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Dissolution behavior of API – 5L – Grade – X52 pipe line steel in Crude oil with 25% connate water environment.

Chinnakkani C.[1*], C. Malarvizhi[1].I, Sangeetha C.[1] and Selvaraj S.[1]

[1*]Postgraduate and Research Department of chemistry, Sri Paramakalyani College, Alwarkurichi – 627 412, [1*]Afffiliated to Manonmaniam Sundaranar University, Abishekapatti, Tirunelveli-17, Tamil Nadu, India.

Email Id: drssspkc@yahoo.com ; ckanichem79@gmail.com Mobile no.9442064252

ABSTRACT

Solanum torvum leaves has shown excellent inhibition effect on API – 5L – Grade – X52 Steel in Crude oil with 25% connate water environment. Inhibition efficiency increased with the increase of inhibitor concentration and attained, maximum of 99.21%.It is due to the very strong adsorption of active inhibitor molecules (viz oxygen, hetero atom) present in the phytochemical constituent may bind with the metal ion, present on the surface. Also, the inhibition efficiency gradually increased with the rise in temperature and suggests that chemisorptions process. The evaluation of thermodynamic parameters viz activation energy (E_a), enthalpy of adsorption (ΔH_{ads}) and free energy changes (ΔG_{ads}) reveals that the adsorption of inhibitor on pipe line surface and follows chemical, endothermic and spontaneous process respectively. The inhibitor is found to obey Langmuir adsorption isotherms. Since the regression co-efficient value(R2 = 0.9938) are very close to unity.

KEY WORDS: API -5L-Grade-X52, Crude oil with 25% connate water, Mass Loss, Green inhibitor, Adsorption isotherm.

***Corresponding author:**

Chinnakkani C.

(Research Scholar-Reg.No.11584)

Postgraduate and Research Department of chemistry,

Sri Paramakalyani College,

Alwarkurichi – 627412,

INTRODUCTION:

Generally a different pipe line of API-5L-Grade-B to X65 widely employed in variety of onshore and off-shore oil and gas industries in world wide. But the main problem of using this material undergoes dissolution inside of the line pipes due to speed of flow velocity and presence of corrosion initiating substances in crude oil. Because of this, problems cause the damage the interior part of the seamless pipe line leads to pipe blisting.Normally these kind of problems may over come by use of inhibitor is one of the best method to prevent metal dissolution is very common.[1, 3] Most of the well-known acid inhibitors are organic compounds containing hetero atoms viz; nitrogen, sulfur, oxygen, heterocyclic compounds with a polar functional group and conjugated double bond.[4,5] These kinds of compounds are adsorbed on the metallic surface and block the active corrosion sites. Most of the synthetic chemicals are costly, toxic to both human being and the environment. In order to overcomes, these difficulties choosing the inhibition are plenty, cheap, nontoxic and environmentally friendly natural products as corrosion inhibitors. These natural organic compounds are either synthesized or extracted from aromatic herbs, spices and medicinal plants. Plant extracts are an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost and are biodegradable in nature. The plant extract are rich sources of molecules which have appreciably high inhibition efficiency and hence termed as “Green Inhibitors”. These inhibitors do not contain heavy metals or other toxic compounds. Recent studies using plants containing heteroatom such as oxygen, nitrogen and sulphur *like Ocimum viridis, Phyllanthus amarus, Annona squamosal, Argan, Psidium guajava, black pepper, Punica granatum, Mentha pulegium, Cnidoscolus chayamans, Solanum Torvum, Pisonia Grandis, mimusops elengi, Sauropus Androgynus, Kingiodendron pinnatum, Wrightia Tinctoria*[6-22] have also been used for inhibition of corrosion. In continuous of our research work, the present investigation is *Solanum torvum* leaves the extract used as corrosion inhibitor on API – 5L – Grade – X52 Steel pipe line in Crude oil with 25% connate water have been investigated with various periods of contact and temperature using the mass loss measurements.

