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Inhibitive effect and adsorption study of *Chromolena odorata* and *Aspilia africana* as corrosion inhibition of zinc in 1 M H_2SO_4 solution

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Abstract

The inhibitive effect of *Chromolena odorata* and *Aspilia africana* as corrosion inhibitors for zinc in 1 M H_2SO_4 was examined using gravimetric method. The plant leaf extracts showed effective and good inhibitor for zinc in 1M H_2SO_4. From the results, *Chromolena odorata* and *Aspilia africana* retarded the corrosion of zinc in the acid medium. The inhibition efficiency of the plant extracts increase as the concentration increases and decrease as the temperature increases respectively. *Aspilia africana* showed better inhibition efficiency than *Chromolena odorata* in the same medium. The apparent activation energy (E_a), heat of adsorption (Q_{ads}) and free energy of adsorption (ΔG_{ads}) were determined. The value of ΔG_{ads} implies that the adsorption of inhibitor on the surface of zinc metal was spontaneous.

Keywords: Zinc, corrosion inhibition, utilization, *Chromolena odorata*, *Aspilia africana*.

1. Introduction

The nature of zinc has fascinated mankind for many centuries, because these materials provided people with accurate tools. The proper utilization of technology as it spun through almost every sphere of life, such as building of houses, construction of bridges, making of knives and kitchen utensils, electricity, automobile and so on. The joy gotten by the use of these metals is however truncated by a menace known as "corrosion". This hazard reduces its efficiency by impairing the metal and leaves it with some terrible characteristic such as a drastic reduction in its physical properties. Corrosion has been defined as the destructive attack of a material by reaction with its environment, and a natural potential hazard associated by industrial productions and transportation facilities (Popoola et al., 2013; Sharma et al, 2010; Uhlig, 1971). In order to curb/prevent the menace associated with corrosion, natural plants extracts (juice from leaves, roots, stems etc) are used as corrosion inhibitors to reduce or mitigate the influence of corrosion in our environments. Many efficient and environmental friendly corrosion inhibitors are used as alternative corrosion inhibitors to reduce the harmful effects on humans, animals and the environment. Some researchers (Ebenso, et al, 2008; Dahmani, et al, 2010; Shah, et al, 2011; Lebrini, et al, 2011;Eno & Obot, 2010; Deepa, et al, 2012; Yamuna and Noreen 2014), has successfully used Green corrosion inhibitors (extract from plant) to reduce corrosion in both acid and alkaline solutions. Green corrosion inhibitors (extract from plant) which happens to be non-toxic organic compound, displaying substantially improved environmental properties will be the inhibitors most widely used in the future. These natural organic compounds are either synthesized or extracted from the aromatic herbs, spices and medicinal plants. Plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost are biodegradable in nature (Rani and Basu, 2012).

2.0 Material and methods

2.1Stock solution of *Aspilia africana* and *Chromolena odorata* extracts

The leaves of *Aspilia africana* and *Chromolena odorata* were collected around the Faculty of Engineering, Nnamdi Azikiwe University, Awka, and shade dried for three days. 200g of dried powder were soaked completely with ethanol and left for 48 hrs. The resulting paste was filtered and the filtrate boiled to remove excess ethanol and the pure leaf extracts were collected respectively.

2.1.1 Specimen preparation

Rectangular specimen of zinc was mechanically pressed cut to form different coupons, each of dimension exactly 5.0 x 3.0 x 0.6cm. The specimens were mechanically polished; a hole drilled at one end for free suspension and numbered by punching. The specimens were decreased with acetone, washed with distilled water and abraded with 200 grade emery paper, cleaned and dried then stored in desiccators for further study.

2.1.1.1 Mass Loss method

In the mass loss measurements, zinc coupon in triplicate was completely immersed in 100ml of the test solution of 1M H_2SO_4 in the presence and absence of the inhibitors. The metal specimens were withdrawn from the test solutions after an hour interval for 8 hours at 303K to 343K. The mass loss was taken as the difference in weight of the specimens before and after immersiondetermined using Electronic analytical balance (JA303P) with sensitivity of $\pm$ 0.001g. 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 measurements, Corrosion rate was expressed in mg cm^{-2} hr^{-1} of the samples (Ali, et al, 2014): The inhibition efficiency (η%) was calculated from weight loss using the following equation:

$$CR = \frac{m_1 - m_2}{At} \qquad (1)$$

Where m_1 and m_2 are the weight loss in (mg) of Zinc before and after immersion, respectively, in test solutions, *A* is the area of specimen (cm^2) and *t* is the exposure time (hr). The inhibition efficiency (η%) was evaluated from corrosion rate as: (Al-Turkustani, et al, 2013),

$$\eta\% = 1 - \frac{CR(inh)}{CR_{(unin\ h)}} \times 100 \qquad (2)$$

Where *CR(uninh)* and *CR(inh.)* are the corrosion rates in the absence and presence of the inhibitor, respectively at same temperature.

