhibitor molecules. It has been observed that adsorption of negatively charged species is facilitated due to the positively charged metal. But positively charged species can also be adsorbed and protect the positively charged metal surface acting with a negatively charged intermediate such as acid anions, adsorbed on metal surface [37, 181, 233]. Obtained values of Gibbs energy were plotted against temperature in Fig.54 in accordance with the following basic Eq.(14) [72,159]. Intercept of graph between ΔG_{ads} versus T in Fig.54 gives value of ΔH_{ads} and by putting the value of intercept in Eq.(14) values of ΔS_{ads} were obtained .These obtained adsorption parameters Gibbs free energy of adsorption (ΔG_{ads}), enthalpy of adsorption (ΔH_{ads}) and entropy of adsorption (ΔS_{ads}), are listed in Table35. A segmented line of two opposite slopes was obtained in Fig.54 indicating two sets of adsorption sites having different ΔH_{ads} values. Similar type of results have been found in previous study between ΔG_{ads} and T(K) by E.A. Noor [159]. The calculated ΔH_{ads} values have been found negative and positive indicating both exothermic adsorption process [85,134,136,162] and endothermic adsorption process [94,237] respectively, depend upon the specific temperature range. Similar type of comprehensive adsorption processes were obtained in previous study [159]. Exothermic process is attributed to either physical or chemical adsorption or mixture of both [42], while the endothermic process is attributed to chemisorption [65]. In exothermic process, values of ΔH_{ads} predict physiorption or chemisorption. For physiorption values of ΔH_{ads} is lower than

40kJ/mol while for chemisorption it approaches to 100kJ/mol [39,251]. Values of ΔH_{ads} in Table35 indicate both physiorption and chemisorption.

Negative values of ΔS_{ads} indicate decrease in entropy of adsorption process. This behaviour can be explained as follows: Before the adsorption of inhibitor molecules onto mild steel surface, inhibitor molecules might freely move in bulk solution (inhibitor molecules were chaotic). But with the process of adsorption, inhibitor molecules were orderly adsorbed onto the steel surface as a result decrease in entropy is observed [132, 133]. The obtained positive values of ΔS_{ads} are the algebraic sum of the adsorption of organic molecules and the desorption of water molecules [78,137] .Therefore the positive values of entropy of adsorption is the result of the substitution process, which can be attributed to the increase in the solvent entropy and more positive water desorption entropy [29, 151]. A more interesting behaviour is observed in Table 35 that negative ΔS_{ads} value is accompanied with negative ΔH_{ads} value. This further agrees that when the adsorption is an exothermic process, it must be accompanied by a decrease in the entropy change and vice versa [159, 228].

CONCLUSIONS:

1. Result showed that AEWHL is good corrosion inhibitor for mild steel in 1M HCl solution.
2. Corrosion rates increase with increase in temperature and decrease with increase in inhibitor concentration.
3. Inhibition efficiencies increases at lower temperature suggest the physiorption process of inhibitor on mild steel surface.
4. Apparent activation energy increases with increase in inhibitor concentrations also suggests pysiorption.
5. Enthalpy of adsorption comes out to be negative and positive showing comprehensive (physical and chemical) adsorption of inhibitor molecules on mild steel surface.
6. The values of Gibbs free energies calculated were negative shows spontaneity of corrosion inhibition process of mild steel in 1M HCl in AEWHL.

4.8 AQUEOUS EXTRACT OF WATER HYACINTH LEAVES IN 1M H_2SO_4

CORROSION RATES:

Corrosion rates were calculated by using Eq.(1)[159]. Table36 shows that corrosion rates of mild steel decrease with increase in concentration of AEWHL as inhibitor at all studied temperatures. This could be subjected to the adsorption of the phyto-constituents of inhibitor molecules with increase in concentration of inhibitor. The corrosion rate obeys Arrhenius type reaction, as it increases with rise in temperature [159].

INHIBITION EFFICIENCY:

From the obtained corrosion rates, inhibition efficiencies were calculated by using Eq.(2) [159,246]. Fig.55 represents the variation of IE% with different concentrations of AEWHL at various studied temperatures. Data in Table37 show that IE% increases or decreases with increasing temperatures at different studied extract concentrations of AEWHL. This indicates the comprehensive adsorption (physical and chemical adsorption) of inhibitor species on mild steel surface [159]. Such type of observation was found in previous study by Noor [159]. Further it has been observed that IE% were increase with increase in inhibitor concentration 64.78% inhibition efficiency is observed at 5% (v/v) concentration of inhibitor at 30°C.

KINETIC PARAMETERS:

Corrosion rates of mild steel specimens were calculated using the kinetic relationship according to Eq.(3) [114,160]. Fig 56 represents plot between logCR and $\log C_{inh}$ values at various studied temperatures. B and K were calculated by slope and intercept of straight lines of the graph.

The obtained results in Table 38 can be discussed as follows [159].

- Negative values of B indicate that corrosion rate is inversely proportional to concentration of inhibitor. In other words the corrosion rates decrease with increase in concentration of inhibitor species.
- The high negative values of B reflect good inhibitive property of inhibitor. High negative value of B can be observed as steep slope in graph [Fig.56].
- Value of B is high at lower temperatures, indicates that inhibitive species is more effective at comparatively lower temperatures.
- The increase in K values with increase in temperature, indicating the increase in corrosion rates with temperatures.

THERMODYNAMIC AND ACTIVATION PARAMETERS:

Thermodynamic and activation parameters like apparent activation energy E_{act}, enthalpy of activation ΔH^*entropy of activation ΔS^* were calculated for steel dissolution process. Activation energies E_{act} were calculated from the slopes of Arrhenius plots drawn between logCR and 1/T in Fig.57 according to the Arrhenius Eq.(4) [232,246]. Table39 represents the calculated data of activation energies. The values of activation energies in presence of inhibitor were found higher than in uninhibited solution. This indicates the formation of higher energy barrier in corrosion reaction by inhibitor molecules. The increase in E_{act} for corrosion process further interpreted as physical adsorption of inhibitor species on mild steel surface [136, 166, 181]. Besides this according to Damaskin [58], the value of activation energy lesser than 80kJ/mol and even smaller than 5kJ/mol represents physical adsorption. This assertion supports the experimental results obtained in the present work. The values of enthalpy of activation ΔH^* and entropy of activation ΔS^* were calculated by using transition state Eq.(5) [232, 246]. A plot of log (CR/T) versus 1/T in Fig.58 gave a straight line with a slope of ($-\Delta H^*/2.303R$) and intercept of [(log R/Nh) + ($\Delta S^*/2.303R$)] from which the values of ΔH^* and ΔS^* were calculated (Fig.58). These values are tabulated in Table 39. Values of ΔH^*were found positive. Positive values indicate endothermic nature of steel dissolution process [37, 153, 246]. Endothermic process further indicates that mild steel dissolution reduces at lower temperatures and increases with increase in temperatures. Negative values of ΔS^* are indicative of formation

of activated complex in rate determining step, which represents association rather than dissociation step, meaning that the decrease in disorder takes place on going from reactants to activated complex [37, 85, 223].

It is also observed from data in Table 39 that E_{act} and ΔH^* vary in the same manner. Values of both E_{act} and ΔH^* increase with increase in concentration of inhibitor, suggesting that energy barrier is increases with increase in inhibitor concentration. This means that corrosion reaction will further be pushed to surface sites that are characterized by progressively higher values of E_{act} as the concentration of inhibitor becomes greater [37, 221, 227]. The values of activation energy were found larger than corresponding values of enthalpy of activation, indicate the involvement of a gaseous reaction, simply hydrogen evolution in corrosion process, associated with a decrease in total reaction volume [159].

ADSORPTION ISOTHERMS:

The nature of adsorption can be explained by understanding the process at metal/electrolyte interface. Further to understand the nature of adsorption, obtained surface coverage (θ) were fitted in different adsorption isotherms. The mathematical expressions for Langmuir adsorption isotherm can be expressed by the Eq.(8) [38,83,161,185,237]. Freundlich and Temkin adsorption isotherms were also drawn according to Eq.(10) [117] and Eq.(11) [152, 172] and straight lines were obtained in Fig.59, Fig.60 and Fig.61 respectively.

ADSORPTION PARAMETERS:

[Gibbs Energy of Adsorption[ΔG_{ads}], Enthalpy of Adsorption[ΔH_{ads}] ,Entropy of Adsorption [ΔS_{ads}] :

