PHYSICOCHEMICAL AND RHEOLOGICAL CHARACTERIZATION OF SOME PLANT GUM EXUDATES AND THEIR INHIBITION OF THE CORROSION OF ALUMINIUM IN ACIDIC MEDIUM

BY

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DECLARATION

I hereby declare that the work in this thesis titled **"Physicochemical and rheological characterization of some plant gum exudates and their inhibition of the corrosion of aluminium in acidic medium"** was performed by me in the Department of Chemistry, under the supervision of **Dr. N. O. Eddy** and **Prof. C. E. Gimba**. The information derived from the literature has been duly acknowledged in the text and a list of references is provided. No part of this work has been presented for another degree or diploma at any institution.

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CERTIFICATION

This project report/thesis/dissertation titled **"Physicochemical and rheological characterization of some plant gum exudates and their inhibition of the corrosion of aluminum in acidic medium"** meets the regulations governing the award of M.Sc. degree in Physical Chemistry of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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ABSTRACT

Trichilia roka (TR), *Newbouldia laevis* (NL), *Ficus sycomorus* (FS) and *Fagara zanthoxyloides* (FZ) gum exudates were tapped from their individual trees and purified. Physical analysis (colour, taste, odour, pH, solubility in various solvents, turbidity, salinity, total dissolved solids, melting point range, conductivity and swelling property) of the gums reveals that the gums are mild acidic, ionic and soluble in water but insoluble in organic solvents. Gas chromatography mass spectrometry and fourier transform infrared analysis of the gums shows the presence of compounds and functional groups typical for polysaccharides. Intrinsic viscosities calculated from Huggins, Kraemer, Tanglertpaibul and Rao plots were relatively comparable. Steady shear properties were studied from speed of rotation versus viscosity plots to obtain yield stress values found to range from 7.79 to 10.35. From thermodynamic parameters of flow, values of ΔH_V and ΔS_V were found to be in the range of 12.42 to 17.93 and from -272.85 to -289.93 J/mol respectively. This suggests exothermic and ordered systems. From Arrhenius-Frenkel-Eyring plots, calculated activation energies of flow (E_F) were found to range from 12.42 to 17.93 J/mol, which indicate the existence of few inter and intra-interactions between polysaccharide chains in the concentration range investigated. This finding has also been supported by the low free energies of flow of the studied gums. Coil conformation phenomenon was studied from the plots of specific viscosity against coil overlap parameter ($C[\eta]$ and transition from dilute to concentrated systems observed with remarkable slope changes of 0.29 to 0.42, 0.69 to 0.43, 0.46 to 0.42 and from 0.74 to 0.29 for TR, NL, FS and FZ respectively, which indicate that transition occurred. The effects of KCl, $CaCl_2$, $AlCl_3$ and urea on the viscosities of the gums were investigated and it was found that the viscosity of TR gum increases by the presence of 1% of urea and KCl while the presence of 1% $AlCl_3$ and $CaCl_3$ decreases the viscosity of the gum. Similarly, 1% solutions of urea, KCl and $AlCl_3$ were found to increase the viscosity of NL gum. On the other hand, 1% of KCl, $AlCl_3$, $CaCl_3$ and urea increased the viscosities of FS and FZ gums. From the chemical composition of the gums, the inhibition of the corrosion of aluminium was suspected and confirmed with average inhibition efficiencies which ranged from 87.93 to 97.15 % and from 72.69 to 91.50 % at 303 and 333 K respectively. The adsorption of the inhibitors was exothermic, spontaneous and was through the mechanism of physical adsorption because of the low free energy of adsorption. The adsorption fitted well with the Langmuir adsorption model.

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CHAPTER ONE

INTRODUCTION

1.1 Background of the study

Gums are defined as molecular structures, having high molecular mass, usually with colloidal properties, such that, in an appropriate solvent, they produce gels or suspensions of high viscosity or solutions of low matter content that can absorb water at ten times their weight. They could be obtained as an exudation from fruit, trunk or branches of the trees spontaneously or after mechanical injury of the plant by incision of the bark, or after the removal of the branch, or after invasion by bacteria or fungi. The exudates become hard nodules or ribbons on dehydration to form a protective sheath against microorganism. They form clear glassy masses, which are usually coloured from dark brown to pale yellow (Umoren *et al*, 2006). According to Jani *et al* (2009), gums are considered to be pathological products resulting from injury to the plant or owing to unfavourable conditions, such as drought, by a breakdown of cell walls (extra cellular formation; gummosis). Gums can also be defined as a group of non- crystalline polysaccharides which usually contain sugars (such as mannose and galactose) and uronic acid derivatives (Ghani, 1988).

Gums are classes of high molecular weight polymeric compounds composed mainly of C, H, O and N which are capable of possessing colloidal properties in an appropriate solvent, or swelling agent at low dry weight. They occur naturally as salts (especially of calcium and magnesium) and in some cases the hydroxyl groups in gums are esterified as acetates. Gums are either hydrophobic or hydrophilic. Hydrophobic gums are insoluble in water (and include resins, rubber, etc) while hydrophilic gums are soluble in water and can be subdivided into natural, semi-synthetic and synthetic gums (Sarah, 1998). Hydrophilic gums serve as a food reserve or to

check excessive transpiration. Tannin protects against frost while resins protect plants against injury. These substances occur in larger quantities in some plants compared to others.

The most fundamental properties of plant gums which make them unique amongst polysaccharides generally are their solubility and viscosity (Meer, 1980). Gums are used in the production of food and pharmaceutical products. The major application of gums is in the food industry where their emulsifying and stabilizing properties are utilized. Gums are also used in the pharmaceutical industry, in addition to other industries such as cosmetics, adhesives, paints and inks. Gums have also been used as corrosion inhibitors recently because they are less toxic, green and eco-friendly.

1.2 Physical Properties of Gums

The solubility, colour, taste, odour and viscosity are important parameters used in the assessment of the uses and commercial values of gums. From solubility true gums are divided into three classes (Howes, 1949); namely:

(i). Soluble gums that dissolve in water forming transparent solution, e.g. *Acacia senegal* gum.

(ii) Insoluble gums which also absorb water but on addition of sufficient water break down into very thick transparent solutions, e.g. tragacanth gum.

(iii) Half- soluble gums that partially dissolve but on addition of more water change into solution; e.g. ghatti gum.

The colour of gums varies from almost colourless through various shades of yellow, orange to dark brown. Some of the best gums such as gum arabic '*Acacia senegal*' are almost colourless. On the other hand, dark or even black gums sometimes occur, e.g. Mesquite gum

(Howes, 1949). The colour of Anogeissus leiocarpus gum may be yellow or light brown (Samia *et al.*, 2009). Gums collected in natural states are represented by a variety of shape and form. Usually the fragments are irregularly globular or tear shaped. The grading of gum is based on shape, size and colour of gum nodules. Moisture content of the gum determines the hardness of the gum and hence the variation in densities and the amount of air entrapped during nodule formation.

1.3 Source of gums

Natural gums are produced from different sources as follows;

Those that can be exudative are produced from plant by incision or injury e.g. gum arabic, karaya gum and trangacanth.

. They that can be extractive when extracted from seaweed e.g. aliginates, agar, etc.

i. Those called seed gums obtained from seeds e.g. locust bean gum, guar gum, etc.

/. Gums obtained from citrus fruits are called pectin while those produced from animal skin and bones are called gelatin.

. Gums can also be produced by fermentation e.g. xanthan and lichen gums.

1.4 Classifications of gums

Gums whether natural or synthetic, can be broadly classifield into two groups. Group I comprises of acid gums, the acid components being L- glucuronic acid, D-glucuronic acid, D-galacturonic acid, sulphate group, phosphate groups while Group II comprises of the neutral gums, the neutral components being hexoses, 6-deoxyhexoses, pentoses, sugar alcohols and ethers of all these classes (Davidson, 1980). Synthetic gums on the other hand also contain basic

groups and have not been classified with these two groups and therefore, provision has been made for these compounds to be classed in Group III whose components are amino acids, polypeptides or proteins and O- and N- alkyl derivatives of all these classes of compounds.

In the classification of plant gums, substances such as resins which are not true gums are often included (Davidson, 1980). True gums exuded by plants are soluble in water and if not soluble, absorb large amount of water to form gluey solutions. Resins on the other hand, are completely insoluble in water but soluble in ethanol, while true gums are precipitated in the presence of ethanol.

The chemical nature of true gums is complex. Generally, they contain carbon, hydrogen, oxygen, calcium, magnesium and potassium in the form of metallic salts which occur in various organic compounds. Ha and Thomas (1988) were able to distinguish the components of various gums. They reported that significant quantities of xylose and fructose were the only sugars found in tragacanth gum while ghatti gum has low quantities of these sugars. Cherry gum has low levels of xylose and rhamnose, and a large amount of arabinose. On the other hand, karaya, guar and locust bean gums contain no arabinose while a large quantity of mannose occurs in the locust bean and guar gums. Trangacanth, ghatti and arabic gums contain arabinose and rhamnose. The gums can be distinguished from one another by these levels of sugars they contain.

Higher levels of these sugars are found in tragacanth followed by ghatti while gum arabic has the least sugar content compared to the other two gums. Karaya and trangacanth were found to contain galacturonic acid while gums arabic, cherry and ghatti contain glucoronic acid. Khaya gum has been reported to contain both D- glucoronic and D-galacturonic acids. Analysis of the gum showed that approximately 50% of its content were in the free acid form and the remainder was largely the calcium salt (Aslam *et al*, 2006).

1.5 Applications of gums

It is very evident that gums have very vast application in pharmaceutical and food industries, as a result of this, there is increasing demands for gums globally, which causes the increase in prices of the existing gums in the local and international markets. For the price to be stable and less expensive there is need to look for alternative or to discover more suitable natural gums which will be of the same quality or even surpass the existing ones (Yusuf *et al*, 2006). According to Hirst *et al*, (1989) the major acacia species is used for pharmaceutical, confectionary, food, textile and beverage production. Additives play an important role in pharmaceutical preparations like tablet, lotions, suspensions, syrups and ointments. Recent trends towards the use of the vegetable and nontoxic products demand the replacement of synthetic excipients with natural ones (Panda *et al*, 2008). Carob bean gum is used as a thickener, stabilizer, emulsifier and gelling agent. Carob bean gum is compatible with xanthan gum and forms gel. It affects the gelling properties of carrageenan and agar. Gum arabic serves as a very efficient emulsifier and a long-term stabilizer in food and cosmetic products containing oil water interfaces (Dror *et al*, 2006).

1.5.1 Gums as pharmaceutical and food additives

Pharmaceutical additives (excipients) are components of dosage forms that enable the formulations to acquire some characteristics which will establish the basic features of the formulated product. These excipients control physicochemical properties as well as the release profiles and availability of the drug in the system (Ram, 2004). The ability of excipients to provide their intended function and perform throughout the shelf life of the product must be established such that the information will justify the choice, concentration and characteristics that may influence the final product (European Medicines Agency, 2004). One of the commonly

used groups of compounds as excipients is natural polymer (gum). Acacia, tragacanth, albizia and guar gum are examples of natural polymers that have been used as excipients in pharmaceutical formulations (Martin *et al*, 1991). They are used as binders and disintegrants in tablets and as suspending and flocculating agents.

Natural gums represent a group of polymers which swell to form highly viscous solutions or dispersions in aqueous media (Talukdar and Vercammen, 1993). They have found wide application in pharmaceutical formulations such as polymer matrices in sustained release solid dosage forms, binders in tablets, stabilizers or suspending agents in liquid dosage forms, and in bio-adhesive drug delivery systems (Middleton *et al*, 1990). Polysaccharide gums used in the pharmaceutical and food industries include guar gum, tragacanth, acacia gum or gum Arabic and xanthan gum amongst others. They have the advantage of biocompatibility, low cost and relatively wide spread availability compared to their synthetic counterparts (Vendruscolo *et al*, 2009). Guar gum has also proven to be a useful substitute for locust bean gum. It is mainly used as a natural thickener, emulsifier, stabilizer, bonding agent, hydrocolloid, gelling agent, soil stabilizer, natural fibre, flocculants and fracturing agent. It is a white to yellowish white, nearly odourless powder with bland taste (Kumar and Shaikh, 2011). Aqueous dispersions of the grewia gum hydrate and swell to form highly viscous dispersions which exhibit pseudoplastic flow (shear-thinning) behaviour. This property has been exploited in the food, cosmetic and pharmaceutical industries. Materials with such properties have therefore been used as stabilizers and suspending agents in foods, cosmetics and in liquid or solid dosage forms. The high thermal stability of the grewia gum as evidenced by the high oxidation onset of 267±6.2 ^{o}C indicates that the gum can be used as excipient even under conditions of high thermal stress (Nep and Conway, 2010).

Some purely natural gums were also investigated as hydrophilic matrices for sustained drug delivery, but they were found to be unable to sustain the drug release for a longer period of time even at the higher concentrations. So in an alternate approach, combinations of hydrophilic and hydrophobic polymers were tried by the scientists for optimized drug delivery, but numerous of them also failed to prolong the drug release beyond 12 hours. Since a wide range of polymers has certain advantages as well as limitations, it is a prerequisite, often, to investigate new polymeric materials for sustained drug delivery. Therefore the study of new drug-release-retarding materials is the motive of research even after the advent of synthetic, semi-synthetic and natural polymers (Tiwari *et al*, 2003). Additives play an important role in pharmaceutical preparations like tablet, lotions, suspensions, syrups and ointments. Recent trends towards the use of vegetable and nontoxic products demand the replacement of synthetic excipients with natural ones. Vegetable gums provide appropriate solution to the current problem. There are several reports about the successful use of hydrophilic polymers derived from plants, like guar, carrageenan, karaya and locust bean gum in pharmaceutical preparations (Sujja-Areevath *et al*, 1996).