MATERIALS AND METHODS

Solanum Torvum leaves used as an inhibitor:

Stock solution of Solanum Torvum Leaves Extract:

Solanum Torvum leaves (STL) was collected from the source and dried under shadow for about 15 days, grained well, then soaked in a solution of ethyl alcohol for about 48 hrs, Then it is filtered followed by evaporation in order to remove the alcohol solvent completely and the pure plant

extract was collected. From this extract, different concentration of 10 to 1000ppm stock solution was prepared using triple distilled water and used throughout our present investigation.

Specimen preparation

Commercially available steel pipeline. API -5L-Grade-X52, specimen was mechanically pressed cut to form different coupons, each of dimension exactly 40.092 cm^2 (5.1 cm × 2.5 cm × 0.96 cm), polished with emery wheel of 80 and 120 mesh, and degreased with trichloroethylene then washed with distilled water, cleaned, dried and then stored in desiccator for the use of our present investigation.

Mass loss method

In mass loss measurements on pipe line steel in triplicate were completely immersed in 50ml of the test solution in the presence and absence of the inhibitor. The metal specimens were withdrawn from the test solutions after 24 to 360 hrs at room temperature and also measured the temperature range 313K to 333K. The Mass loss was taken as the difference in weight of the specimens before and after immersion using digital balance with sensitivity of ±1 mg. The tests were performed in triplicate to guarantee the reliability of the results and the mean value of the mass loss is reported. From the mass loss measurement As, the corrosion rate was calculated using the following relationship.

$$\text{Corrosion Rate}(\text{mmpy}) = \frac{87.6 \times W}{DAT} \qquad \text{---------- (1)}$$

[Where, mmpy = millimeter per year, W = Mass loss (mg), D = Density (gm/cm^3),
A = Area of specimen (cm^2), T = time in hours]

The inhibition efficiency (%IE) and degree of surface coverage (θ) were calculated using the following equations.

$$\%\ IE = \frac{W_1 - W_2}{W_1} \times 100 \qquad \text{---------- (2)}$$

$$\theta = \frac{W_1 - W_2}{W_1} \qquad \text{---------- (3)}$$

(Where W_1 and W_2 are the corrosion rates in the absence and presence of the inhibitor respectively)

RESULTS AND DISCUSSION

Effect of time variation

The dissolution behavior of API – 5L – Grade – X52 Steel pipe line in Crude oil with 25% connate water containing the presence and absence of STL extract with various exposure times (24hrs to 360 hrs) are shown in Table-1**.** Observed values are clearly indicates that the presence of

STL extract, the corrosion rate moderately decreased from 1.4036 to 0.0116 mmpy for 24 hrs and 0.0561 to 0.0054 mmpy after 360 hrs with increase of inhibitor concentration (0 to 1000 ppm). The maximum of 99.21 % of inhibition efficiency is achieved even after 240 hrs exposure time, suggests that the adsorption process occurs through film formation mainly due to the presence of active phytochemical constituents present in the inhibitor molecule especially oxygen containing species and the metal ion from the surface of the steel pipe line.

Table 1 The corrosion parameters of API – 5L – Grade – X52 Steel pipe line in Crude oil with 25% connate water containing different concentration (0 to 1000ppm) of STL extract after 24 to 360 hours exposure time

Conc. of inhibitors (ppm)	24 hrs		72 hrs		120 hrs		240 hrs		360 hrs	
	C.R (mmpy)	% I.E	C.R (mmpy)	% I.E	C.R (mmpy)	% I.E	C.R (mmpy)	% I.E	C.R (mmpy)	% I.E
0	1.4036	-	0.0818	-	0.1684	-	0.1403	-	0.0561	-
10	0.1169	91.67	0.0740	9.53	0.1427	15.26	0.0210	85.03	0.0249	55.61
50	0.0818	94.17	0.0467	42.90	0.0280	83.37	0.0140	90.02	0.0132	76.47
100	0.0233	98.33	0.0467	42.90	0.0251	84.73	0.0128	90.87	0.0124	77.89
500	0.0116	99.17	0.0272	66.74	0.0233	86.16	0.0035	97.50	0.0109	80.57
1000	0.0116	99.17	0.0233	71.51	0.0210	87.52	0.0011	99.21	0.0054	90.37