Values of K_{ads} were calculated by the intercept of Langmuir isotherm drawn according to the Eq.(8) between log (θ/1- θ) and logC_{inh} and by using this Gibbs energy of adsorption was calculated by using Eq.(13) [115,159]. The values of ΔG_{ads} were tabulated in Table40. ΔG_{ads} values has been found negative at all studied temperatures indicating spontaneous adsorption process of inhibitor molecules on metal surface and strong interactions between inhibitor molecules

and metal surface [1, 37, 49, 67, 225, 226]. Generally values of ΔG_{ads} upto -20kJ/mol are consistent with electrostatic interactions (physical adsorption) between charged molecules and charged metal surface and values upto -40kJ/mol or higher involve charge sharing or transfer from inhibitor molecules to metal surface to form coordinate type of bond (chemical adsorption) [37,49,90,132, 163,165,233]. The values of ΔG_{ads} were found from -11.95kJ/mol to-14.72kJ/mol. The obtained values of ΔG_{ads} were found less than -20kJ/mol indicated physical adsorption of inhibitor molecules. It has been observed that adsorption of negatively charged species is facilitated due to the positively charged metal. But positively charged species can also be adsorbed and protect the positively charged metal surface acting with a negatively charged intermediate such as acid anions, adsorbed on metal surface [37,181,233]. Obtained values of Gibbs energy were plotted against temperature in Fig.62 in accordance with the basic Eq.(14) [72,159]. Intercept of graph between ΔG_{ads} versus T gives value of ΔH_{ads} and by putting the value of intercept in Eq.(14) values of ΔS_{ads} were obtained .These obtained adsorption parameters Gibbs free energy of adsorption (ΔG_{ads}), enthalpy of adsorption (ΔH_{ads}) and entropy of adsorption (ΔS_{ads}) are listed in Table40. A segmented line of two opposite slopes was obtained in Fig.62 indicating two sets of adsorption sites having different ΔH_{ads} values. Similar type of results have been found in previous study between ΔG_{ads} and T(K) by E.A. Noor [159]. The calculated ΔH_{ads} values have been found negative and positive indicating both exothermic adsorption process [85, 134, 136, 162] and endothermic adsorption process [94, 237] respectively, depending upon the specific temperature range. Similar type of comprehensive adsorption processes were obtained in previous study [159]. The exothermic process is attributed to either physical or chemical adsorption or mixture of both [42], while the endothermic process is attributed to chemisorption [65]. In exothermic process, values of ΔH_{ads} predict physiorption or chemisorption. For physiorption values of ΔH_{ads} is lower than 40kJ/mol while for chemisorption it approaches to 100 kJ/mol [39, 251]. Values of ΔH_{ads} in Table 40 indicate physiorption. Negative values of ΔS_{ads} indicate decrease in entropy of adsorption process. This behaviour can be explained as follows: Before the adsorption of inhibitor molecules onto mild steel surface, inhibitor molecules

might freely move in bulk solution (inhibitor molecules were chaotic). But with the process of adsorption, inhibitor molecules were orderly adsorbed onto the steel surface as a result decrease in entropy is observed [132, 133]. The obtained positive values of ΔS_{ads} are the algebraic sum of the adsorption of organic molecules and the desorption of water molecules [78,137] .Therefore the positive values of entropy of adsorption is the result of the substitution process, which can be attributed to the increase in the solvent entropy and more positive water desorption entropy [29, 151]. A more interesting behaviour is observed in Table 40 that negative ΔH_{ads} value is accompanied with negative ΔS_{ads} value. This further agrees that when the adsorption is an exothermic process, it must be accompanied by a decrease in the entropy change and vice versa [159, 228].

CONCLUSIONS:

1. Result showed that AEWHL is good corrosion inhibitor for mild steel in 1M H_2SO_4 solution.
2. Corrosion rates increase with increase in temperature and decrease with increase in inhibitor concentration.
3. Inhibition efficiency increases or decreases with increase in temperatures at given concentrations of inhibitor suggesting comprehensive adsorption process.
4. Apparent activation energy increases with increase in inhibitor concentrations also suggests pysiorption.
5. Enthalpy of adsorption comes out to be negative and positive suggests exothermic and endothermic adsorption process.
6. The values of Gibbs free energies calculated were negative show spontaneity of corrosion inhibition process of mild steel in 1 M H_2SO_4 in AEWHL.

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Annexure - 1

ABBREVIATIONS

1. **AAS :** Atomic Absorption Sprectoscopy
2. **AECPL :** Aqueous extract of Calotropis procera leaves
3. **AELCL :** Aqueous extract of Lantana camara leaves
4. **AENOL :** Aqueous extract of Nerium oleander leaves
5. **AEWHL :** Aqueous extract of Water hyacinth leaves
6. **AFM :** Atomic force microscopy
7. **AO :** Argan oil
8. **CC :** Commiphora caudata
9. **EDX :** Energy-Dispersive X-ray Analysis
10. **EFM :** Electron Frequency Modulation
11. **EIS :** Electron Impedance Sprectoscopy
12. **FITR :** Fourier Transform Infrared Spectroscopy
13. **GA :** Gum Arabic
14. **GIE :** Garcina indica extract
15. **HE :** Hydrogen Evolution
16. **LD :** Lavandula dentata
17. **ML :** Mass Loss
18. **OCP :** Open Circuit Potential
19. **PDP :** Potentiodynamic Polarization
20. **SEM :** Scanning Electron Microscopy
21. **TA :** Tryptamine
22. **TSC :** Tri Sodium Citrate
23. **XRD :** X-Ray Diffraction
24. **BLE :** Breadfruit leaves extract

Annexure - 2

RESEARCH PAPERS PUBLISHED/ COMMUNICATED

1. Paper entitled "GREEN APPROACH TO CORROSION INHIBITION OF MILD STEEL IN 1 M HCl SOLUTION BY AQUEOUS EXTRACT OF *LANTANA CAMARA L.* LEAVES" has been published in International Journal of Chemical Sciences, 13(3), (2015), 1157-1162.

2. Paper entitled "CORROSION INHIBITION OF MILD STEEL WITH AQUEOUS EXTRACT OF *CALOTROPIS PROCERA L.* LEAVES IN 1M HCl SOLUTION" has been published in International Journal of Current Research, 8(2) (2016), 26064-26070.

3. Paper entitled " ADSORPTION BEHAVIOUR AND CORROSION INHIBITION PROPERTIES OF AQUEOUS EXTRACT OF LEAVES OF NERIUM OLEANDER L. IN HYDROCHLORIC ACID SOLUTION" has been published in World Journal of Pharmacy and Pharmaceutical Sciences, 6(5) (2017), 40-49.

4. Paper entitled "CORROSION INHIBITION AND ADSORPTION BEHAVIOUR OF AQUEOUS EXTRACT OF LEAVES OF WATER HYACINTH IN 1M HYDROCHLORIC ACID SOLUTION" has been communicated to Corrosion Science.

Annexure - 3

PARTICIPATION IN SEMINARS/ SYMPOSIA/CONFERENCES/ ANNUAL CONVENTIONS

1. Presented a poster in the International Conference on "Frontiers at the Chemistry- Allied Sciences Interface (FCASI-2016)" organized by Centre of Advanced Study, Department of Chemistry, University of Rajasthan, Jaipur (Raj.) during 25-26 April 2016. (Title: Mitigation of Mild Steel Corrosion by Calotropis procera L. Leaves in 1M H_2SO_4 Solution).
2. Presented a poster in the International Conference on "Nascent Developments in Chemical Sciences: Opportunities for Academia-Industry Collaboration" organized by Department of Chemistry, Birla Institute of Technology & Science, Pilani (Raj.), Pilani Campus during 16-18 October 2015. (Title: Green Approach to Protect Mild Steel Corrosion in Acidic Media).
3. Presented a poster in the National Conference on "Recent Advancements in Chemical Sciences" organized by Department of Chemistry, MNIT Jaipur during 21-23 August 2015. (Title: Corrosion Inhibition of Mild Steel in 1M H_2SO_4 Solution by Aqueous Extract of Lantana camara L. Leaves).
4. Presented a paper in 4th International Conference on "Advance Trends in Engineering, Technology and Research" (ICATETR-2015), organized by Bal Krishna Institute of Technology, Kota (Raj.) during 19-20 June 2015. (Title: Thermodynamic and Adsorption Parameters of Aqueous Extract of Lantana camara L. Leaves on Corrosion of Mild Steel Surface in Acidic Medium).
5. Presented a paper in 3rd International Conference on "Advance Trends in Engineering, Technology and Research" (ICATETR-2014), organized by Bal Krishna Institute of Technology, Kota (Raj.) during 22nd-24th December 2014.(Title: Inhibitory Action of Carum Copticum Seeds Extract on Corrosion of Iron in 1M Acetic Acid).

6. Actively participate in 5th National Academic Workshop on "Organic Reaction Mechanisms & Analytical Techniques used in Chemical Sciences" organized by Department of Pure and Applied Chemistry, University of Kota, Kota (Rajasthan) held at University of Kota and sponsored by UGC New Delhi during 21-25 October 2013.
7. Presented a paper in "National Conference on Global Environmental Changes and Disaster Management for Sustainable life on Earth – A burning issue" held at Maharishi Arvind College of Engineering & Technology, Ranpur, Kota on 21st October 2013.

   (Title: Inhibition of the corrosion of mild steel in phosphoric acid solutions by aqueous extract of fenugreek seeds).

PUBLISHED PAPERS

Available online at http://www.journalcra.com

International Journal of Current Research
Vol. 8, Issue, 02, pp.26064-26070, February, 2016

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

ISSN: 0975-833X

RESEARCH ARTICLE

CORROSION INHIBITION OF MILD STEEL WITH AQUEOUS EXTRACT OF *CALOTROPIS PROCERA L.* LEAVES IN 1M HCl SOLUTION

***Priya Bhardwaj, Seema Agarwal and S. Kalpana**

Electrochemistry and Environmental Chemistry Lab, Department of Chemistry, Government College, Kota –324001 (Raj.) India

ARTICLE INFO

Article History:
Received 28th November, 2015
Received in revised form
15th December, 2015
Accepted 15th January, 2016
Published online 14th February, 2016

Key words:

Calotropis Procera L., Corrosion,
Langmuir adsorption isotherm,
Mild steel, Weight loss method.

ABSTRACT

The inhibition of mild steel (MS) in 1 M HCl solution with aqueous extract of *Calotropis procera L.* leaves (AECPL) was studied by weight loss method at 303-333K temperatures. It was found that inhibition efficiency increased with increase in concentration of extract and decreased with increase in temperature. Maximum 60.86%inhibition efficiency was observed at 303 K and at 8% (v/v) concentration of extract. Adsorption of extract at mild steel surface follows Langmuir adsorption isotherm. Physiorption is proposed by the values of Gibbs free energy, variation in inhibition energy with temperature and with activation energy values trend. Negative Gibbs energy reveals the spontaneity of inhibition process in extract at studied temperatures.