Natural materials have been extensively used in the field of drug delivery because they are readily available, cost-effective, eco- friendly, capable of multitude of chemical modifications, potentially degradable and compatible due to their natural origin (Bharadwaj *et al*, 2000). Past research therefore studied and acknowledged various natural gums like agar, konjac, guar gum, chitosan, xanthan gum, sodium alginate and locust bean gum for potential pharmaceutical and biomedical applications (Efentakis and Kouttis, 2001). Gum copal has been used for water-resistant coating and in pharmaceutical and dental industries for its strong binding properties. In India, damar gum has been widely utilized as an indigenous system of medicine. The wide

applications of these gums such as gum gopal and gum damar propose their strong hydrophobic nature, substantial binding property and compatibility with the physiologic environment (Morkhade *et al*, 2006). The ability of excipients to provide their intended function and perform throughout the shelf life of the product must be established such that the information will justify the choice, concentration and characteristics that may influence the final product. One of the commonly used groups of compounds as excipients is natural polymer. Natural polymers are polysaccharides composed of a large group of polymers with varying chemical composition, large derived groups and a wide range of molecular weights. They are characterized by low toxicity, high stability and biodegradability. These properties make them appealing as pharmaceutical excipients (Pendyala *et al*, 2010). Binders are employed in pharmaceutical tablet formulation to provide adequate mechanical properties by promoting the bonding properties existing between the different components of a powder mix in a formulation. Various natural, semi-synthetic and/or synthetic substances like starches, cellulose and gums have been employed in pharmaceutical tablet formulation as binders. Gums are example of hydrophilic substances employed in pharmaceutical solid dosage formulation mainly as binders (Alebiowu and Itiola, 2003).

Locust bean gum is used as a thickening agent and gelling agent in food technology. The bean, when made into powder, is sweet—with a flavour similar to chocolate –and is used to sweeten foods and as a chocolate substitute. It is also used in non-edible products such as pet foods, mining products, paper making, and to thicken textiles. It is used in cosmetics and to enhance the flavour of cigarettes. Shoe polish and insecticides also have locust bean gum powder as an additive. Although there are many types of gums, the most simple and wide-ranging explanation is that gums are plant flours (like starch or arrowroot) that make foods and other

products thick. Gums are used in foods and pharmaceuticals for many reasons besides being used as a thickener. Gums make gels like gelatin (which is derived mostly from pork and beef hides). and gums help to prevent ice crystals in ice cream and frozen foods. They also help to retain moisture in foods so that they stay fresher longer.

1.5.2 Gums as Corrosion Inhibitors

The consequences of corrosion are many and varied and the effects of these on the safe, reliable and efficient operation of equipment or structures are often more serious than simple loss of a mass of a metal. Failures of various kinds and the need for expensive replacements may occur even though the amount of metal destroyed is quite small (Umoren and Ebenso 2008). The corrosion of metals is one of the most significant problems faced by advanced industrial societies. It has been estimated that in the United States alone, the losses of corrosion annually amounts to tens of billions of dollars (Oxtoby *et al.*, 2008). Therefore, there is a need to protect metals against corrosion. The use of inhibitors has been found to be one of the best options available for the protection of metals against corrosion (Eddy *et al*, 2012). Corrosion can be controlled by the addition of chemical substances called inhibitors into acid media. By definition, an inhibitor is a chemical compound which when added in a small amount to the corrosive environment alters the cathodic and or anodic reaction and subsequently reduces the corrosion rate (Hosseini *et al*, 2007).

The choice of inhibitors for the corrosion of metals depends on the ability of the inhibitor to be synthesized from cheap raw materials and for the inhibitor to be environmentally friendly. The use of gums as corrosion inhibitors has attracted considerable attention recently. According to Eddy *et al* (2011), gums have been found to be good corrosion inhibitors due to the following reasons;

i. They form complexes with metal ions and on the metal surfaces through their functional groups

ii. Gum-metal complexes occupy a large surface area, thereby blanketing the surface and protecting the metals from corrosive agents present in the solution.

iii. Because of the presence of arabinogalactan, sucrose, oligosaccharides, polysaccharides and glucoproteins since these compounds contain oxygen and nitrogen atoms which are the centers of adsorption.

iv. Most gums have COOH functional groups, which can enhance the donation of electron or charge transfer and hence facilitate inhibition through adsorption.

v. Most gums are less toxic, green and eco-friendly.

1.6 Rheology

Rheology is defined as the study of the deformation and flow of materials. When a force is applied to a liquid, the liquid will flow to relieve the strain from this force. Different systems will resist this flow more than others and the measurement of this resistance is a measure of the viscosity of the system (Ebewele, 2000). Rheology can also be defined as the study of the flow of matter: mainly liquids but also soft solids or solids under conditions in which they flow rather than deform elastically. It applies to substances which have a complex structure, including muds, sludges, suspensions, polymers, many foods, bodily fluids, and other biological materials. The term rheology was coined in 1920s, and was inspired by a Greek quotation, "panta rei", "everything flows". In practice, rheology is principally concerned with extending the "classical"

disciplines of elasticity and (Newtonian) fluid mechanics to materials whose mechanical behaviour cannot be described with the classical theories (Steffe, 1996).

1.7 Aim and objectives of the study

The aim of this research work is to study the physicochemical and rheological characterization of TR, NL, FS and FZ gum exudates and their potentials for use as corrosion inhibitors for aluminium in acidic medium.

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The objectives of the study are as follows:

i. To carry out some physical analysis (colour, taste, odour, pH, solubility in various solvents, turbidity, salinity, total dissolved solid content melting point range, conductivity and swelling property) of TR NL, FS and FZ gum exudates.

ii. To carry out chemical analysis of gum samples in order to determine their chemical contents and structures, proximate composition and cationic composition using GC-MS.

iii. To determine the active functional groups in each of TR NL, FS and FZ gum exudates using FTIR spectrophotometer.

iv. To study the effect of temperature, pH, concentration and different salts on the viscosity of TR NL, FS and FZ gum exudates.

v. To determine and model the kinetics and thermodynamic parameters of flow for gums. These shall include activation energy of flow, activation entropy and enthalpy of flow and activation free energy of flow.

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vi. To predict possible industrial or domestic applications of the gums based on the results obtained from their chemical and rheological studies.

vii. To investigate the corrosion inhibition potentials of the gums for aluminium in solutions of HCl, using weight loss method.

1.8 Justification for the Study.

The use of these locally sourced gum exudates as pharmaceutical excipients, binders and corrosion inhibitors will solve the problem of high cost and importation of these substances. A positive outcome of this study will increase the growing rate of gum producing plants and thus create job opportunities for the inhabitants of the areas and people nationwide. It requires little or no money to process these naturally occurring substances for use as pharmaceutical excipients or binders, food additives, corrosion inhibitors etc. Therefore there is a need to access the physicochemical and rheological properties for gums that have not been adequately studied and provide a data base for future applications. Current trends in corrosion inhibition researches are directed towards finding inhibitors (green corrosion inhibitors such as gums) that are eco-friendly, less expensive and biodegradable.

CHAPTER TWO

LITERATURE REVIEW

2.1 General chemical composition of gums

The chemical nature of true gums is complex. Generally, they contain carbon, hydrogen, oxygen, calcium, magnesium and potassium in the form of metallic salts which occur in various organic compounds. However it has been established that gums contain polysaccharides and some of their constituents.

Mohammadzadeh *et al* (2007) studied the physicochemical properties of barijch (Ferula gumosa) gum and found that it was composed mostly of polysaccharides. The total sugar content was 83.98 % and the purity of the gum was relatively high, composed mostly of saccharides. Also the gum consisted of uronic acids (galactoronic acid) with a weight ratio of 24.38 %. The polysaccharide extracted from barijch gum by alcoholic solution is of interest for some scientists. The composition of the gums was identified by chemical methods and its analysis showed the presence of galactose, arabinose, rhamnose and uronic acids with galactoronic as its major component. In addition, the study revealed the presence of protein, calcium and magnesium in the gum exudate.

The chemical composition of *Albizia lebbeck* gum exudate was investigated by de Paula *et al*, (2001). The contents of galactose, arabinose and uronic acid are similar to those from Venezuelan and African gums. Mannose in gums from other origins was not identified in Brazilian polysaccharide. 13C NMR spectra of intact and Smith-degraded polysaccharide allowed the chemical shift assignment to be made. The main chain is composed of galactan core (1→3) linked with approximately 33% of substitution at C-6. Gel permeation chromatography (GPC) indicated a major polysaccharide fraction of M_{pk} 2.4 x 10^6 g/mol and two other minor

fractions of M_{pk} 3.6x10^5 and 4.5 x 10^4 g/mol. The whole gum is a low viscosity polysaccharide with apparent flow activation energy of 16.6 and 17.2 kJmol^{-1} for solutions of 2 and 3% (w/v) concentration, respectively. Analysis of *A. lebbeck* gum hydrolysates by TLC chromatography indicates the presence of galactose (R_f =0.48), arabinose (R_f = 0.56), glucuronic acid (R_f =0.05). Rhamnose was detected by high performance liquid chromatography (HPLC) using an amino column.

The complex chemical structure of gum arabic has been widely studied by Dror *et al.* (2006) revealing a multifraction material consisting mainly of a highly branched polysaccharide and a protein–polysaccharide complex (GAGP) as a minor component. This work investigates its mesoscopic structure in aqueous solution by small-angle X-ray and neutron scattering combined with cryotransmission electrons microscopy. Scattering measurements reveal an intricate shape composed of many spheroidal aggregates assigned to the polysaccharide with a small amount of larger coils. A scattering peak was observed at moderate to high concentrations, the spacing of which exhibited a $c^{-1/3}$ power law relation to polymer concentration (c). Upon addition of salt, this peak disappears, indicating its electrostatic nature. The large coils contribute a q^{-2} power law at the low scattering vector (q) range. However, at low concentrations in which inter aggregate peak is not observed, a q^{-1} power law at the low q range indicates the possible existence of a fraction with a locally extended conformation.

However, comparative studies of the physicochemical properties of the gum exudates of three acacia tree species (A senegal, A. sieberiana and A. nilotica) in Batagarawa, Katsina State were carried out by Yusuf (2011). From the data generated, it was confirmed that there were a number of physicochemical differences between the gum exudates. Physicochemical properties vary among the three samples studied within the following ranges: moisture (13.40-16.20 %);

water solubility at 300C (38-45 %); pH of 25% solution (4.50-5.00); relative density of 20 % solution (300C) (1.23-1.32), melting temperature (289-320^{0}C), relative viscosity of 1 % solution (20.18-24.80), total ash (3.30-3.54 %), nitrogen (0.38-0.42 %), protein (2.51-2.77 %) and total soluble fibre (77.99-80.41 %). Analysis of all the samples showed no tannin content. The cationic composition of the gum samples determined shows the presence of calcium (Ca), magnesium (Mg), iron (Fe), sodium (Na) and potassium (K) as the predominant minerals. Copper (Cu), nickel (Ni), cobalt (Co), manganese (Mn), chromium (Cr), zinc (Zn) and lead (Pb) were not detected in this study. Despite the physicochemical differences among the samples studied, levels of physicochemical parameters obtained compare well with those reported in previous studies on acacia gums in many parts of the world.

Grewia gum extracted from the inner stem bark of *Grewia mollis* was characterized by Nep and Conway (2010) using several techniques such as gas chromatography (GC), gel permeation chromatography (GPC), scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and thermogravimetric analysis of the extracted sample. Spectroscopic techniques such as x-ray photoelectron spectroscopy (XPS), fourier-transformed infrared (FT-IR), solid-state nuclear magnetic resonance (NMR), and 1H and 13C NMR techniques were also used to characterize the gum. The results obtained showed that grewia gum is a typically amorphous polysaccharide gum containing glucose, rhamnose, galactose, arabinose and xylose as neutral sugars. GC chromatogram of grewia gum revealed that the polysaccharide gum is composed of five neutral sugars eluting at various retention times. The retention times indicated that grewia gum contains glucose, rhamnose, arabinose, xylose and galactose. The mean relative concentration of these sugars in the polysaccharide is glucose (67.14 %), rhamnose (6.2 %), xylose (2.72 %), galactose (9.61 %) and arabinose (12.71 %).

The physicochemical properties of cashew gum (CG) collected from four cashew growing districts, Sampa, Wenchi, Bole and Jirapa in Ghana were studied by Gyedu-Akoto *et al* (2008) to help promote the utilization of cashew gum in the food industry. The gum was collected from trees of two different age groups, those that were 10 years and below and those above 10 years. Physicochemical properties of CG were compared to those of gum Arabic. Parameters studied included pH (3.8 - 4.2), total ash (0.5 - 1.2 %), protein content (1.27 - 1.80 %), total sugars (0.96 - 2.10 mg/g), total phenols (0.21 - 2.26 %), moisture content (9.8 - 13.2%) and insoluble matter (1.9 - 4.8%). Gum from mature trees was generally found to have higher levels of protein, moisture, sugars and phenols than those from young trees, with the exception of pH which was lower in gum from mature trees. There were also variations in some of the physicochemical properties of the CG from the different locations. The predominant minerals in cashew tree gum were Ca, K, Na and Fe.