3.2. Effect of Temperature

Dissolution behavior of API – 5L – Grade – X52 Steel pipe line in Crude oil with 25% connate water containing various concentration of STL extract at temperature ranges from 303to 333K and the observed values are listed out in Table-2. The observed results reveals that the corrosion rate decreased with increase of inhibitor concentrations and significantly increased with rise in Temperature from 303 to 333K and attain maximum of 73.33% inhibition efficiency at 303K and suggests and support the facts that the process of adsorption follows chemisorptions.

Table 2 The corrosion parameters of API – 5L – Grade – X52 Steel pipe line in Crude oil with 25% connate water containing different concentration of STL extract at 313 to 333 K after one hour exposure time.

Conc. of inhibitor (ppm)	303 K		313 K		333 K	
	C.R (mmpy)	% I.E	C.R (mmpy)	% I.E	C.R (mmpy)	% I.E
0	8.4216	-	7.0180	-	4.2108	-
10	6.4566	23.33	6.4566	7.99	3.3686	20.00
50	6.1758	26.66	3.9301	36.00	2.5265	39.99
100	5.8951	30.00	4.4915	43.99	2.2457	46.66
500	5.6144	33.33	3.3686	52	1.9650	53.33
1000	5.3337	36.66	2.5265	63.99	1.1228	73.33

Activation energy:

The activation energy (E_a) for the corrosion of API – 5L – Grade – X52 Steel in the presence and absence of STL extract is calculated using the following Arrhenius equation (4) and its derived from equation (5).

$$CR = A\exp(-E_a/RT) \quad \text{---------- (4)}$$

$$\log(CR_2/CR_1) = E_a/2.303\ R\ (1/T_1 - 1/T_2) \quad \text{---------- (5)}$$

(Where CR_1 and CR_2 are the corrosion rate at the temperature T_1 and T_2 respectively, E_a is the activation energy and R is the universal gas constant).

The value of activation energy (E_a) for the blank (-19.3855 kJ/mol) is higher than in the presence of inhibitors (Table-3). This observation clearly proved that the adsorption process also is chemisorption.

Heat of adsorption:

Heat of adsorption on the surface of various steel pipe line in the presence of plant extract in crude oil containing 25% connate water environment is calculated by the equation (6).

$$Q_{ads} = 2.303\ R\ [\log(\theta_2/1-\theta_2) - \log(\theta_1/1-\theta_1)] \times (T_2T_1/T_2-T_1) \quad \text{------(6)}$$

(Where R is the gas constant, $\theta_1$and θ_2 are the degree of surface coverage at temperatures T_1 and T_2 respectively).

The calculated Q_{ads} values (Table-3) are ranged from -72.0414 to 43.5713 kJ/mol. This positive value indicate and suggests that the adsorption of STL extract on the API – 5L – Grade – X52 Steel surface is endothermic.

Table 3 Calculated values of Activation energy (E_a) and heat of adsorption (Q_{ads}) of STL extract on API – 5L – Grade – X52 Steel pipe line in Crude oil with 25% connate water environment.

S. No	Conc. of inhibitor (ppm)	% of I.E		E_a ($KJmol^{-1}$)	Q_{ads} ($KJmol^{-1}$)
		30^o	60^o		
1.	0	-	-	-19.3855	--
2.	10	23.33	20.00	-18.1957	-72.0414
3.	50	26.66	39.99	-24.9974	-39.6430
4.	100	30.00	46.66	-26.9915	19.9503
5.	500	33.33	53.33	-29.3614	-15.6550
6.	1000	36.66	73.33	-43.5794	43.5713

Adsorption studies:

Process of adsorption are very important phenomenon to determine the corrosion rate of reaction mechanism. The most frequently use of isotherms are viz: Langmuir, Temkin, Frumkin, Flory- Huggins, Freund lich, Bockris-Swinkles, Hill-de Boer, Parson's and the El-Amady, thermodynamic-kinetic model.

