Bulletin of Pure and Applied Sciences.
Vol.31C-Chemistry (No.2)2012:P.49-58
www.bpas.in

INHIBITORY ACTION OF BILE SALT ON THE DETERIORATION OF ASBESTOS IN ACID RAIN

I. A. Akpan
Department of Chemistry
University of Uyo, Uyo, Akwa Ibom State, Nigeria
*e-mail: iaakpanchem2007@yahoo.com

Received on 20 August 2012: Accepted on 15 November 2012

ABSTRACT

The susceptibility of asbestos in mild acid concentration equivalent to acid rain has been studied. Bile salt was tested on the materials surface as inhibitor. Weight loss measurement reveals that bile salt inhibits the deterioration of asbestos in acidic corrodent with low efficiency. The inhibition effect is more pronounced with increasing temperatures as well as inhibitor concentration. Chemical adsorption mechanism has been proposed for the inhibitor. The low values of inhibition efficiency are probably due to the presence of Ca atoms in the chemical composition of asbestos.

Keywords: Deterioration, Asbestos, Bile salt, Acid rain.

1.0 INTRODUCTION

Initially, building industry greatly depended on the integrity of galvanized steel for roofing sheets[1]. Long-term observation shows that the trust that has been placed on galvanized steel has been challenged by the deleterious effect of corrosion which, first, changes the metallic luster to rust, then pitting, and finally total embrittlement[2]. These manifestations are due to interaction of the metallic structure in contact with aqueous and non-aqueous media. Such damage are severally observed to attract renovations and replacements where the worn-out galvanized steel is alternatively replaced with either aluminium metal sheets or asbestos.

Hitherto, intensive research has been focused on the corrosion of mild steel and aluminium sheets in various media [3-5]. Recently, we have reported on the high efficiency of bile salt on the corrosion inhibition of galvanized steel in tetraoxosulphate (vi) acid[6].

The present work is to test the sensitivity of the biological substance (bile salt) on the surface of asbestos in mild acid condition equivalent to acid rain using weight loss technique.

The inhibition efficiency I(%) has been assessed using the known relation[7].

$$I(\%) = \frac{W_O - W_I}{W_O} \times 100 \quad \ldots \quad \ldots \quad (1.1)$$

where W_O and W_I are the weight loss data in the absence and presence of the inhibitors respectively. The effect of the structural composition of bile salt on its biochemical actions as well as inhibition efficiency has been incorporated into the inhibition studies. The overall results have been assessed kinetically and thermodynamically.

2.0 EXPERIMENTAL

Weight loss corrosion test method as already reported in some previous publications[1-8] were used for this study.

2.1 Materials Preparation

The popular asbestos branded "EMENITE" was used for this study and mechanically press-cut into 5x4 cm coupons of thickness 0.20cm. The coupons were examined carefully to ensure smooth edges to avoid accelerated deterioration at the edges. The coupons were used as supplied and without further polishing, but surface treament of the coupons made use of degreasing in absolute ethanol and drying in acetone. The treated coupons were then stored in a moisture-free desiccator before their use in deterioration studies[9].

The bile salt used for the inhibition was extracted fresh from a dog's liver and used immediately to avoid biodegradation. Inhibitor concentration ranging from 1.0 drop to 5.0 drops were tested in various concentrations of the corrodent. All reagents were of Analar grade, and bi-distilled water was used for the preparation of all solutions.

2.2 Weight Loss Deterioration Test Without Inhibitor

Previously weighed asbestos coupons were suspended in 0.01, 0.02, 0.03, 0.04 and 0.05M H_2SO_4 solutions contained in five 250ml beakers kept at room temperature (30 ± 1^oC) and in a thermostat-controlled bath maintained at 40^oC. The coupons were retrieved from their corrodent solutions at 24h intervals progressively for 168h (7 days), washed separately and gently several times with distilled water, dried in acetone and reweighed[10]. The difference in weight defined as:

$$\Delta W = W_i - W_f \quad \ldots \quad \ldots \quad (2.1)$$

was taken as the weight loss evaluated in g. W_f is the final weight at time t, and W_i is the initial weight at time t = 0. Each reading reported in this paper is an average of two readings recorded on the Mettler H35AR analytical balance to the nearest 0.0001g.