In order to evaluate the physicochemical properties of exudates from Khaya grandifolia gum, Yusuf *et al* (2006) carried out qualitative identification test of the gum. The physicochemical parameters of the gum powder evaluated included; appearance (white), moisture (9.21 ± 0.24 %), ash value (2.23 ± 0.15 %), nitrogen content (0.56 ± 0.03%), protein (3.51 ± 0.03%) and fat content (40.30 ± 0.10%). The percentage of the natural elements in the gum like calcium (0.60 ± 0.01 %), magnesium (8.45 ± 0.0 1 %), iron (0.38 ± 0.02 %), zinc (0.06 ± 0.01%), copper (0.02 ± 0.016 %), lead (0.02 ±0.Ql5 %), potassium (18.59 ± 0.09 %), sodium (3.14 ± 0.10%), were determined using atomic absorption spectrophotometer except Na, and K where flame photometer was used. The gum has substantial amount of potassium, magnesium and sodium. The functional properties revealed that the gum has water and oil absorption

capacities of 3.01 ± 0.03 % and 20.0 ± 0.10 respectively, the least gelation capacity of 6.0 ± 0.20 % and foaming capacity of 8.0 ± 0.01 %.

Determination of the chemical composition of kondagogu, karaya and acacia gums by gas chromatographic technique by Palanuvej *et al* (2012) revealed that kondagogu gum was composed of galactose (14.64 %), rhamnose (17.11%) and galacturonic acid (17.24 %). Karaya gum contained rhamnose (8.91 %), galacturonic acid (9.13%), galactose (14.67%) and glucuronic acid (35.59 %) while rhamnose (10.63 %), arabinose (21.42 %), glucuronic acid (22.54 %) and galactose (42.57 %) were found in Acacia gum. The average molecular weights determined by SEC analysis revealed the large structures of the gums studied (> 2,350 kDa). Qualitative and quantitative compositions and total protein content of the gums studied were carried out by gas chromatography (GC) and Lowry assay respectively. Kondagogu gum contained rhamnose, galactose and galacturonic acid (36: 32: 32 % mole ratios). Karaya gum contained rhamnose, galactose, galacturonic acid and glucuronic acid (13: 23: 12: 52 % mole ratio). Acacia gum was composed of rhamnose, arabinose, galactose and glucuronic acid (10: 26: 43: 21 % mole ratio).

2.2 Studies on rheology of gums

Eddy *et al.* (2012a) carried out studies on the rheological modeling of *Anogeissus leiocarpus* gum (AL gum). Rheological study indicated that the viscosity of the gum increases with increasing pH and concentration but decreases with increase in temperature. The apparent activation energy of flow for *Anogeissus leiocarpus* gum (calculated from Arrhenius-Frenkel-Eyring plot) was 3.16 kJ/mol suggesting the presence of fewer inter and intra molecular interaction. Values of intrinsic viscosity obtained from Huggins and Kraemer plots were similar (8.82 kJ/mol) while those obtained from Tanglertpaibul and Rao plots ranged from 3.50 to 11.82

dL/g. From the plot of speed of rotation *versus* viscosity, viscosity *versus* shear rate and shear stress versus shear rate, a non-Newtonian behaviour (dilatant) with characteristics shear thickening property was verified for *Anogeissus leiocarpus* gum. Calculated b value of 1.108 was obtained through the application of the power law equation and is associated with random coil conformation or entanglement. Analysis of the master's curve shows that random coil conformation or entanglement is proposed to occur at $C[\eta] \sim 4.0$, *i.e.* at $\eta_{sp} \sim 2.19$ ($\eta_{rel} = 3.19$).

In the same vein, Ameh (2012) investigated the rheological behaviour of Ficus glumosa gum. The gum has been adequately modeled using Huggins, Kraemer, Arrhenius, Tanglertpaibul and Rao theories. The results obtained indicated that the viscosity of the gum increases with increasing pH and concentration but decreases with increase in temperature. Values of intrinsic viscosity obtained from Huggins and Kraemer plots were similar (11.197 dL/g). The value of activation energy (E_{vis}) of the gum studied was found to be 1.915 kJ/mol. The low E_{vis} values obtained suggest the existence of few inter and intra-interactions between the molecules of the gums within the temperature investigated.

The rheological properties of aqueous guar gum solutions have been investigated for different concentrations and temperatures in a cone-and-plate rheometer in the linear and in the non-linear viscoelastic regime by Dressler *et al.* (2003). In the linear viscoelastic regime, low amplitude oscillatory shear experiments were performed to measure the complex modulus time-temperature and the time-concentration superposition principles were adopted to increase the window of experimentally accessible frequencies. The time-concentration superposition principle allowed for a frequency shift of approximately one decade towards the high frequency regime. Preliminary modeling efforts in the framework of the theory of linear viscoelasticity have been undertaken to give a theoretical description of the data obtained. In the non-linear

viscoelastic regime, it was found that for low shear rates there is a monotonous increase of the transient shear viscosity, whereas at higher shear rates, a pronounced overshoot in the transient rheological properties has been detected. The steady state values of the shear viscosity and the first normal stress coefficient reveal the characteristic shear-thinning behaviour. The PTT model of polymer rheology has been adopted to describe the non-linear viscoelastic material properties.

Rheological methods were applied to study the effect of sweeteners on the intrinsic viscosity of salep gum in dilute solutions. The concentration of these sweeteners were 0.1, 0.2% w/v for aspartame, acesulfame-K and cyclamate, 0.001, 0.002 % w/v for neotame. The gum was evaluated by Vahid *et al*, (2011) for intrinsic viscosity by various models i.e. Huggins, Kraemer, Tanglertpaibul and Rao equations. The results showed that the values obtained for intrinsic viscosity were different upon various equations used. The plot of relative viscosity versus gum concentration obtained from Tanglertpaibul and Rao model was found as best model. Synthetic sweeteners in these rages of concentration had no significant effect on intrinsic viscosity of salep gum in solutions.

The effects of some synthetic sweeteners on the rheological and physical properties of guar gum in dilute solutions were investigated by Samavati *et al,* (2008). Measurements include the determination of intrinsic viscosity and the particle size, surface weighted mean [D3, 2], volume weighted mean [D4, 3] and specific surface area of guar gum and synthetic sweeteners mixtures. The concentrations of these sweeteners were 0, 0.1, 0.2 % w/w for aspartame, acesulfame-k and cyclamate, and 0, 0.001, 0.002 % w/w for neotame. The gum was evaluated for intrinsic viscosity by various models i.e. Huggins, Kraemer, Tanglertpaibul and Rao equations. The results obtained showed that the values obtained for intrinsic viscosity varied from the various equations used. The plot of relative viscosity versus concentration, obtained

from Tanglertpaibul and Rao model described best the phenomenon. Sweeteners had no significant effect on intrinsic viscosity of guar gum solutions.

Alakali *et al*, (2009) investigated the rheological characteristics (consistency and flow behaviour indices) of food gum (Cissus populnea) exudates obtained from the fresh leaves and stem as well as dried leaves and stem. They were determined at 20, 30, 40, 50 and 60 °C using a rotational viscometer at shear rates of 0.1, 0.2, 0.5, 1.0 and 1.5 rpm for effective design and simulation of its momentum transfer process and system. The experimental design used for the study of consistency and flow behaviour indices of C. populnea at 20 – 60 °C was randomized complete block design (RCBD). The study revealed that consistency index (K) of C. populnea exudates generally increased with increase in temperature. The K values for the fresh were generally higher than the dried materials. The K values of the fresh stem exudates, which are more viscous, were significantly ($P< 0.05$) different from the less viscous fresh leaves exudates, but did not show significant ($P< 0.05$) difference with the dried leaves which became concentrated due to drying. The flow behaviour index did not show any defined trend with changes in temperature, and was not significantly ($P<0.05$) different. The exudates generally exhibited pseudoplastic behaviour at all the temperatures studied. A study of the apparent viscosity of the exudates between temperatures of 20 – 150 °C shows that apparent viscosity increased with increase in temperature below the boiling point of 70 °C. However, above the boiling point, the apparent viscosity decreased with increase in temperature. The viscosity-temperature data were fitted in to the Arrhenius-type equation yielding activation energies between 0.997 to 2.431 KJ/mol°C, corresponding to temperature range between 20 – 70 °C and 1.632 to 2.580 KJ/mol with K corresponding to temperature range between 70 -150 °C.

To investigate the effects of NaCl, KCl, and $CaCl_2$ on visco-elastic properties of xanthan and locust bean gum (LBG) blends in dilute solution, Higiro *et al*, (2007) used oscillatory capillary rheometer. The intrinsic viscosity and elastic component of gums were evaluated. Molecular conformation of the xanthan–LBG complex was assessed by the power-law and Huggins equations. Addition of any of the three salts reduced significantly reduced the intrinsic viscosity and elastic component of the gum blends, with a pronounced effect from divalent ions, compared to that from monovalent ions. The 60 % xanthan to 40 % LBG blend exhibited the strongest attraction between xanthan and LBG. For the three salts, the attraction weakened when 5-mM salt was added and vanished with the addition of 50-mM salt. The strongest attraction between xanthan and LBG molecules was also evidenced by a positive Huggins miscibility coefficient K_m, and a positive attraction–repulsion coefficient α. With addition of 50 mM of any of the three salts, the coefficient α became negative, suggesting a strong repulsion between the two gums. The power-law coefficient b increased as salt concentration and LBG fraction increased in the blends for the three salts, suggesting a more flexible xanthan LBG complex dependent on salt concentrations and LBG.

A gum resin was isolated from Commiphora africana. In order to assess its application to industry, Gundidza *et al* (2011) subjected the gum to rheological studies. A rotational viscometer which had the ability to characterize both Newtonian and non-Newtonian systems was used. The gum resins from C. africana exhibited low shear stress even at high concentrations of the gum resins. The change in shear stress with temperature produced almost a linear graph with a gradient of 0.06. The gum from C. africana was significantly affected and could be used in formulations containing low concentrations of salts. The plots of shear stress versus added ion concentration showed that the gum's shear stresses are reduced by addition of ions (calcium

chloride) until a certain minimum value of shear stress is reached. The gum from C. africana was significantly affected by addition of ions and would have little applications in formulations that contain salts. In addition, the gum resin from this plant species was affected by the addition of salts and would have little application in formulations that contain salts.

Aqueous suspensions of cassava and maize starches with addition of purified cashew gum (5% starch + gum 1 % w/v) were analysed at 25 °C by Andrade *et al*, (2010) using a rotational rheometer, at shear rate ranging from 0 to 100 s^{-1}. The experimental data were fitted to Ostwald de Waale, Casson and Herschel-Buckley rheological model, in order to classify the fluids studied. The results obtained best fitted the Ostwald de Waal (Power Law) model showing a pseudo plastic flow behaviour. The addition of gum favoured the reduction of viscosity in the maize starch slurry, whereas the formulation of cassava starch increased viscosity. These different behaviours could be related to the different interactions between the gum and the cassava and maize starches. The presence of gum may have reduced the mobility of cassava starch molecules in suspension leading to increasing the viscosity.

Mothé and Correia, (2006) studied the rheological behaviour on prepared blends of cashew/xanthan gums in cashew juice. The concentrations of hydrocolloids in the juice were cashew gum (CG) 1 and 1.5 %w/v, xanthan gum (XG) 0.1% w/v. The blends formed were CG: XG (1 % w/v: 0.1 % w/v) and CG: XG (1.5 % w/v: 0.1 %w/v). The results obtained showed that the sample without hydrocolloid had the lowest viscosity and that the samples with cashew gum exhibited slight increase in viscosity compared to that of pure juice. Samples with xanthan gum had the highest values of viscosity. Therefore, samples with blends produced viscosities similar to those samples that contain only xanthan gum.

Gums are integral ingredients in fluid foods used for controlling viscosity and mouthfeel. Advances in rheological instrumentations permit enhanced evaluations of the viscoelastic properties of fluids. Rheological properties of twelve gum solutions were investigated by Yaseen *et al* (2005) at concentrations of 0.05 %, 0.1%, and 0.5 %. The viscous (η") and elastic (η') components of the complex viscosity η*, elastic yield stress, and tan δ were measured as functions of oscillatory shear. Konjac exhibited the highest η' and η" components among all gums at 0.5% and $50s^{-1}$. Gum Arabic, methylcellulose and pectin, exhibited the least η' and no η" component under the same conditions. Konjac exhibited greatest elastic yield stress, whereas microcrystallinecellulose had the least. Modeling result showed that rheological properties of CMC were characterized by an exponential relationship, whereas riota-carrageenan and xanthan were described by a power type relationship. A substantial increase in tan δ was observed for most 0.5% gum solutions at shear rates beyond 10 s^{-1}, indicating a shift from a visco-elastic regime to a purely viscous one. For gums that exhibited substantial viscoelasticity, peak tan δ values ranged from 5.7 to 68.3.

Simas-Tosin *et al* (2010) carried out a rheological analysis of aqueous extract (AE) and polysaccharide precipitate (POLY) of peach tree gum (Prunus persica). Solutions of both fractions at 4% (w/v) had a non-Newtonian shear-thinning behaviour; however that of AE showed higher apparent viscosity than that of POLY. The presence of salts decreased the apparent viscosity of AE dispersion. Dynamic oscillatory analyses showed that 4 % (w/v) AE and POLY had a gel-like structure, being AE hydrogel, a stronger gel compared to POLY. This suggests that other compounds, in addition to polysaccharide, are involved in the gel network in aqueous dispersions of AE. Weaker gels were formed with 2 % (w/v) AE in water and 4 % (w/v)

AE in various salt solutions. These results showed that the peach gum had an interesting rheological behaviour and that it could have a future application.