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Citation: **Priya Bhardwaj, Seema Agarwal and S. Kalpana**, **2016.** "**Corrosion inhibition of mild steel with aqueous extract of *Calotropis procera L.* leaves in 1m HCl solution**", *International Journal of Current Research*, 8, (02), 26064-26070.

INTRODUCTION

Steel corrosion inhibition phenomenon have become an industrial and academic topic especially in acidic media (Bentiss *et al*., 2000). This is because of the increasing industrial applications of acid solutions in acid pickling, industrial cleaning, acid descaling, oil-well acidizing in oil recovery and the petrochemical processes. Besides this corrosion rates are very high in aqueous acidic media especially when soluble corrosion products are formed (Raja *et al*., 2013). Therefore exploring better green corrosion inhibitors are important for its practical applications and environmental friendly point of view .Synthetic organic corrosion inhibitors are effective but costly, environmental polluting and harmful to living beings during their manufacture and applications. So currently researches on corrosion are focused on "green corrosion inhibitors" that show good inhibition efficiency with low risk of environmental pollution (Amin *et al*., 2007) All plant extracts, which have been shown effective corrosion inhibitors are comparatively cheap, easily available, biodegradable and called as green corrosion inhibitors.

***Corresponding author: Priya Bhardwaj,**
Electrochemistry and Environmental Chemistry Lab, Department of Chemistry, Government College, Kota –324001 (Raj.) India.

Different plant parts have been studied as corrosion inhibitors in acidic and alkaline media (Ostovari *et al*., 2009; Alaneme *et al*., 2015; Kamal *et al*., 2012; James *et al*., 2009; Ambrish *et al*., 2010; Ibrahim *et al*., 2011; Bhardwaj *et al*., 2015). In the present study aqueous extract of leaves of *Calotropis Procera L*. has been choosen as corrosion inhibitor for mild steel in 1M HCl solution and findings are discussed in the light of inhibitor concentration, temperature , adsorption properties, kinetic properties, thermodynamic properties .Weight loss (gravimetric analysis) method is applied to obtain inhibition efficiencies.

MATERIALS AND METHODS

Preparation of extract

The leaves of *Calotropis procera L*. plant were taken, washed and air dried for 6-7 days, crushed and grind mechanically. 20 g of ground leaves were heated in 250 ml distill water for one hour using air condenser at 70°C - 80°C. This extract was left overnight and then filtered and make up to 250 ml with distill water for the experiment.

Preparation of steel specimens

Cylindrical mild steel specimens of 4.9 cm length and 0.70 cm diameter were taken and abraded with a series of emery papers,

degreased with acetone, washed with distill water, dried and constant weight was recorded by electronic balance.

Solution Preparation

1M HCl solution was prepared by 37% HCl (Merk Ltd.) using distill water. The employed concentration range of aqueous extract of *Calotropis procera L.* leaves(AECL) was 1% to 8% (v/v).

Gravimetric Measurements

Gravimetric method is widely used method because of its reliability and simplicity in corrosion inhibition experiments. For each experiment 100 ml test solutions were taken in 250 ml beaker and cylindrical specimen was immersed in it with plastic thread for one hour .The experiments were carried out at different temperatures ranges from 303 K to 333K in thermostatic water bath. After one hour specimens were removed, washed with distill water, acetone dried and abraded with series of emery papers and then weighted accurately with electronic balance. It was noted that the surfaces of specimens became more rough in test solutions without the inhibitor than the surfaces of specimens which were immersed in test solutions containing different concentrations of inhibitor.

RESULTS AND DISCUSSION

Effect of temperature on corrosion rates

Corrosion rates were calculated by following equation (Mourya *et al*., 2014; Yadav *et al*., 2014).

$$C\,R\ (g\ cm^{-2}min^{-1}) = \left(\frac{W1-W2}{A\,t}\right) \quad (1)$$

Where CR is corrosion rate, W_1 is weight loss of mild steel specimen without inhibitor and W_2 is weight loss of mild steel specimen with inhibitor, A is area of MS specimen and t is immersion time.

Table 1 represents that corrosion rates increases with increase in temperatures and decreases with increase in concentration of inhibitor. I t is clear that corrosion rates obey Arrhenius type reactions as it increases with increase in solution temperature (31).

Effect of temperature on inhibition efficiency

From the obtained corrosion rates, inhibition efficiencies were calculated by using following equation (Mourya *et al*., 2014; Behpour *et al*., 2011).

$$IE\ \% = \left(\frac{CR - CR_{inh}}{CR}\right) \times 100 \quad (2)$$

Where CR is the corrosion rate in absence of inhibitor and CR_{inh} is corrosion rate in presence of inhibitor. AECL are given in Table 1.

Data in Table 1 reveal that inhibition efficiency increased with an increase in inhibitor concentration. This suggests that the inhibitor species adsorbed on steel /solution interface where the adsorbed species mechanically screen the coated part of steel surface from the action of corrosion medium (31). The variation in inhibition efficiency was detected with increasing temperatures in Table 1.

It is clear from the data that inhibition efficiency decreases with rise in temperatures, suggests possible desorption of adsorbed species. It further suggests physiorption of inhibitor molecules on steel surfaces (39). The surface coverage θ is calculated by in the given equation (Yadav *et al*., 2014).

$$\theta = \left(\frac{CR - CR_{inh}}{CR}\right) \quad (3)$$

θ is the surface coverage , CR is the corrosion rate in absence of inhibitor and CR_{inh} is corrosion rate in presence of inhibitor .

Kinetic parameters

Assuming that corrosion rates of steel specimens against concentration of inhibitor obeys kinetic relationship as equation (Khamis *et al*., 2000; Noor 2005).

$$\log CR = \log K + B \log C_{inh.} \quad (4)$$

Where K is rate constant and equal to CR when inhibitor concentration is unity. B is reaction constant which is measure of inhibitor effectiveness and C_{inh} is the concentration v/v % (ml/100ml) of AECL.

Fig. 2 represents plot between log CR and log C_{inh} values at various studied temperatures. B and K were calculated by slope and intercept of straight lines of the graph.

The obtained results in Table 2 can be discussed as follows (Noor 2007).

- Negative values of B indicates that corrosion rate is inversely proportional to concentration of inhibitor. In other words the corrosion rates decrease with increase in concentration of inhibitor species.
- The high negative values of B reflects good inhibitive property of inhibitor High negative value of B can be observed as steep slope in graph (Fig.1).
- Value of B is high at lower temperatures, indicates that inhibitive species is more effective at comparatively lower temperatures.
- The increase in K values with increase in temperature, indicating the increase in corrosion rates with temperatures.

Thermodyanamic and activation parameters

The thermodynamic and activation parameters like apparent activation energy E_{act} , enthalpy of activation ΔH^*,entropy of activation ΔS^* were calculated for steel dissolution process. Activation energy E_{act} were calculated by following Arrhenius equation (Yadav *et al*., 2014).

$$\log CR = \log A - \left(\frac{Eact}{2.30\ 3R\,T}\right) \quad (5)$$

Table 1. Inhibition efficiencies and corrosion rates of mild steel corrosion in 1MHCl in different concentration of AECL at different temperatures

Conc (v/v)%	CR x 10^{-3} ($g/cm^2/min$)				IE %			
	303 K	313 K	323 K	333 K	303 K	313 K	323 K	333 K
0	0.69	1.37	2.33	3.07	--	--	---	---
1	0.59	1.21	2.17	2.88	14.49	11.67	06.86	06.18
2	0.41	1.08	1.94	2.81	40.57	20.16	16.73	08.46
3	0.38	0.99	1.93	2.74	44.92	27.73	17.16	10.74
5	0.33	0.86	1.86	2.64	52.17	37.22	20.17	14.10
8	0.27	0.72	1.57	2.56	60.86	47.44	32.61	16.43

Table 2. Kinetic parameters and regression coefficients for the corrosion of mild steel in 1M HCl containing AECL at different temperatures

Temp (^{0} K)	Kinetic parameters		
	R^2 values	B	$K(x10^{-3})$ ($g/cm^2/min$)
303	0.974	-0.3584	-0.5736
313	0.968	-0.2514	-1.2755
323	0.898	-0.1363	-2.1923
333	0.956	-0.0538	-2.9080

Table 3. Thermodynamic Activation parameters for the corrosion process of mild steel in solution containing different concentrations of AECL in 1 mol HCl solutions

CONC (v/v %)	E_{act} (KJ/mol)	ΔH^* (KJ/mol)	ΔS^* (J/mol/K)
0	41.26	38.83	-177.64
1	43.20	41.39	-170.56
2	52.93	50.41	-143.63
3	54.91	52.48	-137.55
5	57.86	54.99	--130.48
8	60.93	58.49	-120.69

Table 4. Adsorption parameters obtained from Langmuir adsorption isotherm (A) and Gibbs free energy,entropy and enthalpy for adsorption process of inhibitor at mild steel in 1 M HCl solution in AECL at different studied temperatures

TEMP (K)	R^2	K_{ads}	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (J/mol/K)
303	0.887	0.2358	-13.76		-73.23
313	0.998	0.1389	-12.84	-35.95	-73.83
323	0.912	0.0869	-11.99		-74.17
333	0.994	0.0659	-11.59		-73.15

