Asian Journal of Chemistry Vol. 20, No. 1 (2008), 445-451

Thyme Extract of *Thymus vulgar* L. as Volatile Corrosion Inhibitor for Mild Steel in NaCl Environment

P. PREMKUMAR†, K. KANNAN* and M. NATESAN‡
Department of Chemistry, Government College of Engineering, Salem-636 011, India
Fax: (91)(427)2346458; E-mail: kannan_k2002@yahoo.co.in

Thyme extract of *Thymus vulgar* L. plant was used as volatile corrosion inhibitor for mild steel in sodium chloride environment with 100 % relative humidity. The corrosion rate and inhibition efficiency of the thyme powder was evaluated by weight loss studies and thyme impregnated craft paper was evaluated by weight loss and potentiodynamic polarization studies. It was found that both powder and impregnated craft paper have significant inhibitive effect. The inhibition efficiency increases with increase in concentration from 250 to 1000 mg for the powder and 250 to 1000 mg/sq.ft for impregnated craft paper. This is due to adsorption of inhibitor molecule on the metal surface. The adsorption behavior of thyme obeys Temkin's adsorption isotherm. At higher concentration there is decrease in inhibition efficiency. It may be due to the formation of soluble metal inhibitor complex in NaCl environment. It has also been found that thyme powder of concentration 1000 mg and impregnated craft paper of concentration 1000 mg/sq.ft offered maximum inhibition efficiency of 80.49 and 78.64 %, respectively.

Key Words: Thyme, Thymol, Atmospheric corrosion sensor, Volatile corrosion Inhibitors, Adsorption isotherm.

INTRODUCTION

Among the various methods available for protection of metals from corrosion during storage and transportation, the use of volatile corrosion inhibitors occupies a unique place. The volatile corrosion inhibitor (VCI) protection technique was applied during World War-II to protect military equipments from rusting during storage and climatic conditions. Initially camphor[1] was used to protect military equipment. But during the last two decades numerous investigations are going on in development of organic compounds as volatile corrosion inhibitor for ferrous metals. The organic substances studied as volatile corrosion inhibitor for mild steel were morpholine and its derivatives[2,3], diamino hexane derivatives[4], octylamine[5], cyclohexylamine and dicyclohexylamine[6], amine carboxylates[7], ammonium caprylate[8], *etc*.

†Gnanamani College of Technology, Pachal (PO), Namakkal-637 018, India.
‡Central Electrochemical Research Institute, Karaikudi-630 006, India.

The organic compounds studied and reported as effective VCI were mostly toxic in nature, to reduce the toxicity of VCI, it is decided to study eco-friendly natural compounds.

Thymes vulgar L. plant extract, which is commonly called as thyme was reported as effective corrosion inhibitor for mild steel in acid medium[9,10]. It is known that among the various constituents present in thyme, thymol in high percentage[11,12] and has been known as effective volatile constituent providing inhibitive action against corrosion. So it is decided to investigate thyme as volatile corrosion inhibitor.

EXPERIMENTAL

Test with Thyme powder: Experiments were carried out to find the inhibitor efficiency according to the procedure reported in the literature using mild steel specimens of size (1 cm × 5 cm × 0.2 cm) for weight loss studies. Weight loss experiments were carried out in the absence and presence of thyme at various concentrations ranging form 250 to 1250 mg using modified cell[13]. Modified cell consists of a 1 L bottle with tight fitting rubber cork carrying a glass rod with hooks having provision to suspend the specimens. Just below the specimens a cup with lid was made to place VCI. At the middle part of the cup there is a bend type outlet provision for the vapor to escape and fill the space in Jar. The test was carried out by taking 100 mL of 0.01 N NaCl (100 % relative humidity) in the jar and then specimens were suspended in the hooks. The cell set was kept at 40 °C in a thermostatic water bath for 14 d, after 14 d the specimens were removed and weight loss measurements were made.

Preparation of VCI impregnated paper: VCI coated papers were prepared by using the impregnation methods. A known amount (250 to 1250 mg) of thyme was dissolved in 15 mL of ethanol and one square feet of craft paper was dipped into the solution until completely wet and taken out and the solvent was allowed to evaporate. The VCI impregnated craft paper was stored in airtight containers. It was used for gravimetric experiments and potentiodynamic polarization studies.

Continuous condensation test with impregnate craft paper: Corrosion tests were carried out by using mild steel specimens of size (1 cm × 5 cm × 0.2 cm), wrapped with thyme impregnated and unimpregnated craft papers and suspended in a 1 L jar containing 100 mL of 0.01 N NaCl. The jars were then placed in a thermostatically controlled water bath, which was maintained at 40 °C. This arrangement produced a continuous condensation of water vapour at 100 % relative humidity (RH). The weight loss measurements were made at the end of 14 d.