Tamarind seed gum as seed polysaccharide from Tamarindus indica L. has been characterized for rheological properties by Khounvilay and Sittikijyothin (2011). The Huggins and Kraemer plots obtained by capillary viscometry gave an intrinsic viscosity of 4.7 dlg^{-1} and the viscosity average molecular mass was calculated to be 9.18 x 10^5 $gmol^{-1}$ using the MarkeHouwink relationship. The steady shear and dynamic viscoelasticity properties of tamarind seed gum in aqueous solutions at different concentrations were investigated at 20 °C using a Haake Rheometer RS75. The tamarind seed gum solutions clearly exhibited shear-thinning flow behaviour at high shear rate and the Newtonian region occurred at a low shear rate range, however, at higher concentrations, pronounced shear thinning was observed. The value of zero shear viscosity (η_o) was estimated by fitting Cross and Carreau models. The specific viscosity at zero shear rate (η_{spo}) was plotted against the coil overlap parameter ($C[\eta]$) and the slopes of the plots in the dilute and semi-dilute regions were found to be ~2.2 and 4.3, respectively. The value of the critical concentration (C^*) was about 4.23 g/dl, while the mechanical spectra in the linear viscoelastic region of tamarind seed gum solutions showed the typical shape for macromolecular solutions. Plots of η versus γ and η^* versus ω were superimposable and hence obey the CoxeMerz rule.

2.3 Studies of the effect of pH on viscosity of gums

The stability and efficacy of liquid pharmaceutical preparations depend on the pH of the medium. Such liquid preparations may contain varied additives performing different functions. One of the qualities of oral liquid pharmaceutical preparations is appropriate viscosity for pumping and transfer during manufacture and dispensing to patients. Gums find use in such

liquid preparations as thickening or suspending agents together with different additives that may influence the pH of the environment and hence the stability and quality of the preparation. It is based on this that Ogaji *et al* (2012) carried out anlaysis to determine the effect of pH on the viscosity of grewia gum obtained from Grewia mollis that is a potential pharmaceutical excipient. Aqueous mucilage of grewia (2 % w/v) was prepared and the pH was determined at different shear rates using Brookfield cone and plate rheometer at 25 °C. Adjustment of pH was facilitated by the addition of 0.25 N solution of either hydrochloric acid or sodium hydroxide before the readings were taken. The viscosity of the mucilage was characteristically pseudoplastic and dependent on pH of the medium and storage time. The viscosity ratio generally decreased from 2.046 to 1.470 as the pH of the medium increased from acidic to basic (2.18 to 13.10). The dynamic yields of the dispersion at pH 2.55 and 5.08 were, respectively, 10.5 and 45. The viscosity of grewia gum dispersion changed with change in pH of the medium anomalously. Changes in the viscosity of grewia gum dispersion with change in the pH were observed. This suggests that the use of grewia gum together with other additives in oral liquid preparations should be done with discretion.

In another development, Ameh *et al* (2012) studied the effects of pH on the viscosities of *Fiscus platyphlla* (FP), *Khaya senegalensis* (KS), *Anogeissus leiocarpus* (AL) and *Albizia furrigunea (AF)* gum samples. It was found from the study that the viscosity of the gums tends to increase with increase in pH indicating that the emulsifying properties of the gum is pH dependent. The increase in viscosities of the gums with increase in pH also indicates that the gums are ionic. Viscosity of a liquid is related to the ease with which the molecules can move with respect to one another. Thus the viscosity of a liquid depends on the strength of attractive forces between molecules, which in turn depend on their composition, size, and shape and also

on the kinetic energy of the molecules, which depends on the temperature. This implies that the strength of hydrogen bonding between the molecules of the gums can partly be a factor in accounting for the increase in viscosity with pH. At higher pH (that is increasing alkalinity), the viscosity of the gums is expected to increase.

Effect of temperature and pH on contraceptive gel viscosity was investigated by Owen *et al* (2003). In this study, the rheological properties of four commercially available spermicidal gels (two polyacrylic acid derivatives and two carboxymethylcellulose based) and their dilutions with a vaginal fluid simulant (pH=4.2) and a semen simulant (pH=7.7) were measured at 25 degrees C and 37 degrees C over a biologically relevant range of shear rates. All four gels were shear thinning with temperature-dependent rheological properties. The two types of gels responded differently to dilution. The rheological properties of the polyacrylic acid derivative gels were strongly dependent on the type of diluent used. Their viscosities after dilution with the semen simulant were 100 times greater than thereafter comparable dilutions with the vaginal fluid simulant, this effect being due primarily to the higher pH. The cellulose gels did not exhibit such an effect. These results suggest that the polyacrylic acid and cellulose gels interact differently with the vaginal environment in vivo. Such differences could lead to differences in the extent and durability of epithelial coating.

Knowledge on rheological properties of sludge is important for the design of pumping and transport facilities and as a tool in process control during treatment. Concentrated activated sludge is known to behave as a non-Newtonian material. The contribution to non- Newtonian behaviour is believed to originate from the colloidal properties of solids more than from the molecular properties of the suspension. Considering the fact that the colloidal properties of sludge depend on factors like pH, conductivity, solids concentration and flocculation properties,

Sanin (2002) examines the effects of these variables on the rheology of activated sludge. The results obtained show that the rheograms obtained best fit a power law model indicating that the flow of activated sludge can best be expressed by the pseudoplastic flow model. It is also observed that the apparent viscosity increases sharply with increase of solids concentrations. From the pH values studied, the pH that causes the lowest viscosity is a pH of 5.5. As the pH increases, the viscosity measured increases considerably. This makes sense considering the fact that the isoelectric point of bacteria is at pH 2-4. Conductivity is also found to affect viscosity greatly such that as the conductivity increases, the apparent viscosity decreases. Finally, experimental results reveal that the presence of extracellular polymers and the flocculated nature of activated sludge affect its viscosity.

The influence of pH (3.0-8.0), ionic strength (0.005-0.10 M), and concentration of (50-300 mg L^{-1}) on the viscometric behaviour of solutions of a soil fulvic acid (FA) has been extensively investigated by Rey *et al.* (1996). The results obtained showed a complex influence of the concentration on the specific viscosity with maxima at about 80-100 mgL^{-1} and a minimum at 140-160 mg L^{-1}. The variation of the intrinsic viscosity with pH (for different constant values of ionic strength) for the FA solutions studied revealed a minimum in viscosity between pH 6 and 7. At the lowest pH values, the FA particles remain unchanged, electrostatic repulsions were weak, and the particles had a higher association due to the possible formation of hydrogen bonds, van der Waals forces, and other weak forces. When the pH was increased, the association of the particles was destroyed due to the increase in electrostatic repulsions that were greater than the weak forces. It was found that the aggregates break up because any type of rearrangement disperses the fully ionized molecules to form small, discrete particles. The viscosity of the fulvic acid decreases until a minimum is reached at pH of about 6. At still higher

pH values, the intrinsic viscosity was found to increase again, showing a new aggregation due to mineral bridges and intermolecular interactions.

Anema *et al* (2004) studied the effect of pH on the viscosity of reconstituted skim milk. The reconstituted skim milk was adjusted to pH values between 6.5 and 6.7 and heated (90°C) for up to 30 min. The change in the viscosity, as well as the casein micelle size and the level of whey protein association with the micelles, were monitored for each milk sample. The change in the viscosity was dependent on the pH of the milk during heating. At pH 6.5, the viscosity increased markedly during the early stages of heating, and plateaued on prolonged heating. The magnitude of the change in viscosity decreased as the pH of the milk was increased, so that only small changes in viscosity were observed on heating at pH 6.7. The change in viscosity was linearly correlated with the change in particle volume (calculated from the particle size). This indicates that the viscosity changes were related to a change in the volume fraction of the casein micelles as a consequence of heating. The level of denatured whey proteins associating with the micelles was also markedly dependent on the pH at heating. High levels associated at pH 6.5, and the level associated were lower as the pH was increased to pH 6.7. The changes in viscosity and casein micelle volume were correlated with the levels of denatured whey proteins that were associated with the casein micelles, although there was some deviation from linearity at low levels of association (<15%).

2.4 Studies of the effect of electrolyte on viscosity of gums

An oscillatory capillary rheometer was used by Higiro *et al* (2007) to investigate the effects of electrolytes such as NaCl, KCl, and $CaCl_2$ on visco-elastic properties of xanthan and locust bean gum (LBG) blends in dilute solutions. Gums were evaluated for intrinsic viscosity and elastic component. Molecular conformation of the xanthan–LBG complex was assessed

using the power-law and Huggins equations. Addition of any of the three salts significantly reduced the intrinsic viscosity and elastic component of the gum blends, with a pronounced effect from divalent ions, compared with that from monovalent ions. The 60 % xanthan–40 % LBG blend exhibited the strongest attraction between xanthan and LBG. For the three salts, the attraction reduced when 5-mM salt was added and vanished with the addition of 50-mM salt. The strongest attraction between xanthan and LBG molecules was also noticed by a positive Huggins miscibility coefficient K_m, and a positive attraction–repulsion coefficient a. With addition of 50 mM of any of the three salts, the coefficient α became negative, suggesting a strong repulsion between the two gums. The power-law coefficient b increased as salt concentration and LBG fraction increased in the blends for the three salts, suggesting a more flexible xanthan–LBG complex dependent on salt concentrations and LBG.

In another development, (Xiaodong and Marek, 2007) investigated the effects of lithium, sodium, potassium, and cesium chlorides on the properties of dilute guar gum solutions through viscosity measurements. The results obtained showed that the intrinsic viscosity of guar gum was not significantly affected by the salts up to an electrolyte concentration of 4.1 mol/L. In the same ionic strength range, however, clear differences were observed between individual salts in their ability to influence the Huggins constant. At even higher electrolyte concentrations, only lithium and sodium chlorides markedly increased the intrinsic viscosity of the polymer, pointing towards the formation of a new type of structure in those solutions. The observed trends were attributed to the chaotropic (K+, Cs+) or kosmotropic (Li+, Na+) properties of the background salts. It was suggested that chaotropic electrolytes were capable of enhancing the dissolution of colloidal guar gum aggregates normally present in polysaccharide solutions under ambient conditions. On the other hand, the presence of high concentrations of kosmotropic ions led to enhanced aggregation

of guar gum due to competitive hydration for free water molecules between the polysaccharide chains and the strongly hydrated cations. Comparative tests with the use of urea showed that the solute affected the behaviour of dilute guar gum solutions in a way similar to NaCl, so its dispersing/hydrogen bond-breaking capabilities towards the polymer were not very clear in the system studied.

Khouryieh *et al* (2007) also used oscillating capillary rheometer to investigate the dynamic viscoelastic and intrinsic viscosity properties of deacetylated xanthan (0.025 %), native xanthan (0.025 %), guar gum (0.075 %) and xanthan- guar mixtures in dilute solutions. Influence of ionic strength on xanthan conformation and interaction with guar gum was elaborated. As the salt concentration increased, a significant ($P < 0.05$) decrease in viscosity (η') and elasticity (η'') values was observed for both native xanthan–guar mixtures and deacetylated xanthan-- guar mixtures. In water and 2 mM NaCl solution, the relative viscosity and elasticity of both native xanthan–guar mixtures and deacetylated xanthan–guar mixtures were much higher than of those calculated for mixtures assuming no interaction, whereas no pronounced increase was found for polysaccharide mixtures in 40 mM NaCl. The intrinsic viscosities of deacetylated xanthan–guar mixtures in water and 2 mM NaCl were higher, whereas the intrinsic viscosities of native xanthan–guar mixtures were lower than those calculated from the weight averages of the two individually, assuming no interaction. These results demonstrated that intermolecular interaction has occurred between xanthan and guar mixtures in water and 2 mM NaCl, but may not occur in 40 mM NaCl, and mutual incompatibility may occur. The results obtained suggest that the degree of disordering of xanthan played a critical role in xanthan–guar interaction and may explain the differences in η', η'', and intrinsic viscosity measurements between 2 and 40 mM NaCl.

A study was made by Amorim et al (2007) to determine the influence of ionic strength (S) on the apparent (AV) and plastic (PV) viscosities and water loss (WL) of sodium bentonite suspension with polymers. Na-bentonite was dispersed in water (4.86 % w/w) of different ionic strengths (S = 0.0, 0.015, 0.030 and 0.045 M) followed by the addition of polymer. Three polymer samples were studied i.e. low viscosity carboxymethyl cellulose (CMC BV), polyanionic cellulose (PAC), and partially hydrolyzed polyacrylamide (HPAM). The results obtained indicated that the presence of salts and increased salinity greatly influenced the apparent and plastic viscosities and water loss of bentonite suspensions with polymer. The behaviour of apparent and plastic viscosities presented by the bentonite dispersions treated with CMC BV showed that polymer molecules are absorbed on clay particles even in a saline system. However, at a high ionic strength (S = 0.045 M), this adsorption is limited by the high concentration of calcium and magnesium ions.