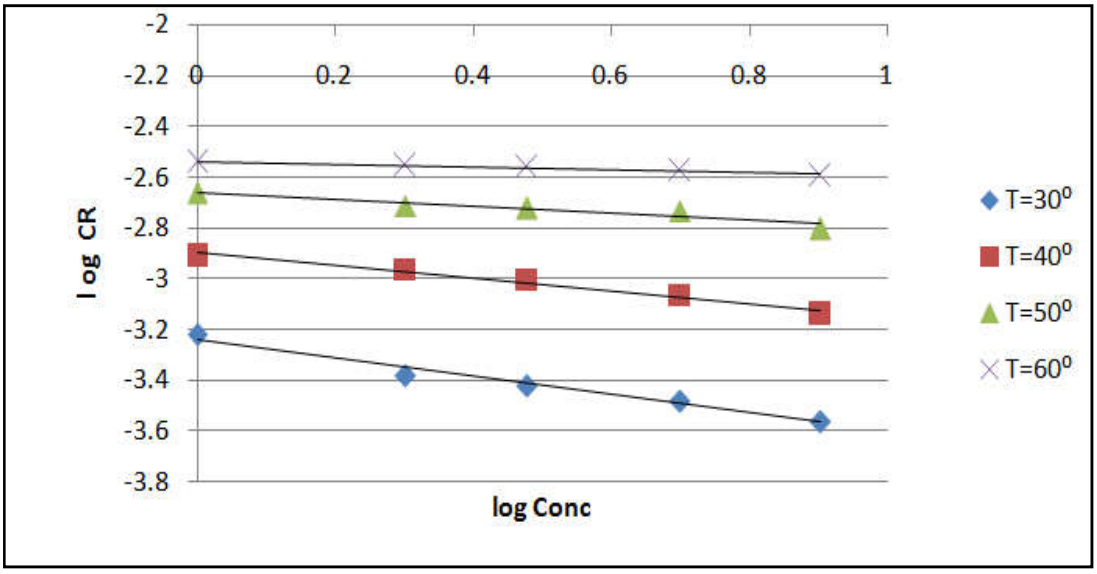
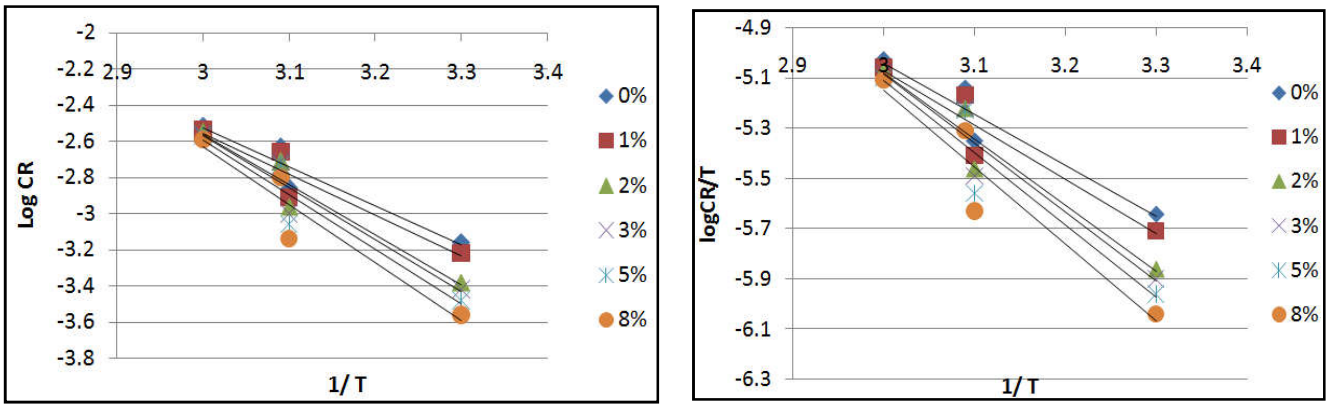


Figure 1. Variation of Log CR vs Log C of corrosion inhibition process by AECL at studied temperatures



(A) (B)

Figure 2. (A) Arrhenius plot and (B) Transition state plot for corrosion of mild steel in 1M HCl in the absence and presence of various concentrations of AECL

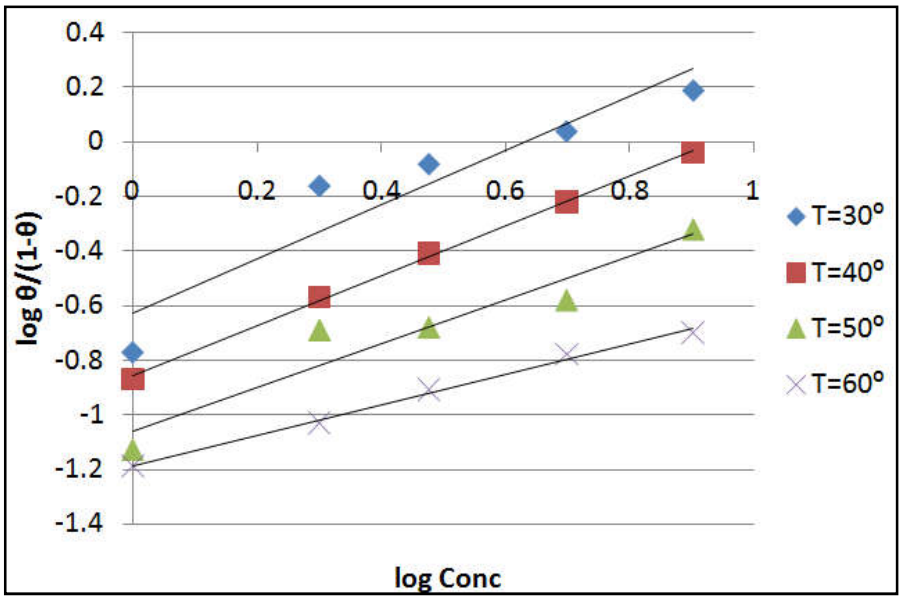


Figure 3. Langmuir adsorption isotherm for corrosion of mild steel in 1M HCl in the absence and presence of various concentrations of AECL at different temperatures

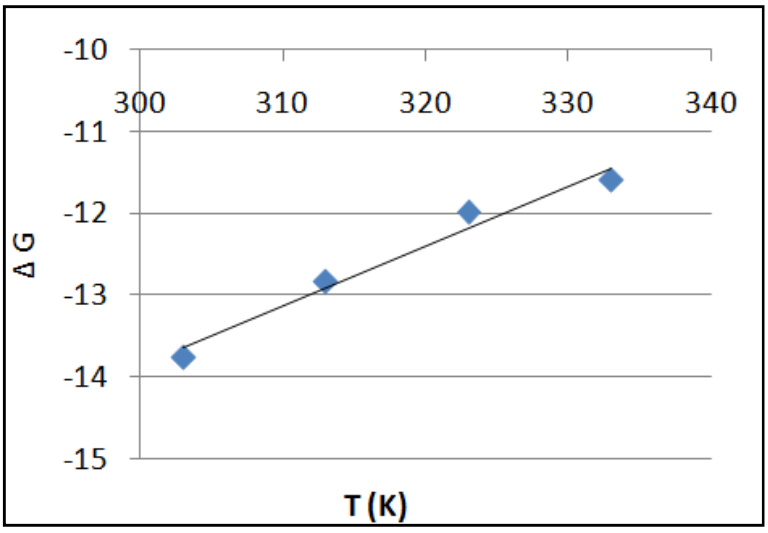


Figure 4. Variation of Gibbs energy change with different studied temperatures

Where A is Arrhenius pre exponential factor, E_{act} is activation energy, R is universal gas constant, T is absolute temperature. The slope of log CR vs 1/T gives the values of activation energies at studied concentrations. Table 3 contains the calculated data of actvation energies. The values of activation energies in presence of inhibitor species were found higher than uninhibited solutions The higher the concentration of inhibitor, the higher the activation energy is observed .It is observed that inhibitive causes a rise in activation energy value when compared to the blank solutions (Manssouri *et al*., 2014). The change in values of activation energies is due to the modification of the mechanism of corrosion process in presence of adsorbed inhibitor molecules (Riggs *et al*., 1967) and could be often interpreted as an indication for the formation of an adsorbed film on metal surface (Schorr *et al*., 1972; Clark *et al*., 1979)). The rise in activation energy indicates the formation of energy barrier in corrosion process in presence of the inhibitor and the increase in activation energy with rise in temperature could be interpreted as physical adsorption (40). The values of enthalpy of activation ΔH^* and entropy of activation ΔS^* were calculated by following transition state equation (Yadav *et al*., 2014).

$$\log\left(\left(\frac{CR}{T}\right)\right) = \left(\log\left(\frac{R}{Nh}\right)\right) + \left[\left(\frac{\Delta S*}{2.30\ 3R}\right)\right) - \left(\left(\frac{\Delta H*}{2.30\ 3RT}\right)\right] \quad (6)$$

Where h is planck's constant, N is Avogadro number R is the gas constant A plot of log (CR/T) vs 1/T gave a straight line with slope of (-ΔH*/2.303R) and intercept of [(log R/N h) + (ΔS^*/2.303 R)] from which the values of ΔH^* and ΔS^* were calculated These values are tabulated in Table 3. The values of ΔH^* and ΔS^* in presence of inhibitor were higher than uninhibited solutions .The positive values of ΔH^* reflects endothermic nature of steel dissolution process (Guan *et al*., 2004) and negative values of ΔS^* indicate the formation of activated complex in rate determining step, represents an association rather than dissociation, means decrease in disorder of system due to adsorption of inhibitor molecules on to the metal surface (Abd-Ei-Nabey *et al*., 1996). This reveals the formation of an ordered stable layer of inhibitor on steel surface (Yurt *et al*., 2004)

Adsorption isotherm and gibbs energy

The mechanism of adsorption can also be predicted by metal/electrolyte interface interaction. To understand the nature of adsorption, obtained surface coverage θ were fitted in different adsorption isotherms. The mathematical expressions for Langmuir (Noor and Al-Moubaraki., 2008).