The fraction of zinc surface covered by the adsorbed extract molecules (θ) was calculated as Deepa Rani P., et al, (2012),

$$\theta = 1 - \frac{CR_{(in\,h)}}{CR_{(unin\ h)}} \qquad (3)$$

3.0 Results and Discussions

3.1 Effect of immersion period on inhibition efficiency

The inhibition efficiency is calculated from the weight loss experiments performed for zinc in 1 M H_2SO_4 for different inhibitor concentrations per 100 ml of corrosive medium and temperature 303K – 343K ± 1°C. It can be observed from Figure 1, that there was a slight increment between 40 and 50%, although there was a sharp increment in inhibition efficiency from 60 – 85% as the immersion period increases implying that inhibition efficiency increases as time progresses. Similar curve was also obtained for *Chromolena odorata but not shown*. The reason behind this increase in inhibitionefficiency initially may be attributed to the formationof a barrier film (Murthy, and Vijayaragavan, (2014).

3.2 Effect of inhibitor concentration on inhibition efficiency

It is seen from Figure 2that the inhibition efficiency of *Chlomolena odorata* and *Aspilia africana* on zinc increases as the inhibitor concentration increases and then decreases as the temperature increases. The increase in efficiency of the inhibitor with increase in concentration may be attributed to increase in number of molecules occupied by the inhibitor on the zinc acid solution interface. As the number of molecules increases, the corrosion reactions are prevented from occurring over the active sites of the zinc surface covered by adsorbed inhibitor species, whereas the corrosion takes place on the surface not covered by the inhibitor molecules. Thereby, one may conclude that the greater the surface coverage the greater the inhibition efficiency. This is in agreement with literature (Ayman, et al, 2014; Durowaye, et al, 2014).

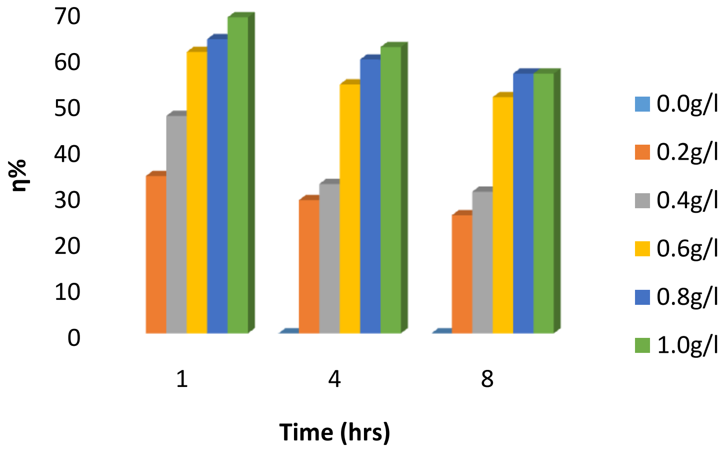


Figure 1: Inhibition efficiency (η%) for corrosion of zinc in 1M H_2SO_4 in the absence and presence of various concentrations of the *Aspilia africana*

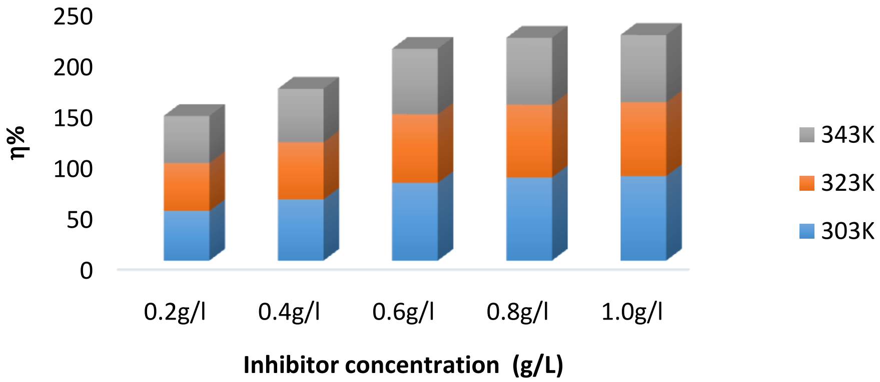


Figure 2. Effect of inhibitor concentration on inhibition efficiency of zinc in free and inhibited solutions