2.5 Corrosion inhibition by gums

Interaction between valuable metals (such as Al) and aggressive media (such as acid, base or salt) is a serious impediment that may risk cost benefit analysis in the operation of some industries. This is because, corrosion of these materials, if not reduced can induce damages to industrial installations (Noor and Al-Moubaraki, 2008). Measures commonly adopted to protect metals against corrosion in industries include panting, electroplating, anodic and cathodic protection, oiling and the use of inhibitors, which is generally regarded as one of the best options. Most inhibitors are organic compounds synthesized from cheap raw materials. They may also be selected from existing compounds that may be aromatic, rich in π-electrons and suitable functional groups (such as C=C, C=O, -OH, etc) (Eddy, 2010). Some inhibitors are products of living organisms (green corrosion inhibitors) and are preferred because they are

cheap, biodegradable and comply with required environmental standards that vitiated the abolition of chromates and other non-eco-friendly inhibitors.

Available literature have also indicated that a wide range of natural polymers have been investigated as possible corrosion inhibitors. The greatly expanded interest on these naturally occurring substances is attributed to the fact that they are cheap, ecologically friendly and possess no threat to the environment. In addition, they are readily available and renewable source of materials. Plant gum exudates from *Pachylobus edulis* (PE) and *Raphia hookeri* (RH), gum arabic, *Dacroydes edulis, guar gum, Anogessus leocarpus (Al) and Ficus glumosa* (FG) have been reported as good corrosion inhibitors (Umoren and Ebenso, 2008, Abdallah , 2004; Eddy *et al*, 2011, Ameh *et al*, 2012). The inhibitive effect of *Ficus glumosa* gum (FG) in the corrosion of mild steel in H_2SO_4 medium has been studied by Ameh *et al*. (2012) using the weight loss, gasometric, thermometric and scanning electron microscopy (SEM) techniques. They found that FG gum is a good adsorption inhibitor. An investigation into the mode of adsorption of the gum revealed that the adsorption is exothermic, spontaneous and fitted the mechanism of physical adsorption. Gum arabic has been investigated and found to be one of the most potent gums for the inhibition of the corrosion of Al (Umoren *et al*, 2006). They attributed the inhibition potential of the gum to the presence of arabinogalactan, oligosaccharides, polysaccharides and glucoproteins, which are rich in hetero atoms. Chemical constituents of *Ficus platyphylla* gum and their corrosion inhibition potentials were investigated using gravimetric and GCMS methods respectively.. The gum was found to be a good adsorption inhibitor for the corrosion of mild steel in solutions of HCl. The inhibition potential of the gum was attributed to the presence of methoxy-phenyl-oxime (0.79 %), 1-methoxyethyl benzoate (4 %), palmitic acid (7.58 %), oleic acid (10.15 %), octadecanoic acid (6.2 %), 1-phenanthrenecarboxylic acid (podoca) (17.78 %),

albietic acid (19.28 %), (6,8,9-trimethyl-4-(1-phenylethyl)-3-oxabicyclo[3.3.1]non-6-en-1-yl) methanol (1.16 %) and tetracosamethyl-cyclododecasiloxane-(2,2,4,4,6,6,8,8,10,10,12,12,14,16,16,18,18,20,20,22,22,24,24-tetracosa methyl cyclododecasiloxane) (31.07 %). Analysis of FTIR spectra revealed that *Ficus platyphylla* gum inhibited the corrosion of mild steel in solutions of HCl through the formation of inhibitor-metal complex (via C=O and NH_2 bonds) and adsorption through OH bond. The adsorption of the inhibitor was also found to be spontaneous, exothermic and supported the mechanism of physical adsorption. Chemical constituents and corrosion inhibition potential of *Daniella olliverri* (DO) gum exudates were investigated by Eddy *et al.* (2012c) and the results obtained showed that the gum is acidic, brownish in colour, ionic and highly soluble in water but insoluble in acetone, chloroform and ethanol. GCMS spectrum of the gum indicated the presence of sucrose, dihex-5-en-2-yl phthalate, stearic acid, 2,6-dimethyl-4-nitrophenol and (E)-hexadec-9-enoic acid. Corrosion inhibition potential of the gum was investigated using weight loss and FTIR methods. *Daniella olliverri* gum has been found to be a good inhibitor for the corrosion of mild steel in HCl solution. The authors attributed the corrosion inhibition potential of the gum to the presence of aromatic compounds, suitable functional groups and heteroatoms as its chemical constituents, which facilitated its adsorption. The adsorption of the gum on the surface of the metal was found to be endothermic, spontaneous and was through the mechanism of physical adsorption. Eddy *et al* (2011) have also found that *Anogessus leocarpus* gum (AL) is a good inhibitor for the corrosion of mild steel due to the presence of sucrose (10.03 %), phthalic acid (2.53 %), n-hexadecanoic acid (11.73 %), oleic acid (30.49 %), pentacenequinone (4.41 %) and 2,3-diphenylnaphthoquinone (21.43 %). The adsorption of the inhibitor on mild steel surface was found to be exothermic, spontaneous, fitted the Langmuir isotherm and was through the

mechanism of charged transfer from the inhibitor's molecule to the charged metal surface. Behpour *et al.* (2011) carried out a comparative study of two oleo-gum resins exudate from Ferula assa-foetida (F. assa-foetida) and Dorema ammoniacum (D. ammoniacum), as inhibitors for mild steel corrosion in 2 M HCl solution using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods. Potentiodynamic polarization curves showed that both oleo-gums behave as mixed type inhibitors. At all temperatures, the experimental data fitted the Langmuir adsorption isotherm for both oleo-gum resin exudates.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

Crude *Fagara zanthoxyloides* and *Trichilia roka* gums were obtained as dried exudates from their parent trees grown at Kanya Babba village in Babura Local Government Area of Jigawa State. The crude *Ficus sycomorus* gum was obtained from Uran Village in Gezawa Local Government Area of Kano State and *Newbouldia laevis* was obtained from the botanical garden situated close to The Postgraduate School, Samaru main campus, Zaria.

3.1.1 Tapping of gums

The gums were collected from the plant species by tapping (Smith and Montgomery. 1959) around mid-December during the day time. A small axe was used to break the outer bark. Tapping was carried out by driving an axe underneath the bark which was pulled back until the bark broke horizontally to give two broken ends. The cut was made about 4.0 cm wide. The bark was then carefully peeled along the length of the wounded trunk. The gum droplets formed were 3.0 – 5.5 cm in diameter. They dried and hardened on exposure to atmosphere.

3.1.2 Purification of the gums

The procedure adopted for the purification of the gum was similar to that used by Femi – Oyewo *et al* (2004) but with some modifications. The gums were dried in an oven at 40°C for 2hours. Their sizes were reduced by blending. It was hydrated in double strength chloroform water for five days with intermittent stirring to ensure complete dissolution of the gum and strained through a 75μm sieve to obtain particulate free slurry which was allowed to sediment. The gum sediment was precipitated from the slurry using absolute ethanol, filtered and defatted

with diethyl ether. The precipitate was again dried in the oven at 40°C for 48 hours. The dried flakes were pulverized using a blender and stored in an air tight container.

3.2 Physicochemical and rheological tests

3.2.1 Percentage yield of the purified gums

The dried, precipitated and purified gums obtained from the crude dried exudates were weighed and the yields were expressed in percentage using the weight of the crude gum(s), as the denominator.

3.2.2 Determination of solubility of the gums in various solvents

The solubilities of gum were determined in cold and hot distilled water, acetone, chloroform and ethanol. The sample of each exudate gum (10 mg) was added to 10 cm^3 each of the above mentioned solvents and left overnight. The clear supernatants (5 cm^3) were taken in small pre-weighed evaporating dishes and heated to dryness over a digital thermostatic water bath. The weights of the dried residue with reference to the volume of the solutions were determined using a digital analytical balance (Model. XP-300, Denver instrument, USA) and expressed as the percentage solubilities of the gums in the solvents (Carter, 2005).

3.2.3 Moisture sorption studies

The method described by Josiah (1991) was adopted. Four dried evaporating dishes were weighed and 2g of each of the gum powder was weighed and transferred into them. The final weight of the dish was noted and then placed over water in desiccators for a period of 5 days, thereafter removed and transferred into other desiccators over activated silica gel (desiccant) for another 5 days. The dish with its contents was weighed on daily basis and its water content calculated.

3.2.4 Swelling properties

The method of Bowen and Vadino (1984) was adopted. A 5 g quantity of each gum powder was placed in a 200 cm^3 measuring cylinder and tapped 200 times. The volume (V_i) of the gum in the cylinder was recorded. Water was added to the gum to reach the 100 cm^3 mark, in the cylinder and left to stand for 24 hours. The new volume of the gums in the cylinder was then recorded as(V_f). The swelling capacity (Φ) was calculated as the ratio of the final volume (V_f) to the initial (V_i). The procedure was repeated to obtain duplicate values.

3.2.5 Determination of the pH of the exudate gum mucilage

This was done by shaking a 1% w/v dispersion of each gum sample in water for 5mins and the pH was determined using an Oaklon pH meter (Model 1100). The pH meter was set to neutral at room temperature of 28 °C and electrode was immersed into the mucilage. The reading of the meter was recorded. Triplicate measurements were made.

3.2.6 Determination of the intrinsic viscosities of the gum mucilage

A Cannon Ubbelohde capillary viscometer (Cannon Instruments, model 1-71) was used. The gum solution was prepared by dispersing 4.5 g of each gum sample separately in 100 cm^3 of distilled water at room temperature. A solution of the prepared sample (12 cm^3) was transferred into the viscometer. The viscometer was immersed in a thermostatic viscometer bath, calibrated using a thermometer with a precision of 0.01 K, to equilibrate for 10 minutes at 25 ^{0}C. After equilibration, the sample was pumped into the bulb and allowed to flow pass the lower mark on the viscometer under the influence of gravitational force. The time of flow of the sample from the upper through the lower mark was noted and recorded in seconds. Triplicate measurements were made and the average values reported. Serial dilution was performed in situ to obtain other

concentrations (3.5, 2.5 and 1.5 %w/v). The relative viscosity was calculated using the equation 3.1

$$\eta_{rel} = \frac{t-t_o}{t_o} \qquad 3.1$$

Where t is the flow time of the gum mucilage in seconds and t_o is the flow time of solvent (water) in seconds.

3.2.7 Determination of apparent viscosity of the mucilage

A digital Brookfield viscometer (Model DV- I PRIME) was used for this study. Spindle number 62 was used throughout. It measures the torque required to rotate an immersed spindle in a fluid. The instrument features a rotating spindle with multiple speed transmission and interchangeable spindles that measure a variety of viscosity ranges. Different concentrations (0.5, 1.0, 1.5 and 2.0 %w/v), of the gum samples were prepared in a 50 cm^3 beaker. The guard-leg was removed and the instrument was recalibrated as specified in the Brookfield Viscometer manual. This was done to allow for immersion of the spindle groove in the fluid. The speed of rotation was varied (10, 20, 50, and 100 r.p.m) to determine its effect on the viscosity values since drag force is known to alter with changes on the spindle size and rotational speed. The experiment was conducted with each of the concentrations kept constant while the speed of rotation was varied and vice versa. For each concentration and at each rotational speed, triplicate measurements were made and the average values reported.

3.2.8 Effects of temperature, pH and electrolytes on viscosities of gum mucilage

The Brookfield viscometer was used as described above. Other parameters such as rotational speed and mucilage concentrations were kept constant. 2 % w/v concentrations of each of the gums were prepared and their viscosities at temperature range 30 - 70 ^{0}C were determined.

Also, with another 2 %w/v concentrations of each of the gums, the pH values were varied ranging from acidic to alkaline using 0.1 M HCl and 0.1 M NaOH as pH adjusters as the case may be. The Oaklon pH meter (Model 1100) mentioned above was used to ascertain the pH values of the mucilage. In another experiment, different concentrations (0.01, 0.1, 1.0 and 1.0 M) of KCl, $AlCl_3$, urea and $CaCl_2$ and 0.5, 1.0, 1.5 and 2.0 %w/v of the exudate gums were prepared. Viscosity values at a fixed concentration of the salts and different concentrations of the gums and vice versa were measured.

3.3 Proximate composition

3.3.1 Determination of moisture content

The method described by AOAC (1984) was adopted. A clean crucible was dried to a constant weight in an air oven at 105 °C, cooled in a desiccator and weighed (W1). Two grams (2.0 g) of finely ground sample was accurately weighed and transferred into the previously labeled crucible and reweighed (W_2). The crucible containing the sample was dried in an oven to a constant weight (W_3). The percentage of moisture was calculated using equation 3.2.

$$\% \text{ Moisture} = \frac{W_2 - W_3}{W_2 - W_1} \times 100 \qquad 3.2$$

3.3.2 Determination of ash content

The AOAC (1984) method was used. The porcelain crucible was dried in an oven at 100 °C for 10 minutes, cooled in a desiccator and weighed (W_1). Two grams (2.0 g) of the finely ground sample was transfered into the previously weighed porcelain crucible and reweighed (W_2). It was ignited and then transferred into a furnace which was set at 550 °C. The sample was left in the furnace for eight hours to ensure proper ashing. The crucible containing the ash was then removed cooled in the desiccator and weighed (W_3). The percentage ash content was calculated as follows using equation 3.3.

$$\% \text{ Ash content} = \frac{W_3 - W_1}{W_2 - W_1} \times 100 \qquad 3.3$$

3.3.3 Determination of crude lipid content

The lipid content was determined as in the AOAC (1984). A clean, dried 500 cm^3 round bottomed flask, containing few anti-bumping granules was weighed (w_1) and 300 cm^3 of petroleum ether (40-60°C) for the extraction was poured into the flask fitted soxhlet extraction unit. The round bottomed and a condenser was connected to the soxhlet extractor, and cold water circulation was put on. The heating mantle was switched on and heating rate adjusted until the solvent was refluxing at a steady rate. Extraction was carried out for six hours. The solvent was recovered and the oil was dried in the oven at 70 °C for one hour. The round bottomed flask and oil was cooled and then weighed (W_2). The lipid content was calculated thus:

$$\% \text{ Crude lipid content} = \frac{W_2 - W_1}{Weight\ of\ sample} \times 100 \qquad 3.4$$

3.3.4 Determination of nitrogen and crude protein contents

The determination of protein contents involved three steps;

i. Digestion

The method of Onyeike and Osuji (2003) was used. Exactly 1.5 g of the ground defatted sample in an ashless filter paper was transformed into 300 cm^3 kjeldahl flask. The sample was digested until a clear green colour was obtained. The digest was cooled and diluted to 100 cm^3 with distilled water.