2.3 Weight Loss Deterioration Test With Inhibitor

The inhibitor investigated is a biological juice (bile salt), extracted fresh from a butchered dog liver. Each of the previously weighed asbestos coupons was introduced into five beakers containing bile salt. Each experiment in the presence of the tested inhbitor was performed at 30 and 40^oC. As before, each asbestos coupon was retrieved from the corrodent-inhibitor solution at 24h intervals for 168h, washed and weighed. The difference in weight of the coupons was again taken as the weight loss.

3.0 RESULT AND DISCUSSION

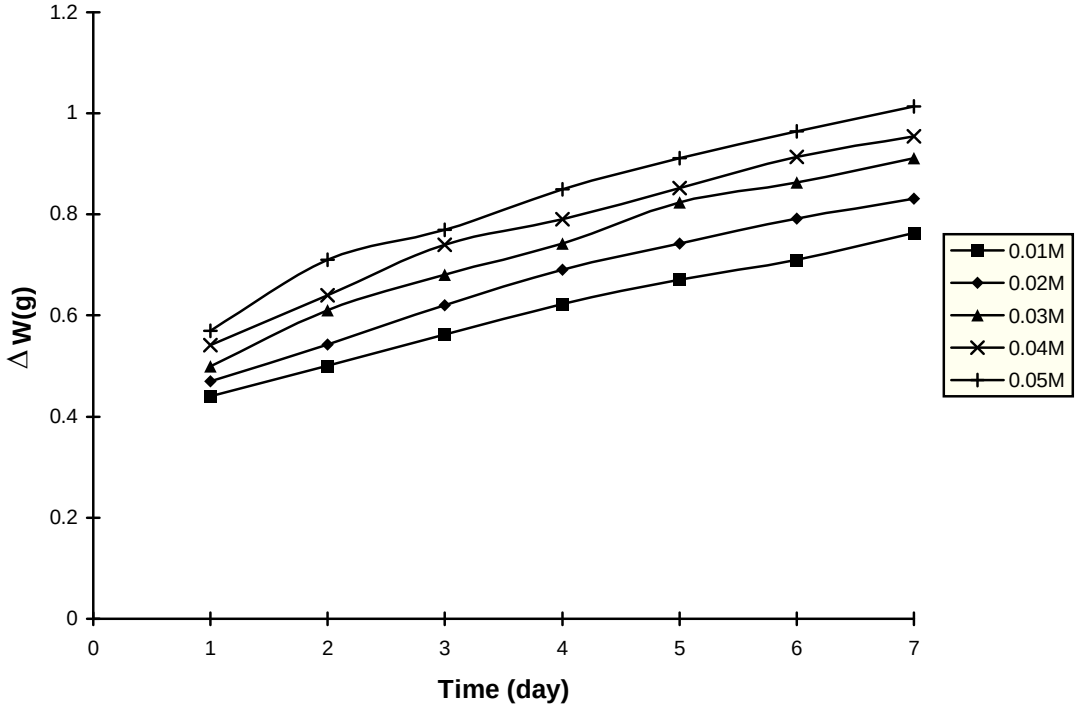

Fig. 3.1: **Variation of Weight Loss with Time for Asbestos Coupon in H_2SO_4 Solution at 30°C without Inhibitor.**

3.1 Deterioration of Asbestos by H_2SO_4 Solution

The deterioration of asbestos in different concentrations of H_2SO_4 solution (Fig. 3.1) and at 30 and 40°C (Fig 3.2) without inhibitor was investigated. The results obtained show that the weight loss of asbestos in H_2SO_4 solutions increases with increasing acid concentration at a given temperature. For instance in Fig. 3.1, the weight loss of asbestos in 0.05M H_2SO_4 solution was about 1.3 times more than those obtained in 0.01M H_2SO_4 solution. This observation is in consonance with the theory of mass action proposed by Guldberg and Waage[11].

Fig. 3.2 reveals that at constant H_2SO_4 concentration, the weight loss increases with increasing temperature. Similar plots were obtained for 0.02, 0.03, 0.04 and 0.05M H_2SO_4 solutions. An increase in temperature favours the formation of activated molecules which may be doubled in number, by a 10°C rise in temperature, thereby increasing the reaction rate [12].