Potentiodynamic polarization experiment: A three-electrode type atmospheric corrosion sensor[14,15] was fabricated by using mild steel with

working electrode area 1 cm^2 and used for potentiodynamic polarization studies. About 1mL of 0.01 N NaCl solution was applied over the well polished atmospheric corrosion sensor, VCI impregnated craft paper was pressed over it. The potentiodynamic polarization measurements were carried out at a sweep rate of 2 mV/s using CH electrochemical analyzer Model CHI 608B instrument. Open circuit potential (OCP) was noted, when a steady state is attained. The potential was varied from OCP within the range of -200 mv to +200 mv then the electrodes were polarized from cathodic to anodic direction. Corrosion kinetic parameters such as E_{corr}, Tafel slopes and I_{corr} were evaluated from E *vs.* log i plot. A similar experiment was carried out using unimpregnated craft paper as control.

RESULTS AND DISCUSSION

FTIR of Thyme: Infrared spectrum of thyme shows that a strong C-H absorption at 2960 cm^{-1}. A strong doublet absorption representing *gem*-methyl was observed at 1422 and 1344 cm^{-1}. A strong and sharp absorption at 1245 cm^{-1} show that the presence of C-O bond of an alcohol and the wide absorption at 3227 cm^{-1} show that the alcohol present is hydrogen bonded. The presence of the aromatic ring in the compound is observed from the absorptions at 1620, 1583, 1520 and 1422 cm^{-1}. From the FTIR it is concluded that the thyme used for the investigation contains the active constituent thymol (Fig. 1.)

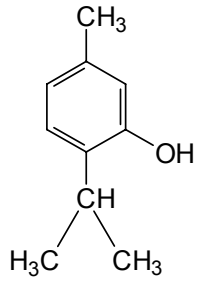

Fig. 1. Thymol

Test with thyme powder: The values of corrosion loss, corrosion rate and the inhibition efficiency obtained by weight loss method in the absence and in the presence of various concentrations of thyme powder as VCI for mild steel in 0.01 N NaCl environments at 40 °C and 100 % RH for a period of 14 d were summarized in Table-1. It could be seen that the weight loss and corrosion rate decreases with increase in concentration of thyme up to 1000 mg further increase in concentration of thyme shows increase in weight loss and corrosion rate. It could also be seen from the

table that the maximum inhibition efficiency 80.49 % was obtained at 1000 mg concentration of thyme. The inhibition efficiency may be due to the formation of a physical barrier between metal and corrosive environment by the intraction of the metal and inhibitor molecule.

TABLE-1
WEIGHT LOSS PARAMETERS AND INHIBITION EFFICIENCY OF VARIOUS CONCENTRATION OF THYME FOR PROTECTION OF MILD STEEL BY MODIFIED CELL METHOD IN 100 % RH USING 0.01 N NaCl AT 40 °C FOR 14 d

Amount of thyme (mg)	Weight loss (mg)	Corrosion rate (μ my^{-1})	Inhibition efficiency (%)
Control	49.2	162.9	-
250	28.3	93.7	42.48
500	21.8	72.18	55.69
750	15.6	51.65	68.29
1000	9.6	31.78	80.49
1250	12.2	40.39	75.21

Continuous condensation test impregnate craft paper: The observations of continuous condensation test with unimpregnated and various concentrations of thyme impregnated craft paper for mild steel in 0.01 N NaCl environment at 40 °C and 100 % RH for a period of 14 d are summarized in Table-2. It could be seen that corrosion rate decreases with increase in concentration of the thyme in the craft paper. The maximum inhibition efficiency 78.64 % was observed at 1000 mg/sq.ft. At higher concentration the inhibition efficiency decreases due to the formation of soluble metal inhibitor complex in the NaCl environment.

TABLE-2
WEIGHT LOSS PARAMETERS AND INHIBITION EFFICIENCY OF VARIOUS CONCENTRATION OF THYME IMPREGNATED CRAFT PAPER FOR PROTECTION OF MILD STEEL BY CONTINUOUS CONDENSATION TEST IN 100 % RH USING 0.01 N NaCl AT 40 °C FOR 14 d

Amount of thyme impregnated on craft paper (mg/sq.ft)	Weight loss (mg)	Corrosion rate (μ my^{-1})	Inhibition efficiency (%)
Control	39.8	131.8	-
250	23.3	77.26	41.46
500	18.2	60.27	54.27
750	13.1	43.38	67.09
1000	8.5	28.15	78.64
1250	10.3	34.11	74.12