$$\frac{C}{\theta} = \frac{1}{Kads} + C_{inh} \text{ (Langmuir isotherm)} \quad (7)$$

Rearranging the above equation

$$(\theta / 1-\theta) = K_{ads}.\ C_{inh} \quad (8)$$

$$\text{Or} \quad \log(\theta / 1-\theta) = \log K_{ads} + \log C_{inh} \quad (9)$$

Where K_{ads} is the equilibrium constant of adsorption , a is the molecular interaction factor in adsorbed layer,θ is the surface coverage, (1-θ) is the uncovered surface, C_{inh} is the concentration of inhibitor

The value of K_{ads} obtained from Langmuir adsorption isotherm (A) of Fig.3 is related by gibbs energy by the following equation (Khamis 1990).

$$K_{ads} = \frac{1}{C_{H_2O}}\ exp^{(-\Delta G/RT)} \quad (10)$$

It can be written as: $\Delta G = -2.303\ RT\ \text{Log}\ (K_{ads.}\ C_{H2})$ (11)

Where C_{H2O} is the concentration of water in (ml / L) at metal/ solution interface, R is universal gas constant and T is absolute temperature. Values of K_{ads} were calculated by the intercept of Langmuir isotherm log (θ /1- θ) vs log C_{inh} . The values of ΔG_{ads} were tabulated in Table 4. Obtained values of Gibbs energy were plotted againt temperature in accordance with the following basic equation (El-Awady *et al*., 1992).

$$\Delta G_{ads} = \Delta H_{ads} - T\ \Delta S_{ads} \quad (12)$$

Intercept of graph between ΔG_{ads} vs T give value of ΔH_{ads} and by putting the value of intercept in equation 12 values of ΔS_{ads} were obtained .These values are listed in Table 4.

The negative values of ΔG_{ads} indicated spontaneous corrosion inhibition process (Abd-El-Rahim *et al*., 2001; Tang *et al*., 2006; Tang *et al*., 2003). Table 4 shows increase (values becomes less negative) in Gibbs energy with temperature ,indicating the exothermic process, at which adsorption was unfavourable with increase in reaction temperature as a result of inhibitor desorption from the steel surface (Noor 2007). The values of of ΔH_{ads} and ΔS_{ads} also predict the mechanism of inhibitor adsorption. The negative values of ΔG_{ads} are between -11.55 KJ/mol to -13.76 KJ/mol indicating physiorption of inhibitor species on steel surface. Generally values of ΔG_{ads} up to -20 KJ/ mol are consistent with electrostatic interaction (physiorption) while more negative values than -40 KJ/mol are due to charge sharing from inhibitor species to metal surface to form a co-ordinate type of bond (Umoren *et al*., 2009) The values of ΔH_{ads} are come out to be negative, shows exothermic adsorption process of adsorption of inhibitor on steel surfaces (Obi-Egbedi *et al*., 2012), and this is further proved by lower inhibition efficiencies in Table 1 at higher temperatures.

The exothermic process is attributed to either physical or chemical adsorption or mixture of both (Bentiss *et al*., 2005), whereas an endothermic process corresponds to chemisorptions (Lebrini *et al*., 2011). In exothermic process values of ΔH_{ads} predicts physiorption or chemisorption process. For physiorption values of ΔH_{ads} is lower than 40 KJ/mol while for chemisorption it is approaches to 100 KJ/mol (Zarrouk *et al*., 2010). The value of ΔH_{ads} in table 4 indicates physiorption process. The negative value of ΔS_{ads} in Table 4 shows decrease in entropy. This is agrees with what expected, when the adsorption is an exothermic process, it must be accompanied by a decrease in the entropy energy change and vise versa (Thomas and Thomas, 1981)

Conclusion

1. Result showed that AECPL is good corrosion inhibitor for mild steel in 1M HCl solution.
2. Corrosion rates increases with increase in temperature and decreases with increase in inhibitor concentration.
3. Inhibition efficiencies increases at lower temperature suggest the physiorption process of inhibitor on mild steel surface.
4. Apparent activation energy increases with increase in inhibitor concentrations also suggests pysiorption.
5. Enthalpy of activation comes out to be negative which show endothermic process.
6. The values of Gibbs free energies calculated were negative shows spontaneity of corrosion inhibition process of mild steel in 1 M HCl in AECPL.

Acknowledgement

The authors are thankful to the Head of Chemistry Department and Principal, Government College, Kota for providing necessary laboratory facilities.

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WORLD JOURNAL OF PHARMACY AND PHARMACEUTICAL SCIENCES
SJIF Impact Factor 6.647
Volume 6, Issue 6, 1417-1430 Research Article ISSN 2278 – 4357

ADSORPTION BEHAVIOUR AND CORROSION INHIBITION PROPERTIES OF AQUEOUS EXTRACT OF LEAVES OF NERIUN OLENDER L. IN HYDROCHLORIC ACID SOLUTION

Priya Bhardwaj[1]*, Seema Agarwal[2] and S. Kalpana[3]

Electrochemistry & Environmental Chemistry Lab, Department of Chemistry, Government College KOTA –324001 (Rajasthan) INDIA.

Article Received on
10 April 2017,
Revised on 30 April 2017,
Accepted on 20 May 2017,
DOI: 10.20959/wjpps20176-9365

***Corresponding Author**
Priya Bhardwaj
Electrochemistry & Environmental Chemistry Lab, Department of Chemistry, Government College KOTA –324001 (Rajasthan) INDIA.

ABSTRACT

The inhibition of mild steel (MS) in 1 M HCl solution with aqueous extract of *Nerium olender L.*leaves (AENOL) was studied by weight loss method at 303-333K temperatures. It was found that inhibition efficiency increased with increase in concentration of extract and decreased with increase in temperature. Maximum 83.76%inhibition efficiency was observed at 303 K and at 10% (v/v) concentration of extract. Adsorption of extract at mild steel surface follows Langmuir adsorption isotherm. Physiorption is proposed by the values of Gibbs free energy, variation in inhibition energy with temperature and with activation energy values trend. Negative values of Gibbs energy reveals the spontaneity of inhibition process in extract at studied temperatures.

KEYWORDS: Nerium oleander L., Corrosion, Langmuir adsorption isotherm, Mild steel, Weight loss method.

1. INTRODUCTION

Steel is widely used alloy in transportation, mechanical and petrochemical industries. However it is suffered from a major problem known as corrosion. Corrosion is the degradation of metals and their alloys by an electrochemical reaction and environment. The introduction of corrosion inhibitors is the best way to prevent metallic corrosion and can save the great economic loss of a country.

This has been provoked the researchers to search new eco-friendly, low cost, easy available effective corrosion inhibitors to foster green environment and for the sustainability of living beings. These compounds are natural products like leaves, roots, barks and stem extracts which effectively absorbs on metal surface and protect metals and their alloys from corrosion in acidic, basic and neutral media.

Literature survey reveals various plant extracts that have been used as corrosion inhibitors for protection of different metals and their alloys. Extract of fenugreek seeds and leaves[18], essential oils of *Mentha spicata, Lavandula multifida, Pulicaria mauritanica*[6,37,38] *Azadirachta indica*[24,27], extract of *Ananas comosus L.*[9], *Embilica officinalis*[26], *Garcina cola and Cola nitida*[8] etc. have been studied. In the continuity of above corrosion inhibition studies, the present work reveals the adsorption behavior and corrosion prevention properties of aqueous extract of leaves of Nerium olender L. for mild steel in 1 M HCl solution.

2. MATERIALS AND METHODS

Preparation of extract

The leaves of *Nerium oleander L*. plant were taken, washed and air dried for 6-7 days, crushed and grind mechanically. 20 g of ground leaves were heated in 200 ml distill water for one hour using air condenser at 70^0C - 80^0C. This extract was left overnight and then filtered and make up to 200 ml with distill water for the experiment.

Preparation of steel specimens

Cylindrical mild steel specimens of 4.9 cm length and 0.70 cm diameter were taken and abraded with a series of emery papers, degreased with acetone, washed with distill water, dried and constant weight was recorded by electronic balance.

Solution Preparation

1M HCl solution was prepared by 37% HCl (Merk Ltd.) using distill water. The employed concentration range of aqueous extract of *Nerium oleander L*. leaves (AENOL) was 1% to 10% (v/v).

Gravimetric Measurement

Gravimetric method is widely used method because of its reliability and simplicity in corrosion inhibition experiments. For each experiment 100 ml test solutions were taken in 250 ml beaker and cylindrical specimen was immersed in it with plastic thread for one hour.

The experiments were carried out at different temperatures ranges from 303 K to 333K in thermostatic water bath. After one hour specimens were removed, washed with distill water, acetone dried and abraded with series of emery papers and then weighted accurately with electronic balance. It was noted that the surfaces of specimens became more rough in test solutions without the inhibitor than the surfaces of specimens which were immersed in test solutions containing different concentrations of inhibitor.