3.3 Effect of inhibitor concentration on corrosion rate

Figure 3 shows plot of corrosion rate of zinc specimens as a function of concentration of the inhibitor. It is seen from the results, that corrosion rate decreases with increase in concentration. It is assumed that as the concentration of inhibitor increases, the number of inhibitor molecules occupying the active site increases, thereby offering resistance to the activity of acid (i.e. decreases the corrosion rate), (Shanthi, and Rajendran, 2013; Deepa, and Selvaraj, 2010). The adsorbed layer combats the action of acid and enhances the protection of metal surface (Amitha, and Bharathi, 2012). Withhigh inhibitor concentrations, a compact and coherent inhibitor over-layer forms on the zinc surface, reducing chemical attack of the metal. The results are inline with the works of (Amitha, and Bharathi, 2012).

3.4 Effect of inhibitor concentration on activation parameters

The effect of the temperature was carried out to determine the performance of the two inhibitors and the nature of adsorption on the dissolution of zinc in 1M H_2SO_4. Based on the information above, Arrhenius equation Eq (4a) and transition state equation Eq (5) was used to calculate the activation thermodynamic parameters such as apparent activation energy E_a, enthalpy of adsorption ($\Delta H°_{ads}$) and entropy of adsorption ($\Delta S°_{ads}$) (Oguzie, et al, 2012).

$$CR = Aexp(-E_a/RT) \qquad (4a)$$

The heat of adsorption Q_{ads} (kJ mol^{-1}), was determined using the expression;

$$Q_{ads} = 2.303R\left[Log\left(\frac{\theta_2}{1-\theta_2}\right) - Log\left(\frac{\theta_1}{1-\theta_1}\right)\right] \times \frac{T_1 \times T_2}{T_2 - T_1} \qquad (4b)$$

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

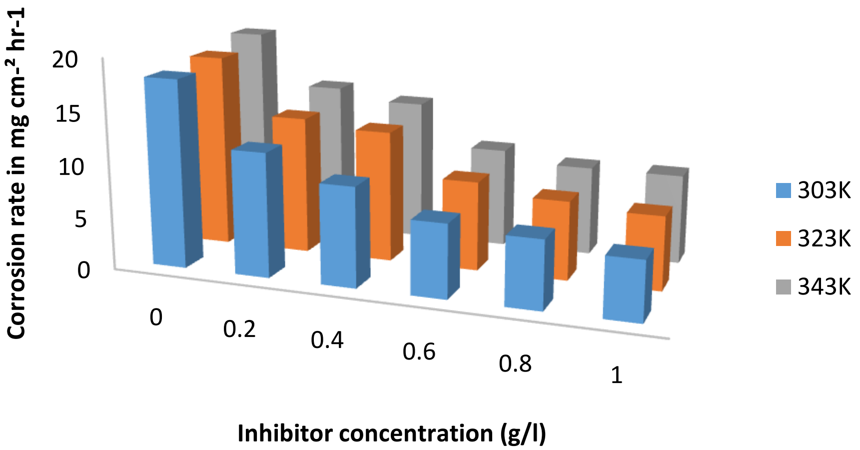


Figure 3: Variation of corrosion rate with concentration of *Chromolena odorata* for the zinc in 1M H_2SO_4

Where CR is the corrosion rate, $E_a$is the apparent activation energy, R is the molar gas constant, T is the absolute temperature, A is the frequency factor, h is the Planck's constant and N is the Avogadro's number. The activation energy $E_a$was calculated from the slope of the plots of Log CR versus 1/T Figures 4 and 5. Plots of Log (CR/T) as a function of 1/T (Figures 6 and 7) give a straight line with a slope of (—ΔH°/ 2.303R) and an intercept of (logR/Nh + ΔS°/2.303R) from which the values of $\Delta H°$ and $\Delta S°$ were calculated, and listed in Table 1.