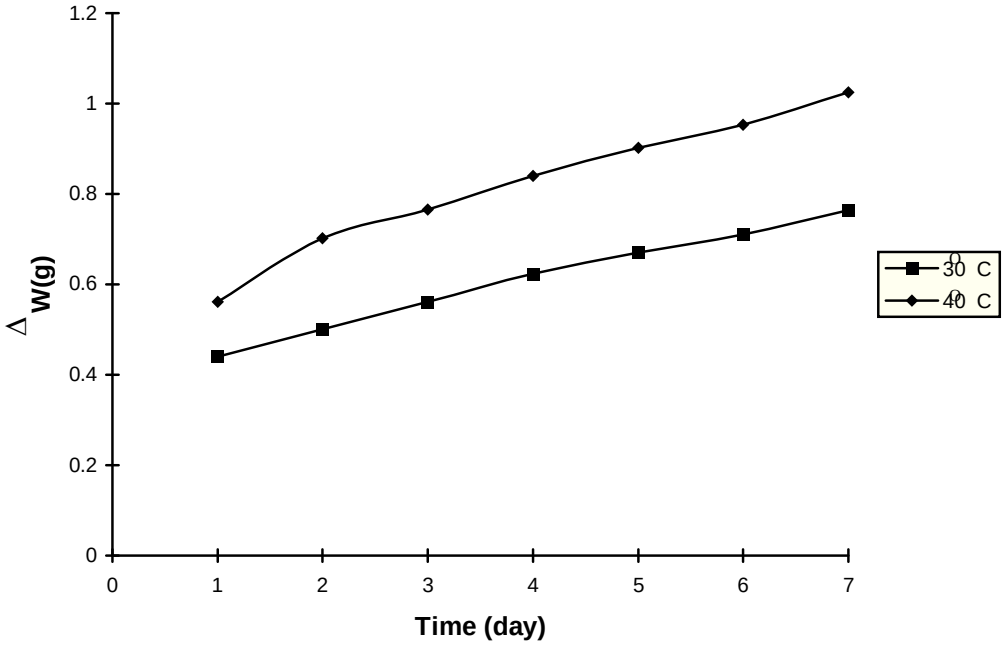

Fig. 3.2: **Variation of Weight Loss with Time for Asbestos Coupon in 0.01M H_2SO_4 Solution at different temperatures without Inhibitor.**

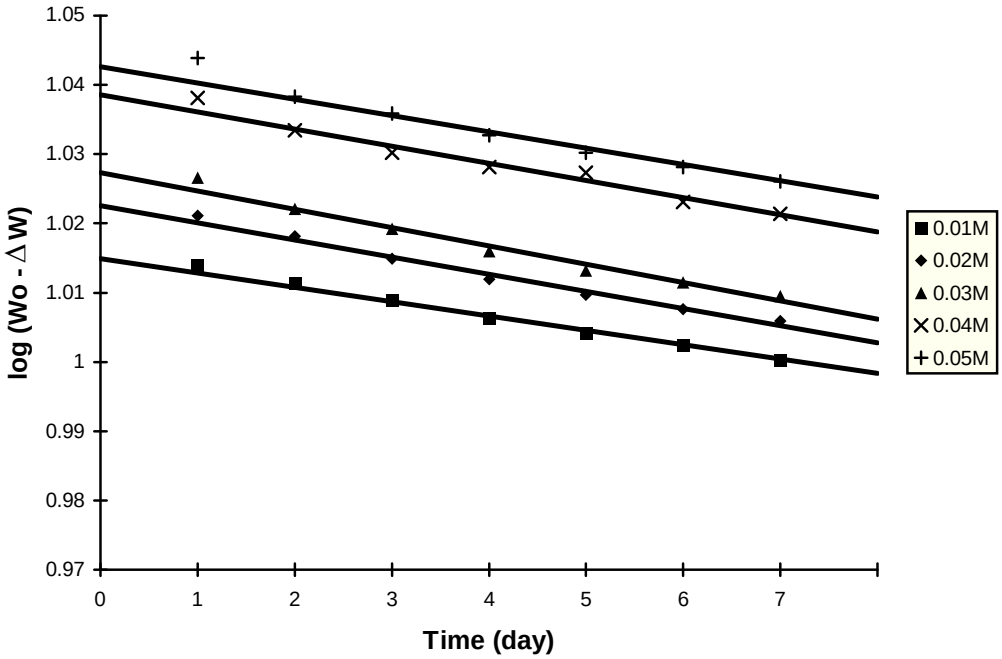

Fig. 3.3: **Variation of log(W_o – ΔW) with Time for Asbestos Coupon in H_2SO_4 Solution at 30°C without Inhibitor.**