Langmuir, El-Awady and Frumkin Adsorption Isotherm

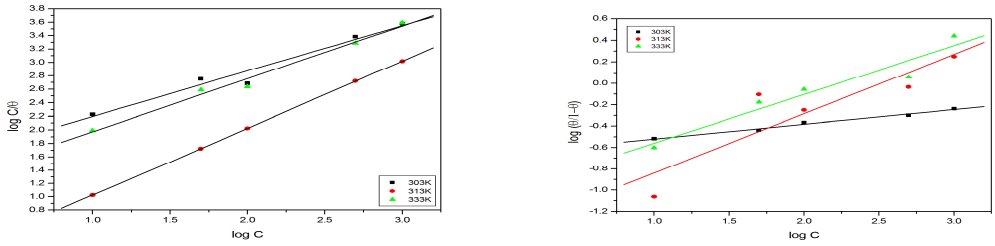
Langmuir adsorption isotherm of STL extract on API – 5L – Grade – X52 steel pipe line surface proceeded according to the following equation (7).

$$\log C/\theta = \log C - \log K \quad \text{--------(7)}$$

(Where θ is the degree of surface coverage, C is the concentration of the inhibitor solution and K is the equilibrium constant of adsorption of inhibitor on the metal surface).

By plotting the values of log(C/θ) Vs log C, linear plots are generated (fig-3). Inspection of this figure reveals that the experimental data fitted with the Langmuir adsorption isotherm, means that there is no interaction between the adsorbed species.

The Figs 2(a-c) shows Langmuir, El-Awady, and Frumkin isotherm model respectively. The values of K, R^2 and ΔG_{ads} are derived from these adsorption isotherm at different temperature ranges from 303K to 333K are given in Table -4. Langmuir adsorption isotherm model best fit the corrosion rate data of STL inhibitor on API – 5L – Grade – X52 strongly and clearly indicates that the average value of Regression co-efficient (R^2=0.9938) is almost very close to unity. The other adsorption isotherm values of El-Awady (R^2=0.9877), are also move near to unity. We also attempt the Frumkin (R^2=0.9621), Freundlich (R^2=0.9511), Temkin (R^2=0.9061), and Florry-Huggins (R^2=0.9002) adsorption isotherm models of STL extract. These observed values relatively so far from unity as compared with the values obtained with Langmuir adsorption isotherm which is clearly indicate that the weak correlation between the two variables (i.e surface coverage, inhibitor concentration). It is concluded that the inhibitor obeys Langmuir adsorption isotherm.



(a) **(b)**

Figure 2 (a) Langmuir, (b) El-Awady isothserm for the adsorption of STL inhibitor on API – 5L – Grade – X52 Steel pipe line in Crude oil with 25% connate water environment.

Free energy of adsorption:

The equilibrium constant of adsorption for various plant extract on the surface of pipe line steel is related to the free energy of adsorption ΔG_{ads} by equation (8).

$$\Delta G_{ads} = -2.303\ RT \log (55.5\ K) \quad \text{---------- (8)}$$

(Where R is the gas constant, T is the temperature, K is the equilibrium constant of adsorption).

The values of intercept (K) obtained from Langmuir, El-Awady adsorption isotherm is substituted in equation (8) and the calculated values of ΔG_{ads} are placed in Table-4. In El-Awady adsorption isotherm, the increase of equilibrium constant (K_{ads}) values suggest that the process is chemisorptions phenomenon, which attributed to electrostatic interaction between the charged steel pipe line and active inhibitor molecules. Also the values of 1/y are less than unity, showing that there is a multilayer adsorption (MLA) of the inhibitor molecule on the inner pipe line surface.[24-25]. In Langmuir adsorption, the negative values of ΔG_{ads} suggested that the adsorption of STL extract onto Mild steel surface is a spontaneous process and the adsorbed layer is more stable one.

