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## THERMODYNAMICS STUDY FOR THE ASSESSMENT OF CORROSION INHIBITION OF MILDSTEEL PIPE BY CASTOR AND RUBBER SEED OILS

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**Abstract:** The thermodynamics for the assessment of corrosion inhibition of mildsteel pipe by Castor and Rubber Seed Oils was studied in this research work. This was prompted due to the fact that temperature factor plays very important role in the corrosion a given material with time. Corrosion Inhibition assessment of the steel pipe, by the castor and rubber seed oil samples was performed at different times (of 4, 8, 16, 24 and 32hours) and temperatures (of 40, 50 and 60°C) to know how much mass of the material will be degraded in a given time. Arrhenius concept was employed to study the temperature-dependence of the process, in which the results shows that corrosion rate increases with time, with the highest rate (42.67% for Castor Seed Oil, **CSO** and 30.66% for Rubber Seed Oil, **RSO**) observed at the highest time of 32hours. Also, enthalpy and entropy changes increases in the direction of increasing temperature and time, indicating an increasing demand for heat energy content. The deepening in the negativity of the free energy value is a response to the increased randomness in the adsorbed molecular layer, which made the reaction entropy-driven and spontaneous. However, the thermodynamic parameters studied were more established in cases involving Sample A (CSO) than in Sample B (RSO).

**Keywords:** Thermodynamics, Corrosion Inhibition, Mildsteel Pipe, Castor Seed Oil, Rubber Seed Oil.

### INTRODUCTION

Corrosion of metals or alloys occurs due to chemical or electrochemical reactions with their environment, which often results in drastic deterioration in the properties of the metals or materials comprising them thereof. Corrosion takes place on a metal (steel) surface, due to the development of anodic and cathodic areas (through oxidation and reduction reactions), forming oxides of metal alloy (Eddy *et al*, 2010; Ha-Won and Vehu, 2007). There are several corrosion-causing agents (corrodents) such as soot, sand, gravels, sulphate salts, chlorides, ions, temperature, and salinity, pH, dissolved gases, humidity, bacteria, stones and mechanical stresses. Also, several protection methods could be employed to check the menace of corrosion; such methods include application of alloys, composites, inhibitors, cathodic and anodic protections, protective linings and

coatings (Ghali *et al*, 2011; Asuquo *et al*, 2012b). Notwithstanding these remedial approaches, corrosion has become a gigantic problem today for almost every nation of the world. The colossal detrimental impact of corrosion on the economy of any country can be manifested in very huge amount of money expendable annually to combat or control it. In the past two decades, research and development efforts in the field have undergone vast changes globally, because of the everyday growing consumer expectations of good quality and performance, coupled with lower cost, enormous hikes in the prices of petroleum-based chemicals (out of fear of depleting stocks by the nearest future), serious concerns pertaining to energy consumption and environmental contamination, regulations such as Clean Air Act Amendments (CAAA) and, above all, the “cost of corrosion”. These predictions, regulations and innovations have posed constant threats and challenges for anti-corrosion industries, forcing to change their gears world-wide. The corrosion chemists, researchers and engineers (in the industries and academics) are actively engaged to explore and formulate new strategies to meet the mandatory limits of performance, cost and legislations.

However, the ultimate solution is foreseen through the *excessive utilization of our naturally/locally available resources*, primarily to cut-off the escalating prices of raw materials, to formulate environmentally benign ones that would expedite their post-service degradation and add value to the waste materials. This idea motivated the assessment of Castor and Rubber Seed Oils for possible large-scale applications. Consequently, environmental-friendly technologies (*Water-borne, powder, high-solid, hyper-branched and radiation-curable*) have evolved, with special emphasis on the excessive utilization of naturally available renewable resources thriving on the acres of our agricultural lands (Derksen *et al*, 1996; Gandini and Belgacem, 2002). These resources, as reviewed, may be formulated as corrosion resistant alloys, corrosion resistant composites, corrosion resistant pigments, corrosion resistant coatings, paints and corrosion inhibitors.

In varying perspectives, Weiss (2012) and Ahmed (2007) reviewed, also, that renewable resource provide cheaper and abundant biological feed stocks with numerous advantages, such as cost effectiveness, low toxicity, inherent biodegradability and environmental friendliness. This yields versatile materials through chemical transformations, with plethora of applications, particularly in corrosion resistance against various corrodents.

## **MATERIALS AND METHOD**

### **Corrosion Inhibition Experiment**

A sizeable mildsteel pipe, of mass ( $W$ ) equals 69.2441g, was held in position on a retort stand by means clips. Using a standard dosing pump (of model: *JM-15774-C07*), a 20g/L concentration inhibitor-in-acid (Castor Seed Oil-in-acid) was

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fed through the pipe from a plastic reservoir (bowl). The reservoir that contains the Castor Seed Oil (CSO) concentration-in-acid was placed moderately in a water bath that is set at a temperature of 40°C. The flow system was designed in such a way that the fluid is systematically recycled in a regular pattern. After 4hours of the cycle, the steel material was removed, rinsed (with distilled water), dried in an oven and weighed to obtain a final weight,  $W_2$ . The difference in mass,  $W_1 - W_2$  was evaluated and recorded. The experiment was repeated for different times of 8, 16, 24 and 32hours at 50°C and 60°C respectively. The same procedure was used for the Rubber Seed Oil (RSO) sample, and the various mass differences were duly computed and recorded as presented in *Table 1*.