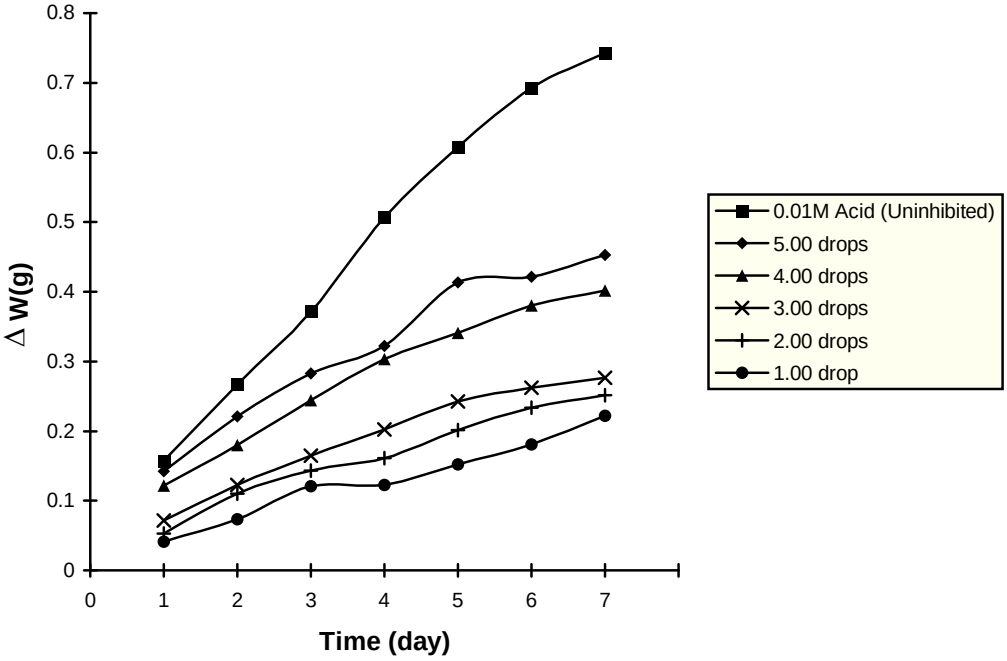

Fig. 3.4: **Variation of Weight Loss with Time for Asbestos Coupon in 0.01M H_2SO_4 Solution containing Bile Salt at 30°C .**

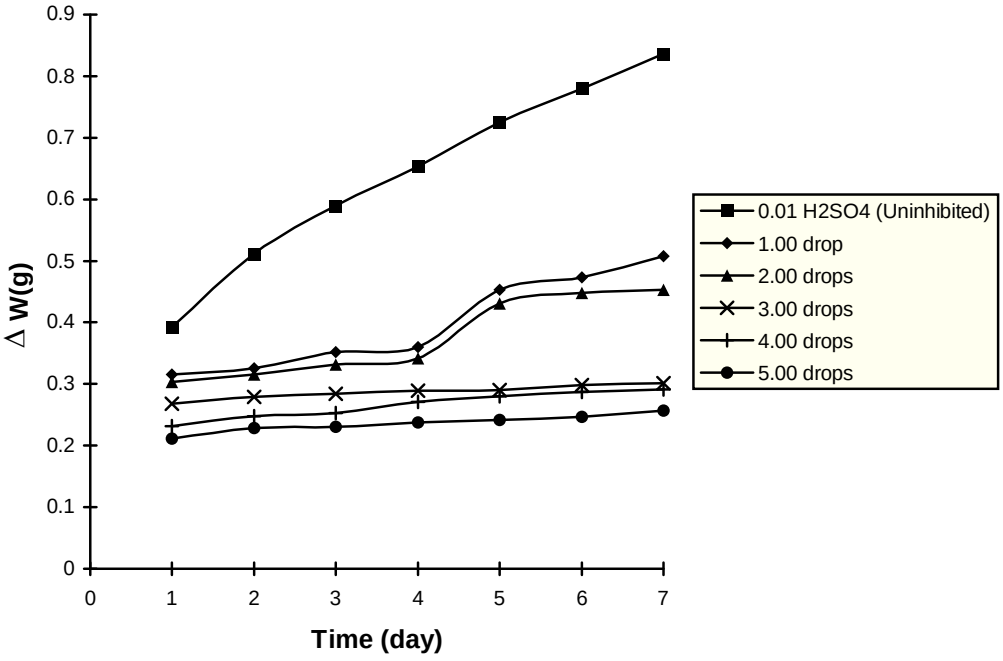

Fig. 3.5 **Variation of Weight Loss with Time for Asbestos Coupon in 0.01M H_2SO_4 Solution containing Bile Salt at 40°C.**