(b) Distillation

The diluted digest (20 cm^3) was transferred into 500 cm^3 Kjeldahl flask containing anti-bumping chips and 40 cm^3 of 40 % sodium hydroxide was slowly added by the side of the flask. A 250 cm^3 conical flask containing a mixture of 50 cm^3 2 % boric acid and four drops of indicator was used to trap the ammonia being liberated. The conical flask and the Kjeldahl were then placed on

a distillation apparatus, with the tube inserted into the conical flask and the Kjeldahl. The flask was heated to distil the ammonia evolved and the distillate collected into the boric acid solution. Distillation was allowed to continue for 10 minutes from the point the boric acid turned green.

(c) Titration

The distillate and the boric acid were then titrated with 0.1 M HCl.

Calculation:

% Crude protein = % Nitrogen (N_2) × 6.25 3.5

$$\% \text{ N} = \frac{14 \times M \times V_1 \times T_v}{Weight\ of\ sample\ (mg) \times V_a} \quad 3.6$$

Where M is actual molarity of acid (M), T_v is the titre value (volume, cm^3) of the HCl used (cm^3), V_t is the total volume of diluted digest (cm^3), V_a is the aliquot volume distilled (cm^3).

3.3.5 Determination of crude fibre content

The method described by AOAC (1984) was used. Two grams (2.0g) of the finely ground sample was weighed into a round bottomed flask. 100 cm^3 of 0.25 M tetraoxosulphate (VI) acid solution was added and the mixture boiled under reflux for 30 minutes. The hot solution was quickly filtered under suction. The insoluble matter was washed several times with hot water until it was acid free. It was quantitatively transferred into the flask and 100 cm^3 of hot 0.3 M sodium hydroxide solution was added and the mixture boiled again under reflux for 30 minutes and quickly filtered under suction. The soluble residue was washed with boiling water until it was base free. It was then dried to constant weight in the oven at 100°C, cooled in a dessicator and weighed (C_1). The weighed sample (C_1) was then incinerated in a muffle furnace at 500 °C for 2 hours, cooled in the dessicator and weighed (C_2).

Calculation:

The loss in weight on incineration = C_1-C_2. The calculation was carried out using equations 3.7.

$$\% \text{ Crude fibre} = \frac{C_1 - C_2}{Weight\ of\ original\ sample} \times 100 \qquad 3.7$$

3.3.6 Determination of carbohydrate content

The total carbohydrate content was determined by difference. The sum of the percentage of moisture, ash, crude lipid, crude protein, and crude fibre content was subtracted from 100 (Muller and Tobin, 1980).

Calculation:

% Total carbohydrate = 100 - (Moisture + Ash + Fat + Protein + Fibre) %. 3.8

3.4 Corrosion monitoring

3.4.1 Materials used

Materials used for the study were aluminium sheets of composition (determined by x-ray diffraction technique); Al (99.94), Cu (0.01), Mg (0.02), Si (0.03), Mn (0.02) and Zn (0.01). The aluminium sheets were mechanically press-cut into different coupons each of dimension, 5×4×0.05 cm. Each coupon used was degreased by washing with ethanol, cleaned with acetone and allowed to dry in air before preservation in a desiccator. All reagents used for the study were of Analar grade and double distilled water was used for their preparation.

3.4.2 Experimental methods

3.4.2.1 Gravimetric method

In the gravimetric experiment, a previously weighed metal (aluminium) coupon was completely immersed in 250 cm^3 of the test solution in an open beaker. The beaker was covered with aluminium foil and inserted into a water bath maintained at 303 K. After every 24 hours, the corrosion product was removed by washing each coupon (withdrawn from the test solution) in a

solution containing 50 % NaOH and 100 gl^{-1} of zinc dust. The washed coupon was rinsed in acetone and dried in the air before re-weighing. The experiment was repeated at 333 K. In each case, the difference in weight for a period of 168 hours was taken as the total weight loss. From the average weight loss (mean of three replicate analysis) results, the inhibition efficiency (%I) of the inhibitor, the degree of surface coverage (θ) and the corrosion rate of aluminium (CR) were calculated using equations 3.9, 3.10 and 3.11 respectively;

$$\%I = 1 - \left(\frac{W_1}{W_2}\right) \times 100 \qquad 3.9$$

$$\theta = 1 - \frac{W_1}{W_2} \qquad 3.10$$

$$CR = \frac{W_2 - W_1}{At} \qquad 3.11$$

where W_1 and W_2 are the weight losses (g) for aluminium in the presence and absence of the inhibitor, θ is the degree of surface coverage of the inhibitor, A is the area of the surface of aluminium coupon (in cm^2), t is the period of immersion (in hours) and ΔW is the weight loss of aluminium after time, t.

3.5 Elemental analysis of the exudate gums

Heavy metals and other elements of interest were determined by wet digestion of the gum samples followed by analysis using Atomic Absorption Spectrophotometry (UNICAMM 969). For this reason, in a 50 cm^3 Pyrex round bottomed flask, 1 g of each of the gum sample was added followed by the addition of 5 cm^3 concentrated per chloric acid ($HClO_4$), 5 cm^3 concentrated nitric acid (HNO_3), and heating at 90 ^0C for $2\frac{1}{2}$ hours. In the digested residue, little amount of distilled water was added followed by filtration using a Whatman filter paper No. 42 and the filtrate made up to 50 cm^3 mark. From the concentrations of magnesium, copper,

manganese, calcium, zinc, iron, lead, cadmium and nickel were determined. Calibration curve for each of the element was made and the concentrations of the above named elements extrapolated from their respective calibration curves.

3.6 Turbidity (by absorptometric method)

A Hach colorimeter (Model: DR/890) was used for this study. The gum sample (1.0 g) was dissolved in 100 cm^3 of deionized water. The sample was properly mixed to form a homogeneous solution before transferring to the sample cell. The sample cell was filled with 10 cm^3 of distilled water (blank). The surface of the cell was wiped with a soft cloth. The blank was then placed in the cell holder and tightly covered with the instrument cap. The value (0 FAU-Formazin Attenuation Unit) displayed was recorded. Another sample cell was filled with 10 cm^3 of the gum sample, the surface of the cell was wiped with soft cloth as before. The sample cell was placed in the cell holder and the READ key pressed to display the value. Triplicate measurements were made and the average values reported.

3.7 Fourier Transform Infrared (FTIR) analysis

FTIR analyses of the exudate gums were carried out using SHIMADZU (Model: FTIR-8400S) Fourier Transform Infrared spectrophotometer. Samples were prepared by mixing thoroughly with KBr before scanning through a wave number range of 4500-400 cm^{-1}.

3.8 Gas Chromatography-Mass Spectrometry (GC-MS) analysis

A Shimadzu GC-MS (Model: QP2010 PLUS), Japan was used with an auto-sampler (Model: AOC-20i). The column capillary has a diameter of 30×0.25 mm. helium gas was used as the carrier gas at a constant flow of 3 cm^3 / min and an injection volume of 8 µL. The column oven temperature was maintained at 80.0 ^0C at an injection temperature of 220 ^0C.

3.9 Determination of wavelength of maximum absorption

A Jenway UV/Vis spectrophotometric (model: 6405) was used for the study. The sample was prepared by dispersing 1 g of each sample in 100 cm^3 of deionized water in a 250 cm^3 beaker. One of the instrument's cuvettes was filled with the gum solution. A second cuvette was filled with deionized water to be used as blank. The spectrophotometer was set to 350 nm. With the sample chamber empty, the transmittance was set to 0 %. The cuvette with the blank was wiped with a piece of soft cloth, placed in the sample chamber and covered. The transmittance was then set to 100 %. With the blank removed, the sample was wiped, placed in the chamber and covered. The absorbance was recorded. Subsequently, absorbance at every 25 nm was recorded. A graph of absorbance against wavelength was plotted. The wavelength of maximum absorption, λ_{max}, was extrapolated.

CHAPTER FOUR

RESULTS AND DISCUSSION

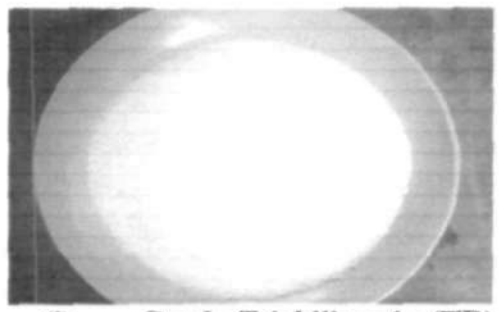
4.1 Physicochemical properties

Table 4.1 presents the physicochemical properties of *Trichilia roka* (*TR*), *Newbouldia laevis* (*NL*), *Ficus sycomorus* (*FS*) and *Fagara zanthoxyloides* (*FZ*) gums while Figure 4.1 shows the photographs of the crude and purified gums. After purification, the yields obtained for TR, NL, FS and FZ gums were 74.00, 78.00, 60.00 and 53.00 % respectively. The corresponding swelling capacities were 15, 8, 10 and 5 respectively. The results obtained, indicated that NL gum had the highest yield after purification while FZ gum had the least. On the other hand, TR gum had the highest capacity to absorb moisture while FZ gum had the least capacity.

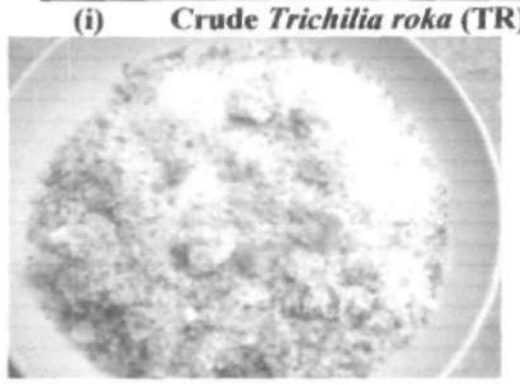
From Figure 4.1, it is evident that TR, NL, FS and FZ gums are whitish-yellow, yellowish-red, reddish-brown and black respectively. All the gums tasted bland except FZ gum, which had a sour taste. NL and FS gums were odourless while TR and FZ gums had the floral and camphor-like odour. The gums studied were also found to be mildly acidic and the acidity increases in the order, FZ>FS>TR>NL indicating that FZ (which had sour taste) was the most acidic. All the studied gums were soluble in cold and hot water but were insoluble in acetone, chloroform and ethanol indicating that the gums are ionic. The solubility of the gums (except that of FS gum) in water was observed to decrease slightly, with increase in temperature. The observed decrease in the solubility of the gum with increasing temperature suggests that the heat given off during the dissolution of the gum is more than the heat required to break the molecules of the gums. Hence the dissolution reaction is exothermic. On the other hand, the dissolution of FS gum in water is endothermic.