3. RESULT AND DISCUSSION

3.1 Corrosion rates

Corrosion rates were calculated by following equation (1).[1, 34]

$$C\,R\ (g\ cm^{-2}min^{-1}) = \left(\frac{W_1 - W_2}{A\,t}\right) \quad (1)$$

Where CR is corrosion rate, W_1 is weight loss of mild steel specimen without inhibitor and W_2 is weight loss of mild steel specimen with inhibitor, A is area of MS specimen and t is immersion time. **Table1** shows that corrosion rates of mild steel decrease with increase in concentration of AENOL inhibitor at all studied temperatures. This could be subjected to the adsorption of the phyto-constituents of inhibitor molecules with increase in concentration of inhibitor. The corrosion rate obeys Arrhenius type reaction, as it increases with rise in temperature.[19]

3.2 Inhibition efficiency

From the obtained corrosion rates, inhibition efficiencies were calculated by using following equation **(2).**[1, 34]

$$IE\ \% = \left(\frac{CR_{blank} - CR_{inh}}{CR}\right) \times 100 \quad (2)$$

Where CR_{blank} is the corrosion rate in absence of inhibitor and CR_{inh} is corrosion rate in presence of inhibitor. AENOL are given in **Table 1.** Data in **Table1** show that %IE increase with increase in extract concentration, which is an indication of an increase in number of components of extract adsorbed on mild steel surface, which block the active sites of metal from acid attack and protect the metallic corrosion.[20] Further the decrease in % I.E. with rise in temperature suggests electrostatic interaction (physical adsorption) of the extract molecules on mild steel surface. This further indicates desorption of adsorbed inhibitor species at higher

temperatures and metal dissolution takes place.[35] 83.76% inhibition efficiency is observed at 10% (v/v) concentration of inhibitor.

Table 1. Mild steel corrosion rates and inhibition efficiencies in 1 M HCl solution in absence and presence of different concentrations of AENOL at different temperatures

Conc (v/v)%	CR x 10^{-3} (g/cm^2/min)				IE %			
	303K	313K	323K	333K	303K	313K	323K	333K
0	1.17	1.75	3.72	3.85	-	-	-	-
1	0.83	1.41	3.08	3.19	29.05	19.42	17.20	17.14
2	0.79	1.32	2.84	3.14	32.47	24.57	23.65	18.44
3	0.44	0.89	2.27	2.97	62.39	49.14	38.97	22.85
5	0.34	0.79	1.73	2.74	70.94	54.85	53.49	28.83
10	0.19	0.45	1.00	1.77	83.76	74.28	73.11	54.02

3.3 KINETIC PARAMETERS

Assuming that corrosion rates of steel specimens against concentration of inhibitor obeys kinetic relationship as equation (3).[19,38]

$$\log CR = \log K + B \log C_{inh.} \quad (3)$$

Where K is rate constant and equal to CR when inhibitor concentration is unity. B is reaction constant which is measure of inhibitor effectiveness and C_{inh} is the concentration v/v % (ml/100ml) of AENOL. Figure 2 represents plot between log CR and log C_{inh} values at various studied temperatures. B and K were calculated by slope and intercept of straight lines obtained in Figure 1. The obtained results are summarized in **Table 2** which can be discussed as follows[19]

- Negative values of B indicate that corrosion rate is inversely proportional to concentration of inhibitor. In other words the corrosion rates decrease with increase in concentration of inhibitor species.
- The high negative values of B reflects good inhibitive property of inhibitor High negative value of B can be observed as steep slope in graph (Fig.1).
- Value of B is high at lower temperatures, indicates that inhibitive species is more effective at comparatively lower temperatures.
- The increase in K values with increase in temperature, indicating the increase in corrosion rates with temperatures.

Table2. Kinetic parameters for mild steel corrosion in 1 M HCl solution in AENOL

Temp (K)	Kinetic Prameters	
	B	K x 10^{-3} (g cm^2 min^{-1})
303 K	-0.6753	0.9831
313 K	-0.5013	1.6084
323 K	-0.5002	3.6132
333 K	-0.2466	3.6157

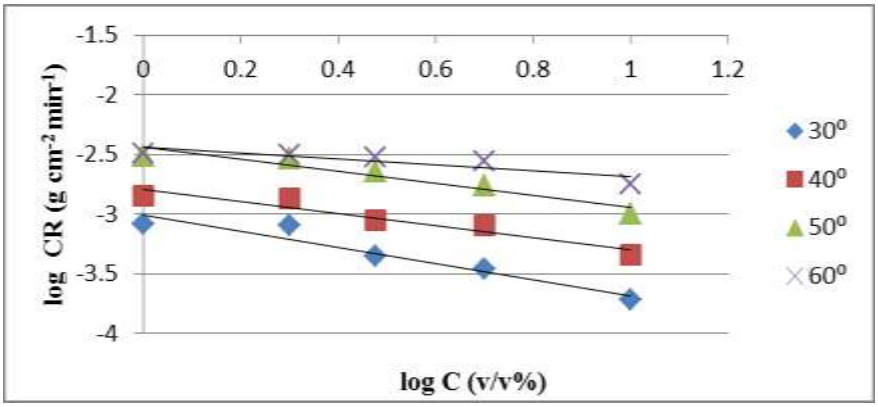

Figure 1. Variation of log CR with log$C_{inh.}$ for mild steel corrosion in 1M HCl in presence of different concentrations of AENOL at various temperatures

3.4 THRMODYNAMIC AND ACTIVATION PARAMETERS

Thermodynamic and activation parameters like apparent activation energy E_{act}, enthalpy of activation Δ H^*entropy of activation ΔS^* were calculated for steel dissolution process. Activation energy E_{act} were calculated by following Arrhenius equation (4).[34,35]

$$\log CR = \log A - \left(\frac{E_{act}}{2.303\ R\ T}\right) \quad (4)$$

Where A is Arrhenius pre-exponential factor, E_{act} is activation energy, R is universal gas constant, T is absolute temperature. The slope of log CR vs 1/T in Figure 2 gives the values of activation energies at studied concentrations. **Table 3** represents the calculated data of activation energies. The values of activation energies in presence of inhibitor were found higher than in uninhibited solution. This indicates the formation of higher energy barrier in corrosion reaction by inhibitor molecules. The increase in E_{act} for corrosion process in inhibitor solution further interpreted as physical adsorption of inhibitor species on mild steel surface.[16, 23, 25] Besides this According to Damaskin[47], the value of activation energy lesser than 80kJ/ mol and even smaller than 5kJ /mol represents physical adsorption. This assertion supports the experimental results obtained in the present study. The values of enthalpy of activation ΔH^* and entropy of activation ΔS^* were calculated by following transition state equation (5).[34, 35]

$$\log\left(\frac{CR}{T}\right) = \left[\log\left(\frac{R}{Nh}\right) + \left[\left(\frac{\Delta S^*}{2.303\ R}\right)\right] - \left[\left(\frac{\Delta H^*}{2.303\ RT}\right)\right] \quad (5)$$

Where h is planck's constant, N is Avogadro number R is the gas constant A plot of log (CR/T) vs 1/T gave a straight line with slope of (-ΔH*/2.303R) and intercept of [(log R/Nh) + (ΔS*/2.303 R)] from which the values of ΔH^* and ΔS^* were calculated (see Figure 3). These values are tabulated in **Table 3**. Values of ΔH^*were found positive. Positive values indicate endothermic nature of steel dissolution process.[1, 17, 35] Endothermic process further indicates that mild steel dissolution reduces at lower temperatures and increases with increase in temperatures. Negative values of ΔS^* are indicative of formation of activated complex in rate determining step, which represents association rather than dissociation step, meaning the decrease in disorder takes place on going from reactants to activated complex.[1, 11, 30]

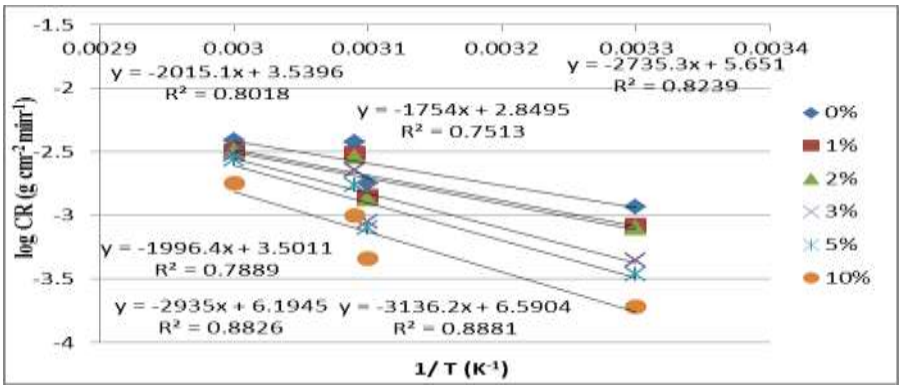

Figure 2. Arrhenius plots for mild steel corrosion rates in 1 M HCl in absence and presence of various concentrations of AENOL

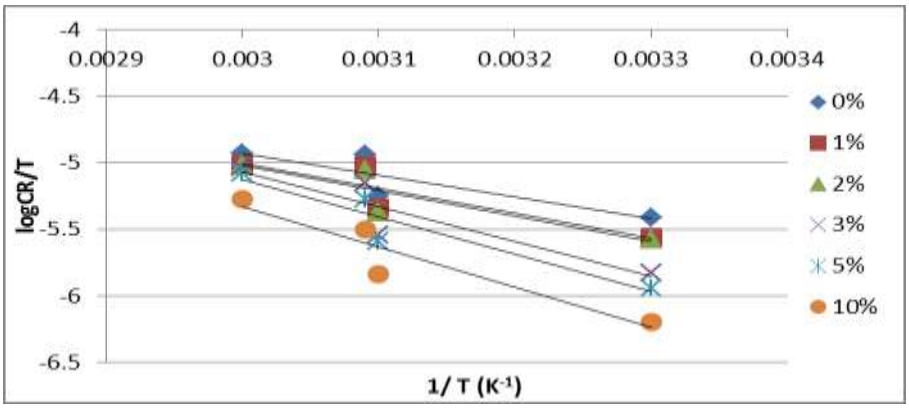

Figure 3. Transition state plots for mild steel corrosion in 1 M HCl in absence and presence of various concentrations of AENOL