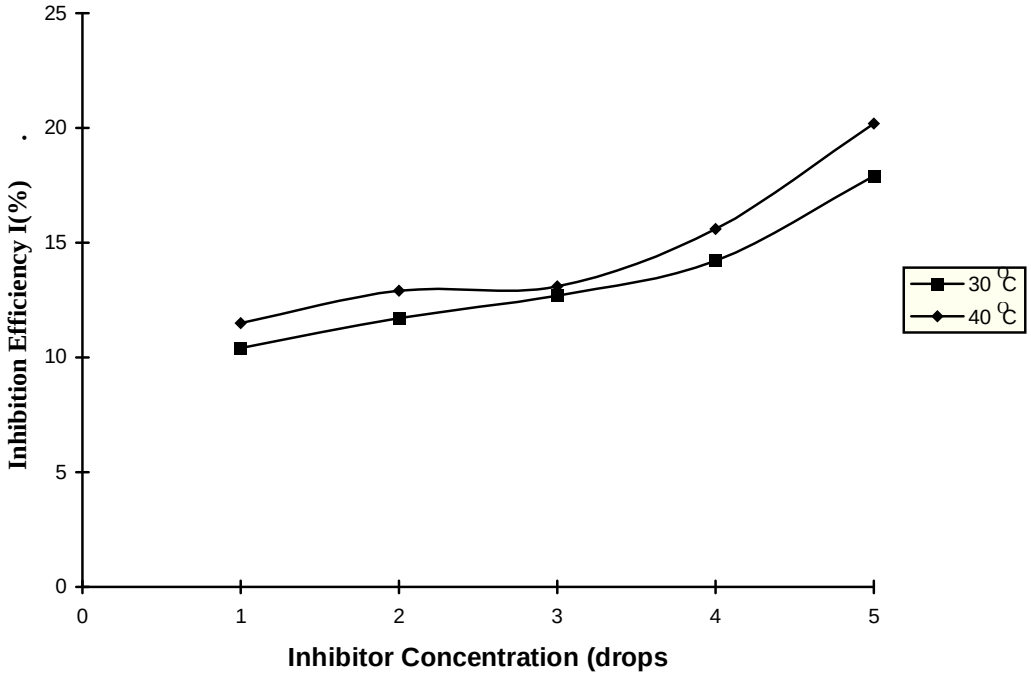

Fig. 3.6: **Variation of Inhibition Efficiency I(%)with Inhibitor Concentration for Asbestos in 0.01M H_2SO_4 Solution containing Bile Salt.**

Table 3.1: **Deterioration rate of uninhibited and inhibited asbestos coupons in various corrodent concentrations at 30 and 40°C (inhibitor concentration = 2.0 drops).**

Corrodent Concentration (M)	Deterioration Rate (Uninhibited (MPY)		Deterioration Rate (Inhibited (MPY)	
	30°C	40°C	30°C	40°C
0.01	2.12×10^{-4}	2.53×10^{-4}	1.74×10^{-4}	2.02×10^{-4}
0.02	2.35×10^{-4}	2.75×10^{-4}	2.02×10^{-4}	2.32×10^{-4}
0.03	2.65×10^{-4}	3.02×10^{-4}	2.32×10^{-4}	2.62×10^{-4}
0.04	2.76×10^{-4}	3.16×10^{-4}	2.43×10^{-4}	2.75×10^{-4}
0.05	2.79×10^{-4}	3.19×10^{-4}	2.50×10^{-4}	2.82×10^{-4}

Application of Markov Chains[13] to plot the course of this reaction shows that the deterioration of asbestos by H_2SO_4 solutions does not progress by simple homogeneous process, but by heterogeneous one involving several intermediates. This assertion is further confirmed from the non-uniformity of the plots in fig. 3.1. Based on this observation, the results were tested for the various order of reactions. A plot of log(Wo - ΔW) against time (days) reveal a first-order kinetics with respect

to asbestos coupons in H_2SO_4 solution (Fig. 3.3). The half lives, $t_{½}$ (days), obtained for asbestos in 0.01M H_2SO_4 without inhibitor are 87.0 and 74.0 days at 30 and 40°C, respectively.