### Thermodynamics Study

The thermodynamics of the process was studied for both samples, using the Arrhenius concept. The Arrhenius equation gives the dependence of the rate constant of a chemical reaction on absolute temperature, pre-exponential factor and other relevant reaction constants (Silberberg, 2006; Bauer *et al*, 2013). The heat energy requirement for corrosion reaction on the mildsteel, in the presence and absence of the inhibitor samples, at varying times, was evaluated using the Arrhenius formulation of *equation 1* as contained in both Eastop and McConkey (1993) and Levine (2005):

$$r_c = A \frac{-\Delta H}{RT} \quad (1)$$

Where:

$r_c$  = Corrosion rate (*percentage weight loss at a given inhibitor concentration in a given time*).

A = Arrhenius constant (*2.1 exp.9 sec<sup>-1</sup>*)

$\Delta H$  = Change in heat energy content

R = General gas constant (*8.31KJmol<sup>-1</sup>K<sup>-1</sup>*)

T = Reaction temperature

The rate of corrosion,  $r_c$  was evaluated using *equation 2*, as presented in *Table 1*.

$$r_c = \frac{(W_1 - W_2)}{W_1} \times 100 \quad (2)$$

Where:  $W_1$  = Initial mass of the material (before corrosion)

$W_2$  = Final mass of material (after corrosion)

**Table 1: Thermodynamics Data (for  $C_0=20g/L$ ) at Various Times**

Time (hour)	SAMPLE A (CSO)		SAMPLE B (RSO)	
	Weight Loss, $g$	$r_c$	Weight Loss, $g$	$r_c$
4	9.0422	13.06	7.7218	11.15
8	12.1285	17.52	9.0291	13.04
16	16.1819	23.37	10.8469	15.66
24	23.4251	33.83	18.9342	27.34
32	29.5454	42.67	21.2275	30.66

The enthalpy change of the reaction,  $\Delta H$  is given by equation 3.

$$\Delta H = \frac{1}{A} \cdot (RT) \cdot (r_c) \quad (3)$$

The values of the  $\Delta H$  at the respective conditions were duly computed. Also, the values of the corresponding changes in Entropy ( $\Delta S$ ) and Free Energy ( $\Delta G$ ) were respectively evaluated using equations 4 and 5 as contained in Philip (2003); the values  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  are duly presented in Table 2.

$$\Delta S = \frac{\Delta H}{\Delta T} \quad (4)$$

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

**Table 2: Thermodynamic Parameters**

Sample	Time (hr)	$\Delta H$ (KJ/mol)			$\Delta S$ (KJ/mol/K)			$-\Delta G$ (KJ/mol)		
		313K	323K	333K	313K	323K	333K	313K	323K	333K
A (CSO)	4.00	2.00	2.06	2.12	0.200	0.206	0.212	60.600	64.478	68.476
	8.00	2.68	2.76	2.85	0.268	0.276	0.285	81.204	86.388	92.055
	16.00	3.57	3.69	3.80	0.357	0.369	0.380	108.171	115.497	122.740
	24.00	5.17	5.34	5.50	0.517	0.534	0.550	156.651	167.142	177.650
	32.00	6.52	6.73	6.94	0.652	0.673	0.694	197.556	210.649	224.162
B (RSO)	4.00	1.70	1.76	1.81	0.170	0.176	0.181	51.510	55.088	58.463
	8.00	1.99	2.06	2.12	0.199	0.206	0.212	60.297	64.478	68.476
	16.00	2.39	2.47	2.55	0.239	0.247	0.255	72.417	77.311	82.365
	24.00	4.18	4.31	4.45	0.418	0.431	0.445	126.654	134.903	143.735
	32.00	4.69	4.84	4.99	0.469	0.484	0.499	142.107	151.492	161.177

From the thermodynamic parameters obtained (Table 2), it can be observed that enthalpy change ( $\Delta H$ ) increases with increase in time of the corrosion reaction. This demonstrates the continuous heat energy demand for the sorption process. The positive values of the entropy change ( $\Delta S$ ), also increase down the table, showing that the reaction at the solid-liquid interface occurs in the direction of increasing randomness. Also, the free energy values, at all cases, were negative; the negativity of the values deepened with increase in temperature of the reaction. This is traceable to the fact that effect of temperature tends to increase the degree of randomness in adsorbed molecular layer (Eddy and Odoemelam, 2008). In

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other words, there are higher collisions at higher temperatures, which result in higher kinetic energy (as well as the overall energy demand) of the reaction. The result, thus, confirms that the reaction is more spontaneous in the direction of increasing temperature change, and it is entropy-driven; any reaction that has a positive enthalpy change must be entropy-driven if it is spontaneous (Philip, 2003). This is because the combination of a rise in temperature and a large  $\Delta S$  value has the ability to make  $T\Delta S$  a large positive value, hence  $-T\Delta S$  becomes a large negative number that overcomes  $\Delta H$ .

Generally, the enthalpy change for **Sample A** (CSO) is higher than that of **Sample B** (RSO), indicating that more energy is required for the reaction involving the CSO to occur than is required in the case of the RSO. The results, however, were in agreement with the ones obtained in related works done by Undiandeye *et al* (2014b) and Ostovari (2009).

## CONCLUSION

This study shows that change in enthalpy of a corrosion reaction increases with time. The sorption process occurred in the direction of increasing randomness; it is spontaneous and enthalpy-driven. The thermodynamics parameters considered were higher in **Sample A** (CSO) than in **Sample B** (RSO).

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