It is also observed from data in **Table 3** that E_{act} and ΔH^* vary in the same manner. Values of both E_{act} and ΔH^* increase with increase in concentration of inhibitor, suggesting that energy

barrier is increases with increase in inhibitor concentration. This means that corrosion reaction will further be pushed to surface sites that are characterized by progressively higher values of E_{act} as the concentration of inhibitor becomes greater.[1, 29, 31]

Table 3. Activation and thermodynamic parameters for mild steel corrosion in 1M HCl solution with AENOL

Conc. (v/v)%	E_{act} (KJ/mol)	ΔH^* (KJ/mol)	ΔS^* (J/mol/K)
0	33.58	30.93	-199.27
1	38.22	35.79	-186.02
2	38.58	36.06	-185.61
3	52.37	49.94	-144.85
5	56.19	53.76	-134.45
10	60.05	57.66	-126.74

The values of activation energy were found larger than corresponding values of enthalpy of activation, indicate the involvement of a gaseous reaction, simply hydrogen evolution in corrosion process, associated with a decrease in total reaction volume.[19]

3.5. ADSORPTION ISOTHERM AND GIBBS ENERGY

The nature of adsorption can be explained by understanding the process at metal/electrolyte interface. Further to understand the nature of adsorption, obtained surface coverage θ were fitted in different adsorption isotherms. Langmuir adsorption isotherm was the best fit. The mathematical expressions for Langmuir adsorption isotherm can be expressed by the following equation.[10,40,42- 44]

$$\frac{C}{\theta} = \frac{1}{Kads} + C_{inh} \qquad (6)$$

Rearranging the above equation (6) we get

$$\left[\frac{\theta}{(1-\theta)}\right] = K_{ads}\, C_{inh} \qquad (7)$$

$$\text{Or} \quad \log\left[\frac{\theta}{(1-\theta)}\right] = \log K_{ads} + \log C_{inh} \qquad (8)$$

Where K_{ads} is the equilibrium constant of adsorption, θ is the surface coverage, (1-θ) is the uncovered surface, C_{inh} is the concentration of inhibitor. Values of K_{ads} were calculated from the intercept of Langmuir adsorption isotherm drawn according to the equation (8) between

log (θ /1- θ) and log C_{inh} (see Figure 4). The value of K_{ads} obtained from Langmuir adsorption isotherm is related to Gibbs energy according to the following equation (9).[19, 38]

$$K_{ads} = \frac{1}{C_{H_2O}} \exp^{(-\Delta G/RT)} \quad (9)$$

It can be written as: $\Delta G_{ads} = -2.303\ RT\ Log\ (K_{ads.}\ C_{H2O})$ (10)

Where C_{H2O} is the concentration of water in (ml / L) at metal/ solution interface, R is universal gas constant and T is absolute temperature. The values of ΔG_{ads} were tabulated in **Table 4**. Obtained values of Gibbs energy were plotted against temperature in accordance with the following basic equation.[19,39]

$\Delta G_{ads} = \Delta H_{ads} - T \Delta S_{ads}$ (11)

Intercept of graph between ΔG_{ads} vs T in Figure 5 gives value of ΔH_{ads} and by putting the value of intercept in equation (11) values of ΔS_{ads} were obtained. These obtained adsorption parameters Gibbs free energy of adsorption (ΔG_{ads}), enthalpy of adsorption (ΔH_{ads}) and entropy of adsorption (ΔS_{ads}) are listed in **Table 4.** ΔG_{ads} values has been found negative at all studied temperatures indicating spontaneous adsorption process of inhibitor molecules on metal surface.[1,4,5,7,19,28] Generally values of ΔG_{ads} upto -20 KJ/mol are consistent with electrostatic interactions (physical adsorption) between charged molecules and charged metal surface and values upto -40 KJ/mol or higher involve charge sharing or transfer from inhibitor molecules to metal surface to form coordinate type of bond (chemical adsorption).[1, 4, 5, 12, 13, 21, 22, 33] The obtained values of ΔG_{ads} were found less than -20kJ/mol indicated physical adsorption of inhibitor molecules. It has been observed that adsorption of negatively charged species is facilitated due to the positively charged metal. But positively charged species can also be adsorbed and protect the positively charged metal surface acting with a negatively charged intermediate such as acid anions, adsorbed on metal surface.[1, 25, 33] Values of ΔH_{ads} has been found negative indicating the exothermic adsorption process[11, 14, 16,20, 34], which further indicates lower %IE at higher temperatures, due to desorption of inhibitor molecules. The exothermic process is attributed to either physical or chemical adsorption or mixture of both.[3] In exothermic process, values of ΔH_{ads} predict physiorption or chemisorption. For physiorption values of ΔH_{ads} is lower than 40kJ/mol while for chemisorption it approaches to 100kJ/mol.[36,2] Values of ΔH_{ads} in **Table 4** indicate physiorption. Negative values of ΔS_{ads} indicate decrease in entropy of adsorption process. This behavior can be explained as follows: Before the adsorption of inhibitor molecules onto

mild steel surface, they might freely move in bulk solution (inhibitor molecules were chaotic). But with the process of adsorption, inhibitor molecules were orderly adsorbed onto the steel surface as a result decrease in entropy is observed.[13] A more interesting behavior is observed in **Table 4** that negative ΔH_{ads} value is accompanied with negative ΔS_{ads} value. This further agrees that when the adsorption is an exothermic process, it must be accompanied by a decrease in the entropy change and vies versa.[20,35]

The obtained positive values of ΔS_{ads} are the algebraic sum of the adsorption of organic molecules and the desorption of water molecules.[15, 46] Therefore the positive values of entropy of adsorption is the result of the substitution process, which can be attributed to the increase in the solvent entropy and more positive water desorption entropy.[45]

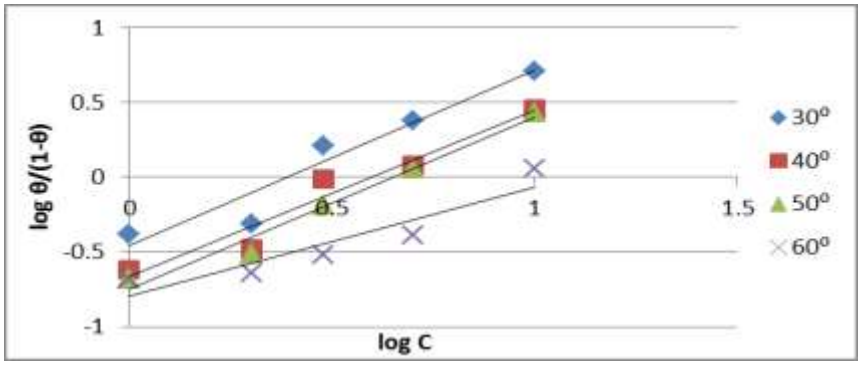

Figure 4. Langmuir adsorption isotherm of AENOL on mild steel surface in 1 M HCl at various studied temperatures

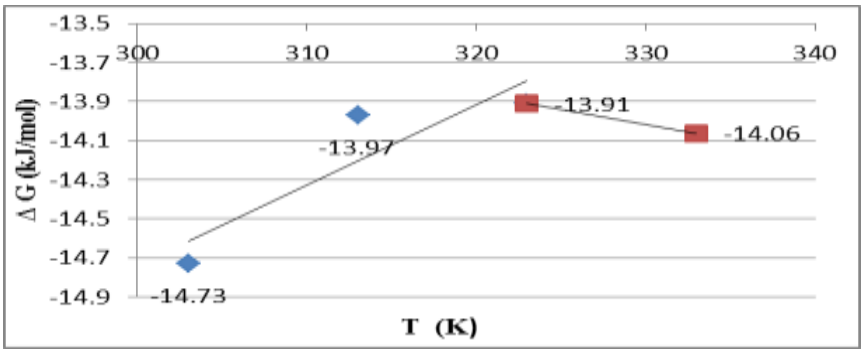

Figure 5. The variation of ΔG_{ads} (kJ/mol) with T (K) for mild steel corrosion in 1M HCl at different studied temperature in AENOL

Table 4. Adsorption parameters for mild steel corrosion in 1 M HCl solution with AENOL

Temp (k)	ΔG_{ads} (kJ/mol)	ΔH_{ads} (kJ/mol)	ΔS_{ads} (J/mol/K)
303	-14.73	-27.04	-40.63

313	-13.97	-27.04	-41.76
323	-13.91	-27.04, -09.07	- 40.65, 14.98
333	-14.06	-09.07	14.98

4. CONCLUSIONS

1. Result showed that AENOL is good corrosion inhibitor for mild steel in 1M HCl solution.

2. Corrosion rates increase with increase in temperature and decrease with increase in inhibitor concentration.

3. Inhibition efficiencies increases at lower temperature suggest the physiorption process of inhibitor on mild steel surface.

4. Apparent activation energy increases with increase in inhibitor concentrations also suggests pysiorption.

5. Enthalpy of adsorption comes out to be negative and lower than 40kJ/mol, which shows exothermic and physical adsorption process of inhibitor.

6. The values of Gibbs free energies calculated were negative shows spontaneity of corrosion inhibition process of mild steel in 1 M HCl in AENOL.

5. ACKNOWLEDGEMENT

The authors are thankful to the Head of Chemistry Department and Principal, Government College, Kota for providing necessary laboratory facilities.

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SUMMARY

The thesis consists of four different chapters.

Chapter 1: Introduction and Review of Literature:

This chapter contains an introduction about corrosion phenomenon and corrosion of mild steel and its importance .It contains brief idea about natural corrosion inhibitor substances and corrosion inhibition of mild steel using natural plant products. It also contains a concise report of review of literature of subject along with the objective and significance of study.