Table 4.1: Physicochemical parameters of *Trichilia roka* (*TR*), *Newbouldia laevis* (*NL*), *Ficus sycomorus* (*FS*) and *Fagara zanthoxyloides* (*FZ*) gums

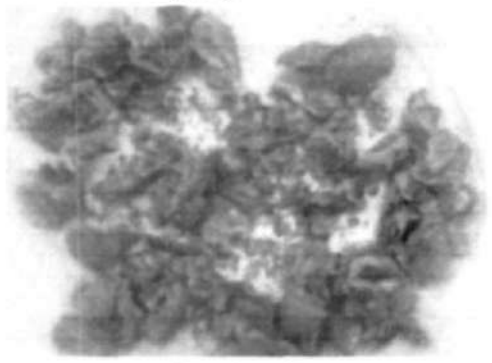
Parameters	GUMS			
	TR	**NL**	**FS**	**FZ**
Colour	Yellowish-white	Yellowish-red	Reddish-brown	Black
Odour	Floral	Odourless	Odourless	Camphor-like
Taste	Bland	Bland	Bland	Sour
pH	5.22	5.43	5.21	4.81
Solubility(% w/v) in Cold water	9.2	7.8	8.4	9.4
Hot water	8.5	7.6	9.2	9.0
Acetone	0.00	0.00	0.00	0.00
Chloroform	0.00	0.00	0.00	0.00
Ethanol	0.00	0.01	0.00	0.00
Percentage yield (% w/w)	74.00	78.00	60.00	53.00
Swelling capacity	15.00	8.00	10.00	5.00
Turbidity (FAU)	1100	80	224	93
Salinity (%)	0.0	0.1	0.1	0.0
Electrical conductivity (µS/cm)	78.8	268.0	160.9	36.0
Total dissolved solids (mg/l)	37.0	127.5	76.0	16.5
λ_{max} (nm)	325	310	380	307
Melting point (^{0}C)	224-226	217-219	274-276	210-212



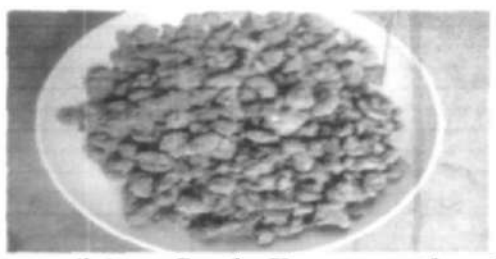
(i) Crude *Trichilia roka* (TR)



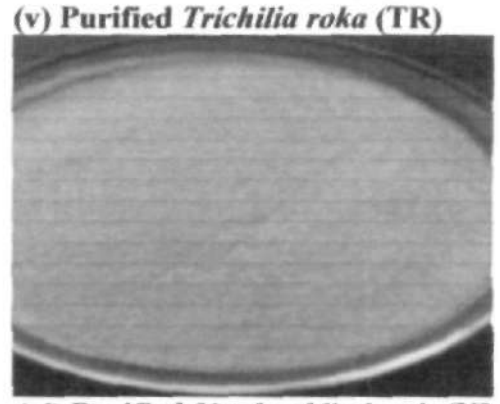
(ii) Crude *Newbouldia laevis* (NL)



(iii) Crude *Ficus sycomorus* (FS)

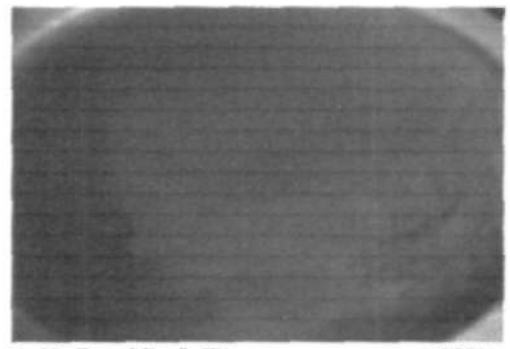


(iv) Crude *Fagara zanthoxyloides* (FZ)

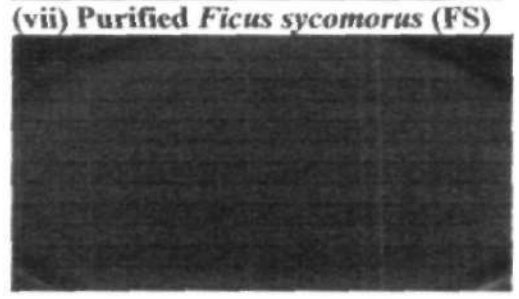


(v) Purified *Trichilia roka* (TR)

(vi) Purified *Newbouldia laevis* (NL)



(vii) Purified *Ficus sycomorus* (FS)



(viii) Purified *Fagara zanthoxyloides* (FZ)

Figure 4.1: Plates of the crude and purified TR, NL, FS and FZ gums exudates

The results obtained for physicochemical parameters of the gums studied (Table 4.1). also revealed that although the salinity of the gums was very low, it correlated strongly with conductivity (r =0.889). However, values the conductivities were very high compared to those obtained for salinity. These suggest that the conductivities of the gums may not primarily be due to the presence of chloride ions but may be due to the movement of charge within the colloidal system (Milani *et al.*, 2007).

The Melting points for TR, NL, FS and FZ gums were very similar (Table 4.1) and ranged from 217 to 276 °C. This clearly indicates that the gums are unstable above these temperatures. Other physicochemical parameters measured for TR, NL, FS and FZ gums included turbidity, total dissolved solids (TDS) and wavelength of maximum absorption. These parameters are closely related to each other. Turbidity is a measure of the amount of insoluble content in the polysaccharide such as gum (Pablyana *et al.*, 2007). It is also a measure of the emulsifying property of the gum (Yadav *et al.*, 2008). From the results obtained, turbidities of TR, NL, FS and FZ gums were 110, 80, 224 and 93 FAU respectively. Therefore, FS gum had the highest ability to scatter light while NL gum had the least. According to Dror *et al.* (2006), turbidity is related to light scattering according to equation 4.1.

$$\frac{I_t}{I_0} = exp\{-\tau l\} \qquad 4.1$$

where I_t and I_0 are the intensities of the transmitted and incident light beam, l is the path length of the sample and τ is the turbidity. From the logarithm and rearrangement of equation 4.1, equation 4.2 was obtained and by comparison with the Beer-Lambert equation, equation 4.3 was obtained

$$2.303log\left(\frac{I_t}{I_0}\right) = -\tau l \qquad 4.2$$

$$A = \epsilon Cl = log\left(\frac{I_t}{I_0}\right) = \frac{-\tau l}{2.303} \qquad 4.3$$

where A is the absorbance of the system, ε is the molar absorption coefficient, which is defined as the specific absorption coefficient associated with a concentration of 1 mole/l. and a path length of 1 cm. From equation 4.3, it can be assumed that if the path length is constant, the turbidity of the gum will vary linearly with the concentration of its active constituent. Curve fitting between turbidity and TDS was linear (Figure 4.2). Linear plot was also obtained between turbidity and wavelength of maximum absorption (Figure 4.2) indicating that the turbidity of the gums correlated excellently well with TDS and with the wavelength of maximum absorption.

4.2 Proximate composition

Table 4.2 presents the proximate composition of TR, NL, FS and FZ gums. These included nitrogen content, protein, carbohydrate, fibre, ash and lipid contents. From the results obtained, the nitrogen contents of TR, NL, FS and FZ gums were less than unity and ranged between 0.35 to 0.70 %. The lower the nitrogen content of a polysaccharide, the better its emulsifying property. The concentrations of nitrogen in the gums studied are higher than the range of levels reported for the nitrogen content of gum Arabic (i.e 0.26 – 0.39 %) by Karamalla *et al.* (1998) and *Acacia senegal* gum by Elmanan *et al.* (2008), Idris *et al.* (1998), Lelon *et al.* (2010), Siddig *et al.* (2005). However, the observed concentrations are within the range reported for *Ferula gumosa* gum by Milani *et al.* (2007) and are also comparable to those reported for some *Albizia* gums (Mhinzi, 2003). Nitrogen content of polysaccharides is a measure of its protein content. Thus the higher the nitrogen content, the higher its protein content. The protein content of gums is a significant index for assessing its emulsifying properties and its pharmaceutical applications.

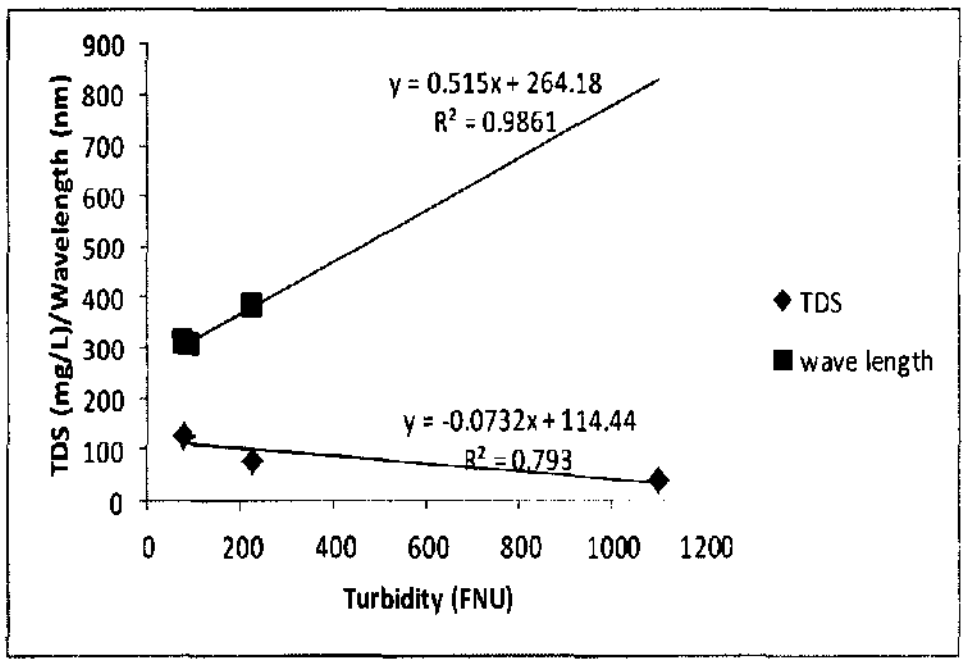


Figure 4.2: Variation of TDS/wave length of maximum absorption with turbidity for TR, NL, FS and FZ gums

Table 4.2: Proximate composition of TR, NL, FS and FZ gums

Proximate parameters	Concentration (%)			
	TR	NL	FS	FZ
Nitrogen	0.3488	0.5248	0.4960	0.7008
Protein	2.18	3.28	3.10	4.38
Moisture	1.00	5.00	12.00	24.00
Ash	2.00	1.00	5.00	33.00
Lipid	21.50	16.00	18.00	12.90
Fibre	11.90	6.40	4.60	3.40
Carbohydrate	61.42	68.32	57.30	22.32

The moisture contents of TR, NL, FS and FZ gums were 1.00, 5.00, 12.00 and 24.00 % respectively. This indicated that TR gum had a low moisture content compared to its swelling capacity, which was highest for all the gums studied. On the other hand, FZ gum had the highest moisture content and also had the least swelling index. Moisture contents of other gums were also found to vary with their respective swelling capacities. Correlation between moisture content and swelling index of the gums was excellent and negative (r = 0.90). The observed moisture contents of FS and FZ gums are within the range reported for *Cochlospermum gossypium* gum (15.25 ± 1.18 %), Senegal and Kerensis species of gum Arabic (15.50 ± 0.50 and 17.50 ± 1.60 % respectively), Acacia Senegal gum (9.15 ± 0.89 %) and Anarcardium occidentale (7.2 %) (Akinhanmi *et al.*, 2008; Kramalla *et al*, 1998; Lelon *et al.*, 2010; Vinod and Sashidhar, 2010).

The ash contents of the various gums were found to range from 2.00 to 33.00 %. The results obtained indicated that FZ gum had the highest ash content indicating that the inorganic content of this gum is expected to be the highest while that of NL gum with the least concentration of ash is expected to be least. Generally, the concentrations of ash in the gums studied are relatively comparable to those reported for some plant gums (Akinhanmi *et al.*, 2008; Kramalla *et al*, 1998; Lelon *et al.*, 2010; Vinod and Sashidhar, 2010).

The lipid content of the various gums was found to increase in the order FZ > NL>FS>TR indicating that TR had the highest lipid content. On the order hand, the fibre content of the gums studied were found to increase in the order, FZ>FS>NL>TR indicating that TR gum had the highest fibre content while FZ gum had the least.

The most essential component of polysaccharides including plant gum exudates is their carbohydrate content. In this study, carbohydrate contents of the gums were found to increase in

the order, FZ>FS>NL>TR and FZ>FS>NL>TR which indicated that TR gum is essentially richer in carbohydrate than others.

4.3 Concentrations of some cations

Table 4.3 presents the concentrations of major ions, trace metals and heavy metals in TR, NL, FS and FZ gums. The concentrations of calcium (Ca) ions in the four gums were 14.227, 21.496, 28.572 and 24.689 ppm for TR, NL, FS and FZ gums respectively. These levels are higher than those reported for some gums including *Anogeissus leiocarpus* gum (Eddy *et al*., 2012a), *Barijeh* gum (Milani *et al*, 2007), *Khaya grandifolia* gum (Yusuf *et al*, 2006), Acacia Senegal gum (Mhinzi, 2003) and that of *Anacardium occidentale* gum (Zakaria *et al*, 1997). However the concentrations were found to be lower than those reported for Cashew gum (Gyedu-Akoto *et al*., 2008) and gum *Tragacanth* (Balaghi *et al*, 2010). The concentrations of magnesium (Mg) ions in the four gums were 4.210, 16.924, 8.595, and 4.096 ppm for TR, NL, FS, and FZ gums respectively. These concentrations are also higher than those reported for *Anogeissus leiocarpus* gum (Eddy *et al*, 2012a), *Barijeh* gum (Milani *et al*., 2007), Acacia Senegal gum (Mhinzi, 2003), *Anacardium occidentale* gum (Zakaria *et al*, 1997) but lower than those reported for Cashew gum (Gyedu-Akoto *et al*, 2008) and gum *Tragacanth* (Balaghi *et al*, 2010). However the concentrations of magnesium ions found in Khaya grandifolia gum (Yusuf *et al*, 2006), was higher than that of TR and FZ but lower than that of NL and FS gums.

The measured concentrations of sodium (Na) ions obtained in TR, NL, FS, and FZ gums were 21.960, 21.389, 19.760 and 23.513 ppm respectively. These are higher than those reported for *barijeh* gum (Milani *et al*, 2007), *Khaya grandifolia* gum (Yusuf *et al*, 2006), Acacia Senegal gum (Mhinzi, 2003), *Anacardium occidentale* gum (Zakaria *et al*, 1997) but lower than those of cashew gum (Gyedu-Akoto *et al*., 2008) and gum Tragacanth (Balaghi *et al*, 2010).