Table 4 Langmuir and El-Awady adsorption parameters for the adsorption of STL inhibitor on API – 5L– Grade – X52 Steel pipe line in Crude oil with 25% connate water environment.

Temperature (Kelvin)	Langmuir			El-Awady			
	K	R^2	$-\Delta G_{ads}$ kJ/mol	K	1/Y	R^2	$-\Delta G_{ads}$ kJ/mol
303K	7.0840	0.9883	12.2068	$1.1x10^{-2}$	0.5107	0.9802	6.0120
313K	8.1722	0.9952	14.2019	$3.6x10^{-3}$	0.4940	0.9759	4.6078
333K	21.008	0.9950	18.5009	$3.9x10^{-4}$	0.3449	0.9929	9.3220

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Thermodynamics parameters

Another form of transition state equation which is derived from Arrhenius equation (4) is shown below (9)

$$CR=RT/Nh \exp(\Delta S/R) \exp(-\Delta H/RT) \text{ ----- (9)}$$

Where h is the Planck's constant, N the Avogadro's number, ΔS the entropy of activation, and ΔH the enthalpy of activation. A plot of log (CR/T) Vs. 1000/T gives a straight line (Fig. 4) with a slope of (−ΔH/R) and an intercept of [log(R/Nh)) + (ΔS/R)], from which the values of ΔS and ΔH were calculated and listed in Table-11. The negative value of enthalpy of activation clear that the exothermic nature of dissolution process is very difficult. The entropy (ΔS) is generally interpreted with disorder which may take place on going from reactants to the activated complex.

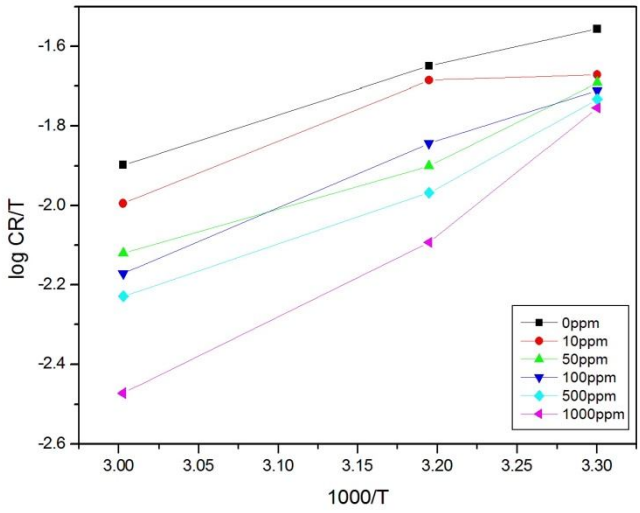

Figure-4 The relation between log (CR/T) and 1000/T for different concentrations of STL extract.

Table 11 Thermodynamic parameters of API – 5L – Grade – X60 Steel in Crude oil with 25%, connate water obtained from weight loss measurements.

S.No	Concentration of STL (ppm)	ΔH ($kJ\ mol^{-1}$)	ΔS ($J\ k^{-1}mol^{-1}$)
1	0	-9.7115	35.5993
2	10	-9.5760	35.3382
3	50	-11.6961	27.6286
4	100	-13.0297	23.3702
5	500	-13.5817	21.0572
6	1000	-19.1296	0.8318

CONCLUSIONS

- *Solanum Torvum* has shown excellent inhibition performance for API – 5L – Grade – X60 Steel in Crude oil with 25%,connate water environment.
- The inhibition efficiency increased with the increase of inhibitor concentration and the maximum of 99.21% was achieved.
- Inhibition efficiency increased with the rise in temperature 73.33% for 333K . It follows chemical adsorption mechanism.
- The value of activation energy (E_a), enthalpy of adsorption (ΔH_{ads}) and free energy changes (ΔG_{ads}) indicates that the adsorption of inhibitor on steel pipe line surface follows chemical, endothermic and spontaneous process respectively.

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