Polarization studies: Potentiodynamic polarization behaviour of mild steel in 0.01 N NaCl environment in presence of various concentration of thyme impregnated paper and unimpregnated paper were studied at a sweep rate of 2 mV/s. The polarization curves were shown in Fig. 2. The corrosion kinetic parameters such as E_{corr}, I_{corr}, anodic and cathodic tafel slopes (b_a and $-b_c$) were obtained from the anodic and cathodic polarization curves and the results were summarized in the Table-3. It can be seen from the table that all different concentrations of thyme impregnated paper exhibited a less negative E_{corr} value than the control sample, showing thereby that mild steel was protected to some degree from corrosion in the presence of thyme. Tafel slopes both ba and bc were affected slightly, it shows that thyme impregnated craft paper is acting as mixed type inhibitor. The I_{corr} values decreases with increase in concentration of thyme up to a concentration of 1000 mg/sq.ft, then there is a slight increase at 1250 mg/sq.ft. It can also be seen from the table that the inhibition efficiency increases with increase in concentration of thyme up to 1000 mg/sq.ft and then decreased. The maximum inhibition efficiency 66.78 % was observed at 1000 mg/sq.ft.

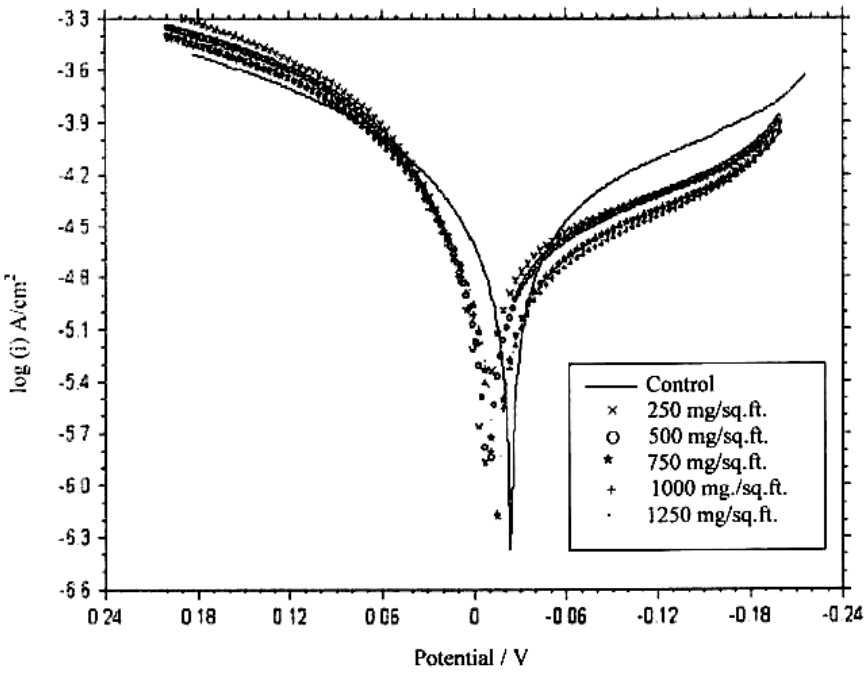

Fig. 2. Potentiodynamic polarization curves for mild steel wrapped with unimpregnated and impregnated papers containing different amounts of thyme in 0.01 N NaCl

TABLE-3
ELECTROCHEMICAL POLARIZATION PARAMETERS FOR VARIOUS CONCENTRATION OF THYME IMPREGNATED CRAFT PAPER FOR MILD STEEL

Amount of thyme impregnated on craft paper (mg/sq.ft)	E_{corr} (V)	Tafel slopes (mV/dec)		I_{corr} ($\mu A/cm^2$)	Inhibition efficiency (%)
		b_a	$-b_c$		
Control	-0.043	117	133	30.64	-
250	-0.005	81	165	19.84	35.25
500	-0.009	80	152	16.47	46.25
750	-0.001	80	149	13.24	56.79
1000	0.002	77	145	10.18	66.78
1250	0.001	79	150	11.80	61.49

Adsorption isotherm: Adsorption isotherms plays vital role in the determination of the mechanism of organo-electrochemical reactions. The frequently used isotherms are Langmuir, Frumkin, Parsons, Temkin, Flory-huggins and Bockris-sinkles[16]. All these isotherms are of the general form

$$f(\theta, x) \exp(-2a\theta) = kc$$

where, $f(\theta, x)$ = configuration factor, a = interaction factor, k = equilibrium constant, c = concentration, θ = surface coverage (IE/100)

Fig. 3 shows the plot of surface coverage (θ) *vs.* log c for mild steel in NaCl environment in presence of various concentration of thyme impregnated craft paper. It could be seen from the figure that the straight lines indicating that the adsorption of the thyme on mild steel surface follows Temkin's adsorption isotherm both in the weight loss and polarization method, thyme adsorbs from the impregnated paper on mild steel surface according to Temkin's isotherm.