Table 1: Activation parameters and head of adsorption for dissolution of zinc in 1M H_2S0_4 using *Aspilia africana* and *Chromolena odorata*

Aspilia africana					***Chromolena odorata***			
Con of Inhibitors (g/l)	**Ea (KJ/mol)**	**ΔH (KJ/mol)**	**ΔS (KJ/mol)**	**Qads (KJ/mol)**	**Ea (KJ/mol)**	**ΔH (KJ/mol)**	**ΔS (KJ/mol)**	**Qads (KJ/mol)**
0.0	7.93	5.80	-3.98		13.0	9.11	-11.1	
0.2	8.55	5.56	-4.27	-1.72	13.3	11.2	-10.8	-2.07
0.4	31.7	28.9	-27.7	-1.78	50.5	47.2	-45.7	-0.05
0.6	45.9	43.7	-40.8	-12.07	68.3	65.1	-60.3	-10.21
0.8	50.3	47.8	-45.0	-17.27	68.0	66.2	-62.2	-16.16
1.0	64.6	61.9	-60.0	-17.59	70.3	68.3	-66.6	-17.54

Inspection of Table 1 reveals that the presence of plant leaves extracts increases the values of $E_a$as compared to the blank (without *Aspilia africana* and *Chromolena odorata* extracts) indicating physical adsorption of the extracts on the metal surface. The positive values of $\Delta H°$ reflect the endothermic nature of the zinc dissolution process in the 1 M H_2SO_4. The values of $\Delta S°$ in the presence and absence of the extracts are large and negative implying that the activation complex in the rate determining step represents association rather than dissociation. This is an indication that a decrease in disorder takes place on going from reactants to the activated complex (Obot, & Obi- Egbedi, 2009). The heat of adsorption, Q_{ads} was calculated from Equation (4b) and presented in Table 1.

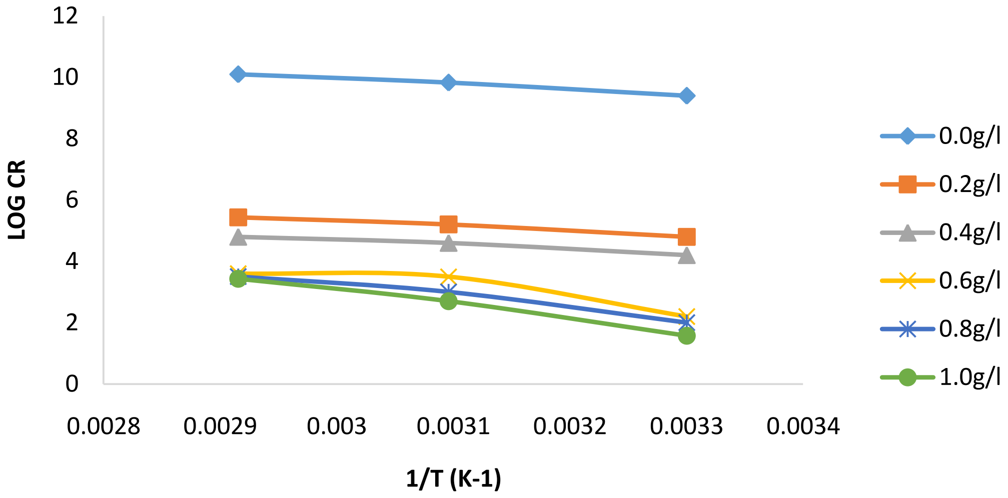


Figure 4: Arrhenius plot for zinc corrosion in 1M H_2S0_4 in the absence and presence of various concentrations of *Aspilia africana*