Table 3.2: **Kinetic Data for the Deterioration of Asbestos in H_2SO_4 Solution and Inhibition Efficiency of Bile Salt at 30 and 40°C.**

Inhibition Concentration (drops)	Rate Constant K (day^{-1})		Half life $t_{½}$ (days)		Activation Energy E_a ($kJmol^{-1}$)	Inhibition Efficiency I(%)	
	30°C	40°C	30°C	40°C	30 – 40°C	30°C	40°C
0.00	0.0096	0.0137	72.0	51.0	28.1	-	-
0.01	0.0080	0.0094	87.0	74.0	12.7	10.4	11.5
0.02	0.0073	0.0082	95.0	85.0	9.2	11.7	12.9
0.03	0.0062	0.0071	112.0	98.0	10.7	12.7	13.1
0.04	0.0054	0.0063	128.0	110.0	12.2	14.2	15.6
0.05	0.0047	0.0056	148.0	124.0	13.8	17.9	20.2

The deterioration rate ($k_{det.}$) for asbestos in H_2SO_4 solution was calculated in millimeter penetration per year (MPY) using Eq 4.1

$$k_{det.}\ (MPY) = \frac{W/A}{D} \times \frac{0.36525}{\rho} \quad \ldots \quad \ldots \quad (4.1)$$

where W = weight loss (g)
A = area of coupon (cm^2)
D = number of days of exposure
ρ = density of asbestos (gcm^{-3})

Results obtained from Eq. (4.1) reveal 1.74×10^{-4} and 2.02×10^{-4} MPY at 30 and 40°C respectively in 0.01M H_2SO_4 solution, as deterioration rates. The results also show that the deterioration rate is higher at 40°C than at 30°C and is in good agreement with the observed higher weight loss at 40°C than at 30°C without inhibitor (Fig. 3.2).

3.2 Effect of Inhibitor Concentration

Figs. 3.4 and 3.5 reveal that bile salt actually inhibits the acid deterioration of asbestos to an appreciable extent. Compared with Figs. 3.1 and 3.2 lower weight loss data are recorded. Fig. 3.6 shows that inhibition efficiency increases with increasing inhibitor concentration as well as temperature.

3.3 Proposed Inhibition Mechanism of Bile Salt on Asbestos Surface Based on Thermo-kinetic Data.

It is generally acknowledged that the temperature dependence of inhibition efficiency and the comparison of the apparent activation energy of the deterioration process

both in the absence and in the presence of the inhibitors leads to some conclusions concerning the mechanism of the inhibiting action.

According to Popova *et al*.[14], a decrease in inhibition efficiency with increasing temperature accompanied with increase in deterioration activation energy in the presence of the inhibitor compared to its absence, is often interpreted as an indication of the formation of an adsorptive film of a physical (electrostatic) character.

The opposite effect corresponding to lower E_a in the inhibited solution compared to the inhibited solution, and an increase in inhibition efficiency with increase in temperature indicates the formation of chemisorptive bonds between inhibitor species and the metal surface.

In the present study, the results given in Table 3.2 indicate that the inhibition efficiency of the studied biological juice increases with an increase in the temperature of the system from 30 to 40^{o}C. This as a first instance suggests that the bile salt was chemically adsorbed on the asbestos surface. The fact that inhibition efficiency increases with temperature is probably due to likely specific chemical interaction between the asbestos surface and the inhibitor. Correspondingly, the data in Table 3.2 illustrate that the activation energies for the corrosion process in the presence of the studied compound (bile salt) in various concentrations were lower than the value obtained in the blank corrodent. This is further evidence for the proposed chemisorption mechanism of the bile salt.

3.4 Inhibition Efficiency of bile salt with reference to molecular structure

Bile is composed of a variety of substance which composition is determined both by secretory and excretory activities of the liver. With respect to function and therapeutic application, the most important constituent of bile are the bile acids and their conjugates. The bile acids are derivatives of cholanic acid, which is a steroid. The conjugates are referred to as bile salt which are polar derivatives of cholesterol. The structures of cholanic acid and glycocholate (bile salt) are shown in Fig. 4.1 and 4.2 respectively.