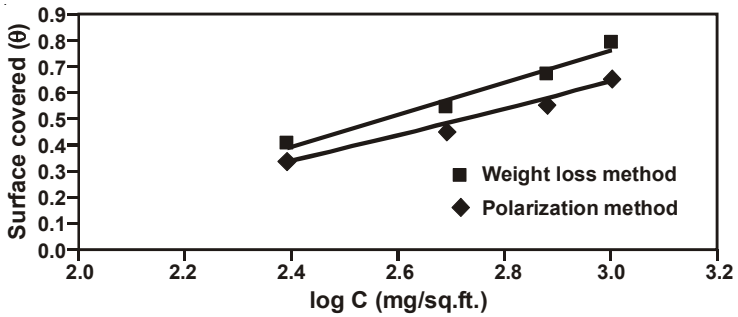

Fig. 3. Temkin adsorption isotherm plot for mild steel in NaCl environment

Conclusion

The investigation brings out the following conclusions: (i) The FTIR study indicates that the presence of thymol in the thyme sample used for the investigation. (ii) The thyme powder of concentration 1000 mg for 1 L of vapour phase provided the maximum inhibition efficiency of 80.49 % for mild steel in NaCl environment. (iii) Thyme impregnated craft paper of concentration 1000 mg/sq.ft provided the maximum inhibition efficiency of 78.64 % in continuous condensation test. (iv) Polarization studies of impregnated craft paper given the maximum efficiency of 66.78 % at 1000 mg/sq.ft and it shows that thyme acts as a mixed type inhibitor in NaCl environment. (v) The adsorption of thyme on mild steel obeys Temkin adsorption isotherm.

ACKNOWLEDGEMENTS

The authors are grateful to Dr. T. Arangannal and Mrs. P. Mala Leena, Chairman, Gnanamani College of Technology and Dr. K. Srinivasan, Prof. of Chemistry, GCE, Salem for providing all necessary facilities, constant encouragements and for giving valuable comments throughout this work.

REFERENCES

1. E.G. Vernon and H.J. Stroud, *J. Appl. Chem.*, **2**, 178 (1952).
2. A. Subramanian, R. Gopalakrishnan, C. Boopathy, K. Balakishnan, T. Vasudevan, M. Natesan and N.S. Rangasawamy, *Bull. Electrochem.*, **14**, 289 (1998).
3. E. Vuorinen, P. Ngobent, G.H. Van der Kalashorst, W. Skinner, E. De Wet and W.S. Ernst,, *Br. Corros. J.*, **29**, 120 (1994).
4. M.A. Quraishi and D. Jamal, *Corrosion*, **58**, 387 (2002).
5. A. Subramanian, R. Rathinakumar, M. Natesan and T. Vasudevan, *Anti Corros. Methods Mater.*, **49**, 354 (2002).
6. A. Subramanian, P. Rajendran, M. Natesan, K. Balakrishnan and T. Vasudevan, *Anti Corros. Methods Mater.*, **46**, 346 (1999).
7. E. Vuorinen and W. Skinner, *Br. Corros. J.*, **37**, 153 (2002).
8. W. Skinner, F. Du Preez and E. Vuorinen, *Br. Corros. J.*, **34**, 151 (1999).
9. E. Khamis and N. Al-Andis, *Materialwissenschaft und Werkstofftechnik*, **33**, 556 (2002).
10. A. Chetouani and B. Hammouti, *Bull. Electrochem.*, **20**, 343 (2004).
11. N. Asfaw, H.J. Storesund, L. Skattubol, F. Tonnesen and A.J. Aasen, *Flav. Fragr. J.*, **15**, 123 (2000).
12. M. Hudaib, E. Speroni, A.M. Di Pietra and V. Cavrini, *J. Pharm. Biomed. Anal.*, **29**, 691 (2002).
13. A. Subramanian, M. Natesan, A. Gopalan, K. Balakrishnan and T. Vaasudevan, *Bull. Electrochem.*, **15**, 54 (1999).
14. A. Subramanian, M. Natesan, V.S. Muralidharan, K. Balakrishnan and T. Vasudevan, *Corrosion*, **56**, 144 (2000).
15. D.M. Bastidas, E. Cano and E.M. Mora, *Anti Corros. Methods Mater.*, **52**, 71 (2005).
16. V. Chandrasekaran, K. Kannan and M. Natesan, *Asian J. Chem.*, **17**, 1921 (2005).

(*Received*: 14 November 2006; *Accepted*: 14 September 2007) AJC-5844