Chapter 2: Materials, Methods And Methodology :

This chapter consists of description of four selected plants for corrosion inhibition studies viz. *Lantana camara* , *Nerium oleander* , *Calotropis procera* and *Eichhornia crassipes* , two selected acids for preparation of different aggressive media viz. hydrochloric acid and sulphuric acid. It also includes detailed description of standard methods adopted for determination of weight loss, corrosion rates, inhibition efficiency, kinetic parameters, thermodynamic parameters, adsorption parameters and complete adopted methodology. Weight loss is determined gravimetrically , corrosion rates and inhibition efficiencies are calculated by using equation [1] and [2].Kinetic parameters , different thermodynamic parameters like activation energy (E_{act}),enthalpy of activation (ΔH^*) , entropy of activation (ΔS^*) and adsorption parameters like Gibbs energy of adsorption , enthalpy of adsorption , entropy of adsorption are calculated at four different temperatures with the help of corrosion rates using the equation [3] , [4] , [5] , [6] , [7] ,[13], [14] respectively. These all were studied at various concentrations of leaves extract of selected plant materials in different aggressive media.

Selection of plants as corrosion inhibitors;

Four different plants viz. *Lantana camara*, *Nerium oleander*, *Calotropis procera* and *Eichhornia crassipes* were taken as natural green corrosion inhibitors for mild steel in two different aggressive media. Aqueous extract of *Lantana camara*

leaves (AELCL), aqueous extract of Nerium *olender* leaves (AENOL), aqueous extract of *Calotropis procera* leaves (AECPL) and aqueous extract of *Eichhornia crassipes* (water hyacinth) leaves (AEWHL) were prepared for corrosion studies.

Acids selected for different aggressive media;

Hydrochloric acid and sulphuric acid were selected for preparation of aggressive media. 1M solutions of each acid were prepared for experimental studies.

Methods adopted for determination of weight loss , corrosion rates , inhibition efficiency , kinetic parameters , thermodynamic and activation parameters , Gibbs energy and adsorption parameters :

Determination of weight loss ;

Gravimetric technique was used for weight loss determination. Weight loss method described by Mettson was adopted for corrosion studies. For weight loss determination cylindrical mild steel specimens of various dimensions (5.0 cm in length and 0.80 cm in diameter), (4.7 cm in length and 0.50 cm in diameter), (4.9 cm in length and 0.70 cm in diameter), (4.8 cm in length and 0.60 cm in diameter) were taken, abraded with different emery papers, degreased in acetone and washed with distilled water, dried and then the constant weight was recorded by electronic balance Citizen model CY204. Stock solutions of leaves extracts viz. AELCL was prepared by heating 20 g of powdered leaves in 500 ml of distilled water for one hour, of AECPL was prepared by 20 g of powdered leaves in 250 ml of distilled water for one hour, of AENOL was prepared by 20 g of powdered leaves in 200 ml of distilled water for one hour ,of AEWHL was prepared by 20 g of powdered leaves in 500 ml of distilled water for one hour at 70°C-80°C in round bottom flask respectively. These extracts were left overnight filtered and then made up to above-mentioned volume with distilled water. Aggressive media were prepared by 1M HCl and 1M H_2SO_4 in distilled water. The cylindrical mild steel specimens were hanged by plastic thread and glass rod in 250 ml borosil glass beakers, each containing 100 ml of aggressive media for one hour at four different temperatures in presence and absence of different

concentrations of extracts of four selected plants. After completion of immersion time, specimens were taken out washed with distilled water, dried and again abraded mildely with emery paper to remove the adhered material and weighed accurately by electronic balance and weight loss is calculated. The employed concentration range of palnt extracts were 2%-6%(v/v) for AELCL, 1%-10%(v/v) for AENOL, 1%-8%(v/v) for AECPL, and 1%-5%(v/v) for AEWHL extract. The observations were taken at four different temperatures (303K, 313K, 323K, 333K).

Determination of Corrosion Rates (CR);

In 1M HCl and 1M H_2SO_4, corrosion rates of mild steel specimens at different temperatures were calculated by equation (1)

$$C\ R\ (gm\ cm^{-2}\ min^{-1}) = \left(\frac{\Delta W}{A\,t}\right) \quad (1)$$

Where ΔW is the weight loss calculated of mild steel specimen before and after immersion in acidic media. A is the total surface area of different specimen and t is immersion time in minute.

Determination of Inhibition Efficiency (IE%);

By using corrosion rate data, inhibition efficiency was calculated by following equation (2).

$$IE\ \% = \left(\frac{CR_{blank} - CR_{inh}}{CR_{blank}}\right) \times 100 \quad (2)$$

Where CR_{blank} and CR_{inh} are the corrosion rates of mild steel in the absence and presence of the specific concentration of inhibitor respectively.

Determination of Kinetic Parameters;

Kinetic parameters B (reaction constant) and K (rate constant) were calculated by the equation (3).

$$\log CR = \log K + B \log C_{inh} \quad (3)$$

where K is equal to CR at the inhibitor concentration of unity. B is the reaction constant which is the measure of inhibitor effectiveness and C_{inh} is the concentration in %(v/v) of inhibitor.

Determination of the thermodynamic and activation parameters;

Thermodynamic and activation parameters like energy of activation (E_{act}), enthalpy of activation (ΔH^*) entropy of activation (ΔS^*) were calculated by equation (4), (5).

$$\log CR = \log A - \left(\frac{E_{act}}{2.303\ R\ T}\right) \quad (4)$$

Where A is Arrhenius pre-exponential factor, CR is corrosion rate and T is temperature in Kelvin. For calculating E_{act} values, the graph was plotted between log CR values and (1/T) values.

$$\log\left(\frac{CR}{T}\right) = \left[\left(\log\left(\frac{R}{Nh}\right)\right) + \left(\left(\frac{\Delta S^*}{2.303\ R}\right)\right] - \left[\left(\frac{\Delta H^*}{2.303\ RT}\right)\right] \quad (5)$$

Where N is Avogadro`s number, h is Planck's constant. For calculating the values of (ΔS^*) and (ΔH^*), graph was plotted between log (CR/T) and (1/T) values.

Adsorption Isotherms;

To study the adsorption process of inhibitor, different adsorption isotherms viz. Langmuir adsorption isotherm, Freundlich adsorption isotherm, Temkin adsorption isotherm were drawn by using the following equations (8), (10) , (11)

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (6)$$

Rearranging the above equation

$$\frac{\theta}{1-\theta} = K_{ads}.C_{inh} \quad (7)$$

$$\text{Or} \quad \log\left(\frac{\theta}{1-\theta}\right) = \log\left(K_{ads}.\right) + \log\left(C_{inh}\right) \quad (8)$$

Where θ is the degree of surface coverage and is equal to IE%/100, K_{ads} is the equilibrium constant of adsorption in ($ml^{-1}L$), (C_{inh}/θ) is the inhibitor bulk concentration in ($ml\ L^{-1}$).

Freundlich isotherm is given by the following equations.

$$\theta = K_{ads}\ C^{n}_{inh} \quad (9)$$

$$\text{or } \log\theta = \log(K_{ads}) + n \log C_{inh} \quad (10)$$

Where θ<n<1 θ and K_{ads} is the equilibrium adsorption constant and C_{inh} is the inhibitor concentration in ml/L.

Temkin adsorption is given by the following equation.

$$-2a\theta = \ln(K_{ads}) + \ln(C_{inh}) \quad (11)$$

<u>Dtermination of Adsorption Parameters</u>:

<u>Gibbs Energy ΔG_{ads}</u>:

Different adsorption parameters Gibbs energy of adsorption (ΔG_{ads}), enthalpy of adsorption (ΔH_{ads}), entropy of adsorption (ΔS_{ads}) were calculated by following equations (13), (14), (15) respectively.

$$K_{ads} = \frac{1}{C_{H_2O}} \exp(-\Delta G_{ads}/RT) \quad (12)$$

It can be written as

$$\Delta G_{ads} = -2.303RT \log(K_{ads} . C_{H_2O}) \quad (13)$$

Where K_{ads} is the equilibrium adsorption constant calculated from Langmiur adsorption isotherm C_{H_2O} is the concentration of water in (1000 ml/L). ΔG_{ads} is Gibbs energy change in adsorption process. R is universal gas constant and T is the temperature in Kelvin.

Enthalpy of Adsorption(ΔH_{ads}) and Entropy of Adsorption (ΔS_{ads});

Enthalpy and entropy of adsorption (ΔS_{ads}) are calculated by the following equation (14).

$$\Delta G_{ads} = \Delta H_{ads} - T\,\Delta S_{ads} \qquad (14)$$

Where ΔH_{ads} is enthalpy of adsorption process, ΔS_{ads} is entropy of adsorption process and ΔG_{ads} is Gibbs energy of adsorption.

Chapter 3: Observations and Results:

This chapter contains all observations and results in tabular and graphical forms for corrosion studies of mild steel in selected media. These tables show the data of calculated corrosion rates, inhibition efficiencies, kinetic parameters, thermodynamic activation parameters and adsorption parameters in absence and presence of corrosion inhibitors. The graphs include Arrhenius plots, various adsorption isotherms, transition state plots, plots between logarithm of corrosion rates and logarithm of concentrations of inhibitors etc. for various plant extracts taken for study.

Chapter 4: Discussions on findings and conclusions:

This chapter includes interpretation of findings. Obtained results revealed that corrosion rate generally increases with temperature and decreases with increase in concentration of inhibitor. Moreover inhibition efficiencies also increase with increase in inhibitor concentrations. Mechanisms of inhibition at mild steel surface are explained and discussed by various adsorption isotherms and Arrhenius plots.

Systematic alphabetically arranged bibliography is given at the end of thesis.