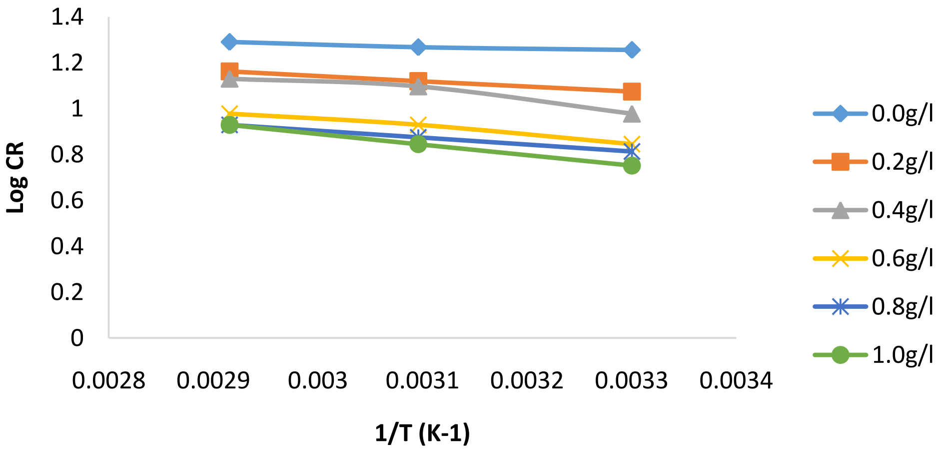


Figure 5: Arrhenius plot for zinc corrosion in 1M H_2S0_4 in the absence and presence of various concentrations of *Chromolena odorata*

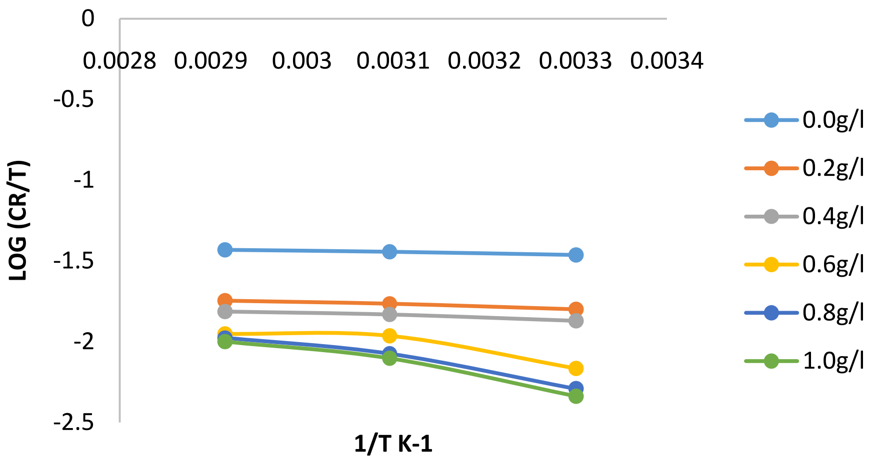


Figure 6: Transition plot for zinc corrosion in 1M H_2S0_4 in the absence and presence of various concentrations of *Aspilia africana*

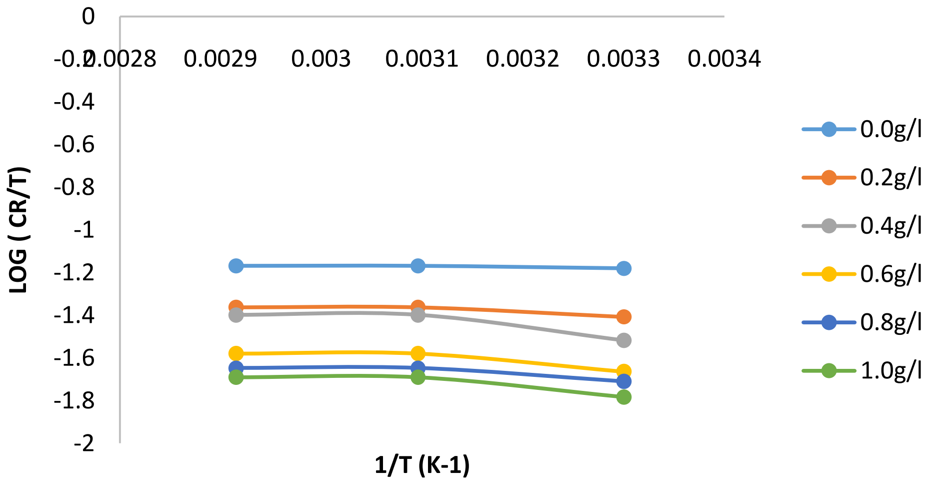


Figure 7: Transition plot for zinc corrosion in 1M H_2S0_4 in the absence and presence of various concentrations of *Chromolena odorata*

3.5 Adsorption isotherms

The fundamental information on the interaction between the inhibitors and the zinc surface (Murthya, &Vijayaragavana, 2014) and mechanism of electrochemical reaction (Ikeuba, et al, 2014) may be provided by the adsorption isotherm.

Table 2: Adsorption properties for the corrosion inhibition of Zn in H_2SO_4 by *Aspilia africana* leaf extracts.