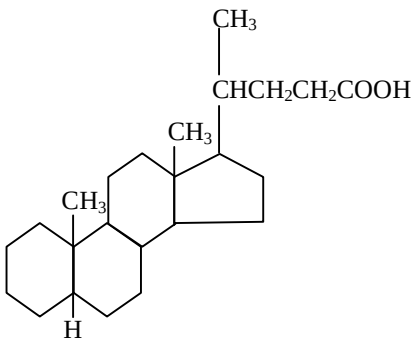

Fig. 4.1: **Structure of Cholanic Acid.**

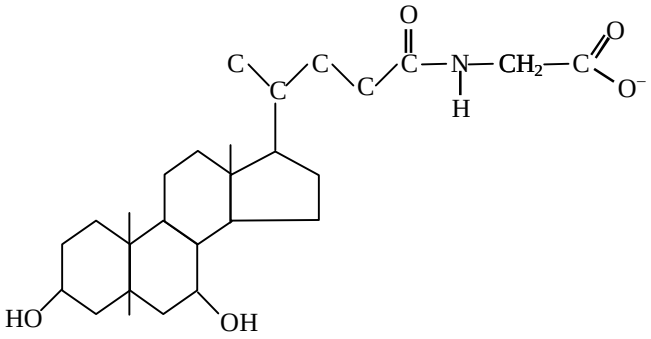

Fig. 4.2: **Structure of Glycocholate (Bile Salt).**

The molecular structure of bile salt shows that it is amine type of organic compound containing nitrogen atom and benzene rings, with carbonyl group attached to the amino group. The lone pairs on the oxygen and nitrogen atoms furnishes the inhibitor with electrons for co-ordinate bonding with calcium atoms on the asbestos surface, shielding the asbestos from acid attack. The low values of inhibition efficiency recorded at both temperatures (30 and 40^{o}C) is attributed to the presence of calcium atoms on asbestos surface[15].

4.0 CONCLUSION

The deterioration of asbestos in H_2SO_4 solution without inhibition increases with increasing acid concentration and temperature. Bile salt inhibits the deterioration of asbestos in the acidic corrodent probably by being chemically adsorbed onto the asbestos surface. The inhibition efficiency increases with increasing inhibitor concentration and temperature. The inhibitory activity of bile salt on asbestos surface is greatly hindered, probably by the presence of Ca atoms.

5.0 ACKNOWLEDGEMENTS

The authors are thankful to Mr. Monday Inyang Udoh for performing measurements. Useful suggestions offered by Dr. B. I. Ita of the Department of Pure and Applied Chemistry, University of Calabar, are greatly acknowledged.

REFERENCES

1. Corrosion Basics. An Introduction. National Association of Corrosion Engineers, Houston, TX, 1984.

2. Onuchukwu,A.I. and Trasatti,S.(1988). *Electrochemic Acta*, 33:1425 – 1430.

3. Granese,S.L.(1988).*Corros Sci.*, 44 : 322 – 327.

4. Mengoli,G. , Musiani, M.M., Pagura,C. and Paolucci,F.(1991). *Corros. Sci.*, 32 : 743 – 753

5. Gurmeet,S. and Kaur,G. (1984). *Trans. Soc. Adv. Elkectrochem. Sci. Technol*. 19 : 106 – 117.

6. Akpan, I.A. and Ekop, A.S.(2007). *Trop. J. Appl. Sci.,* (2007). In Print.

7. Ekpe, U. J., Ibok, U.J.,B. I. Ita,B., Offiong,O.E. and Ebenso,E.E.(1995). *Mater. Chem. Phys*. 40 : 87 – 93.

8. Onuchukwu,A.I. and Lori,J.A.(1984). *Corros. Sci.,* 24: 833 – 841.

9. Onuchukwu,A.I. and Baba,A.I.(1987). *Mater. Chem. Phys*. 18: 381 – 390.

10. Ekpe,U.J., Ebenso,E.E. and Ibok,U.J. (1994). *J. W. Afric. Sci. Assoc.* 37 :13 – 18.

11. Chadwick,T.F. Chemistry: A Modern Introduction for Sixth Forms and Colleges. Part 3: Physical Chemistry. Second Edition. George Allen and Unwin Ltd. London, 1977; pp.156 – 157.

12. Gross,J.M. and Wiseall,B. Principles of Physical Chemistry. MacDonald and Evans, London,1972.

13. Sebatiao,J.F. and Maria da Graca,M.M.(1979). *Journal of Chem Edu*. 9 :583 – 585.

14. Popova, A., Sokolova, E., Raicheva, S. and Christov, M.(2003). *Corros. Sci.,* 45 : 33 – 58.

15. Hoffman,G.N.(2002). *Trop. Journ. Of Biotechnol*. 7 : 312 – 322.