Adsorption Isotherm	Temp (K)	R^2	Log K	K_{ads}	Slope	ΔG_{ads} (kJ/mol)	Isotherm value
Flory-Huggins Isotherm	303	0.9999	-0.7288	0.1867	1.2179	-5.8911	x 1.218
	343	0.9991	-0.4623	0.3449	0.7728	-8.4194	0.729

The surface coverage of different concentrations of inhibitor in acidic media has been evaluated from weight loss measurements and attempted to fit these values to different adsorption isotherms. In this study, Flory-Huggins adsorption isotherm was found to be suitable for the experimental findings and has been used to describe the adsorption characteristic of the inhibitors. The Flory-Huggins theory allows the most basic presentation of adsorption on an ideal surface. The Flory-Huggins adsorption isotherm may be written in the form: Flory-Huggins isotherm:

$$Log\left(\frac{\theta}{C}\right) = LogK + \alpha Log(1-\theta) \qquad (6)$$

(Ating, et al, 2010), θ is the surface coverage, C is the inhibitor concentration, α is the molecular interaction parameter, and K is the equilibrium constant of adsorption process. K is related to the free energy of adsorption by the equation:

$$K = \left[\frac{1}{55.5}\right] exp\left[\frac{\Delta G^{\circ}{}_{ads}}{RT}\right] \qquad (7)$$

Where θis the degree of surface coverage, K_{ads} is the equilibrium constant of adsorption process, and ΔG°_{ads} is the free energy of adsorption values.

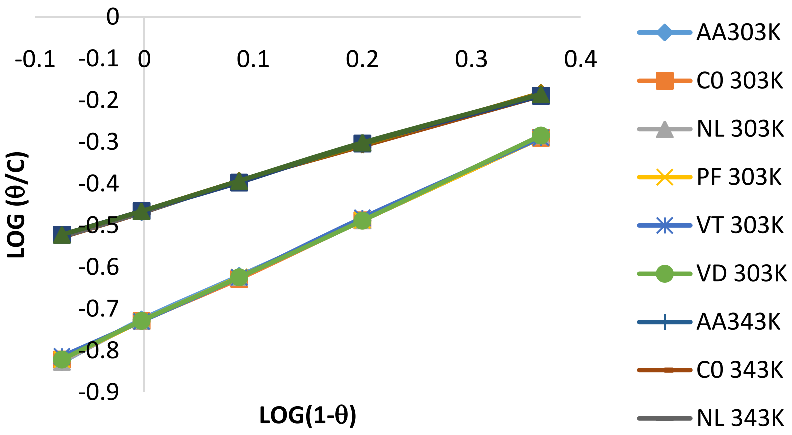
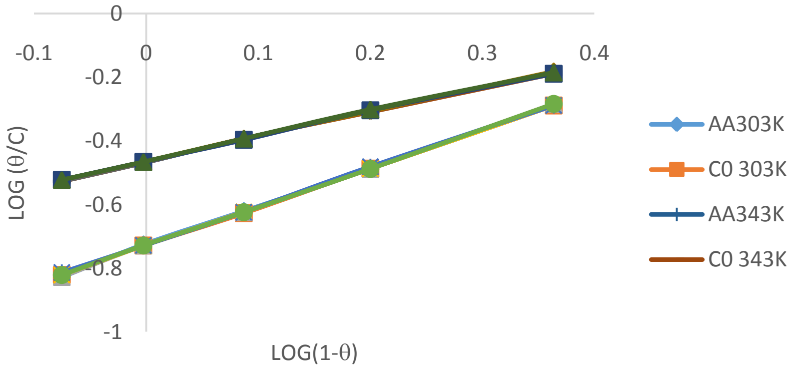


Figure 8: Plot of Log (θ/C) versus Log (1-θ) for corrosion inhibition of Zn in H_2S0_4 using different inhibitors at 303K and 343K.



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4.0. Conclusion

The following conclusions were drawn from the results of the study:

1. Acid extracts of *Aspilia africana* and *Chromolena odorata*leaves proved to be a good corrosion inhibitors for zinc in 1M H_2SO_4 solution.
2. The inhibition efficiency of *Aspilia africana* and *Chromolena odorata* increases as inhibitor concentration increases and decrease with increase in temperature.
3. The adsorption properties was found to obey physical adsorption phenomena and followed Flory- Huggins adsorption isotherm which exhibited the best fit to the experimental data.

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