Table 4.3: Mean concentration of some cations in *TR*, *NL*, *FS* and *FZ* gums

Cation	Concentration (ppm)			
	***TR* gum**	***NL* gum**	***FS* gum**	***FZ* gum**
Na	21.960	21.389	19.760	23.513
K	0.625	1.061	0.611	11.175
Zn	1.324	0.282	0.264	0.591
Al	0.452	1.161	-0.290	1.194
Pb	0.705	2.950	0.022	1.026
Mg	4.210	16.924	8.595	4.096
Cd	0.003	0.004	0.007	0.015
Ca	14.227	21.496	28.572	24.689
Cu	0.049	0.032	0.219	0.055
Ni	0.136	0.077	0.532	0.107
Fe	0.042	0.326	1.526	4.129
Mn	-0.078	-0.062	0.214	0.672

The measured concentrations of potassium (K) ions in TR, NL, FS, and FZ gums were 0.625, 1.061, 0.611 and 11.175 ppm respectively. These are lower than those reported for some plant gums such as *Khaya grandifolia* gum (Yusuf *et al*, 2006), *Acacia senegal* gum (Mhinzi, 2003), *Anogeissus leiocarpus* gum (Ahmed *et al*, 2009), cashew gum (Gyedu-Akoto *et al*, 2008) and gum tragacanth (Balaghi *et al*, 2010). However, these concentrations are higher than those in *Anacardium occidentale* gum (Zakaria *et al*, 1997).

The concentrations of iron (Fe) ions in TR, NL, FS, and FZ gums were 0.042, 0.326, 1.526 and 1.529 ppm respectively. These concentrations are comparable to the range of levels reported for some plant gums including *Anogeissus leiocarpus* gum (Eddy *et al*., 2012a), *Acacia Senegal* gum (Mhinzi, 2003), gum *Tragacanth* (Balaghi *et al*, 2010) and those of *Khaya grandifolia* gum (Yusuf *et al*., 2006). The measured concentrations of copper (Cu) ions in TR, NL, FS, and FZ gums obtained were 0.049, 0.032, 0.219 and 0.055 ppm respectively. These concentrations are within the range reported for some plant gums such including *Anogeissus leiocarpus* gum (Eddy *et al*, 2012a) and acacia species gum (Mhinzi, 2003). However these concentrations were lower than those reported for some species of *Khaya grandifolia* gum by Yusuf et al. (2006).

Concentrations of zinc (Zn) ions in these gums were found to range from 0.264 to 1.324 ppm and are comparable to those reported for some plant gum exudates including *Anogeissus leiocarpus* gum (Eddy *et al*, 2012a), acacia species gum (Mhinzi, 2003), gum tragacanth (Balaghi *et al*, 2010), and *Khaya grandifolia* gum (Yusuf *et al*, 2006). Similarly, the concentrations of aluminium (Al) ions in TR, NL, FS, and FZ gums were 0.452, 1.161, -0.290 and 1.194 ppm respectively. However the literature is scanty on the concentrations of aluminium ions in gums.

The concentrations of manganese (Mn) ions in the four gums were -0.078, -0.062, 0.214 and 0.672 ppm for TR, NL, FS, and FZ gums respectively. The results obtained, indicated that these gums are not rich in Mn. However, the observed concentrations are within the range reported for some plant gums including *Anogeissus leiocarpus* gum (Eddy *et al.*, 2012a). In TR, NL, FS and FZ gums, the concentrations of lead (Pb) ions were 0.705, 2.950, 0.022 and 1.026 ppm respectively while the concentrations of nickel ions were 0.136, 0.077, 0.532 and 0.107 ppm respectively. The concentrations of Pb and Ni obtained were comparable to those obtained for most plant gums and were below the threshold concentrations needed for their toxicity (Ahmed *et al.*, 2009). Finally the concentrations of cadmium (Cd) ions in TR, NL, FS, and FZ gums were 0.003, 0.004, 0.007 and 0.105 ppm respectively and are lower than the range reported for some food and pharmaceutical gums (Eddy *et al.*, 2012a, 2012b, 2012c).

It can be seen from the results obtained that TR, NL, FS and FZ gums are richer in the essential minerals than those of trace and heavy metals. Therefore, the gums may be a good source of mineral nutrition and are suitable for use as pharmaceutical excipients and food additives. The trend for the decreasing concentration of elements in the gum studied samples is Ca>Na>Mg>K>Fe>Pb>Ni>Al>Zn>Mn>Cd.

4.4 Gas chromatography – mass spectrometry (GCMS) study

GCMS spectra of *Trichilia roka* (*TR*), *Newbouldia laevis* (*NL*), *Ficus sycomorus* (*FS*) and *Fagara zanthoxyloides* (*FZ*) gums are shown in Figures 4.3 to 4.6. The concentrations of active constituents of each gum, associated retention time, molar mass and chemical formula of compounds identified from the spectrum are presented in Tables 4.4 to 4.7. In Figures 4.7 to 4.10, the chemical structures of compounds identified from the spectra are presented in Figures 4.7 to 4.10 respectively.

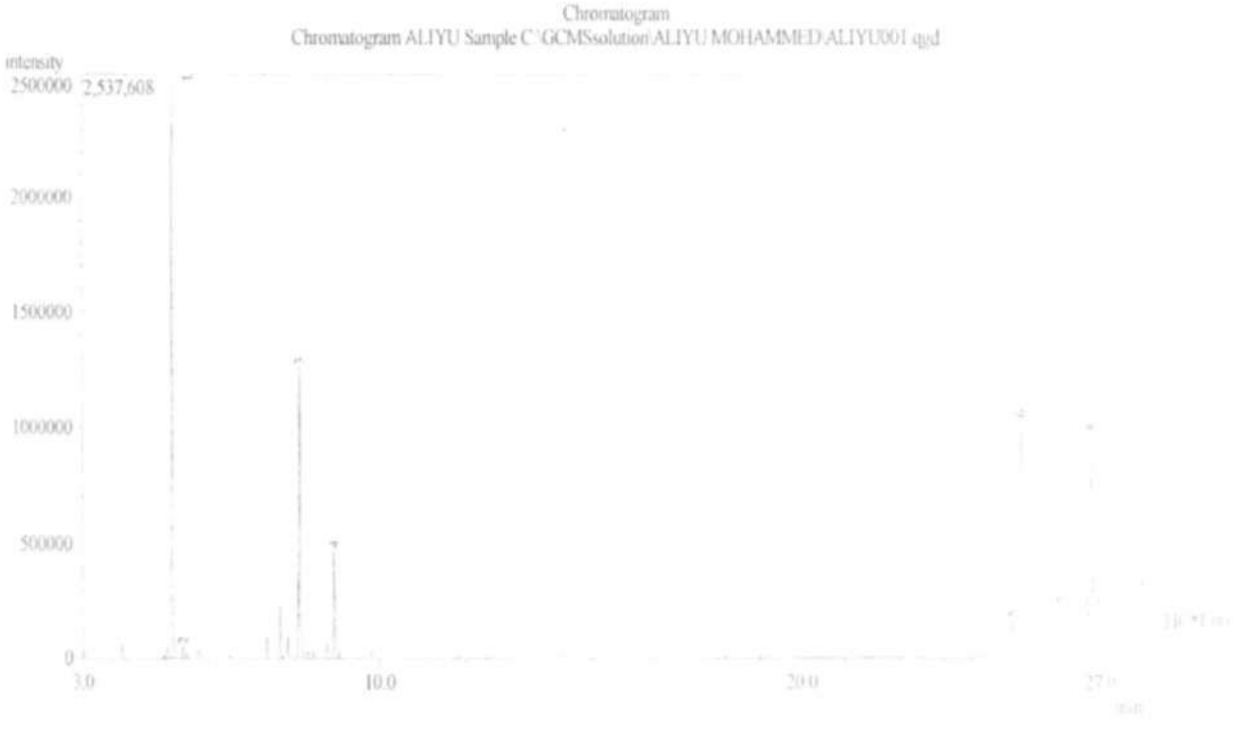


Figure 4.3: GCMS spectrum of *Trichilia roka* (TR) gum exudate



Figure 4.4: GCMS spectrum of *Newbouldia laevis* (NL) gum exudate



Figure 4.5: GCMS spectrum of *Ficus sycomorus* (FS) gum exudate

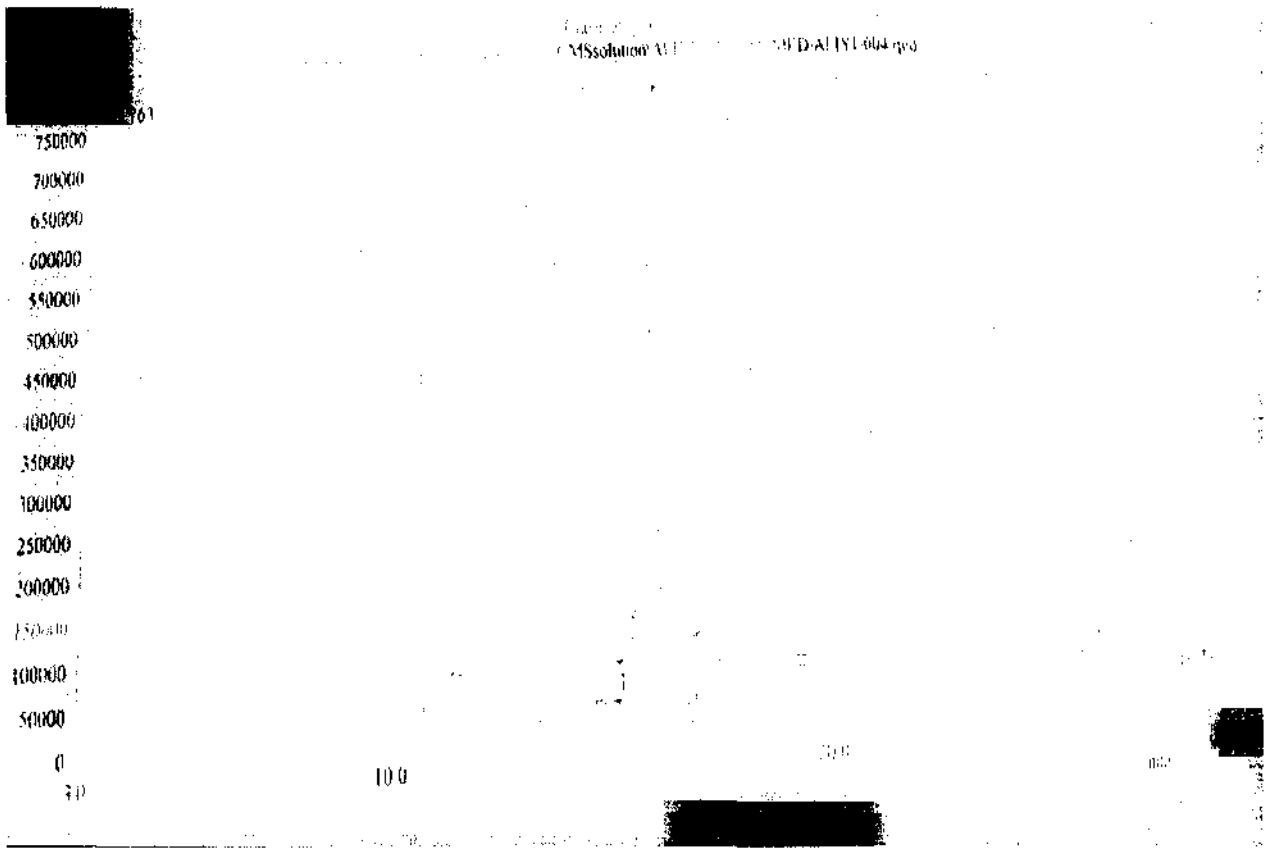


Figure 4.6: GCMS spectrum of *Fagara zanthoxyloides* (FZ) gum exudate

Table 4.4: Parameters deduced from GCMS spectrum of *TR* gum

Line number	IUPAC name	Molecular formula	Molar mass (g/mol)	Retention time (m)	Concentration (%)
1	Alpha purene	$C_{10}H16$	136	5.158	40.12
2	Camphene	$C_{10}H_{16}$	136	5.408	1.20
3	Verbenol	$C_{10}H_{16}O$	152	8.158	20.36
4	Pinen-4-one	$C_{10}H_{14}O$	150	8.950	7.78
5	Neodihydrocarveol	$C_{10}H_{11}O$	154	24.917	1.20
6	Limonene diepoxide	$C_{10}H_{16}O_2$	168	25.142	14.97
7	erythro(cis)(1',4')-4,4'-dihydroxybicyclooctyl	$C_{16}H_{30}O_2$	254	26.092	1.80
8	isopregol,	$C_{10}H18O$	154	26.767	12.57

Table 4.5: Parameters deduced from GCMS spectrum of *NL* gum

Line number	IUPAC name	Molecular formula	Molar mass (g/mol)	Retention time (m)	Concentration (%)
1	2,3-bis[(9E)-9-octadecenoate	$C_{57}H_{104}O_6$	884	24.658	18.60
2	4,4,11,11,14b-penta methylicosahydropicen-3(4H)-one	$C_{30}H_{48}O$	424	25.692	22.09
3	Perhydropyrene	$C_{16}H_{26}$	218	27.617	59.30

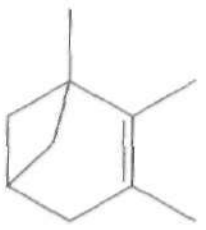
Table 4.6: Parameters deduced from GCMS spectrum of *FS* gum

Line number	IUPAC name	Molecular formula	Molar mass (g/mol)	Retention time (m)	Concentration (%)
1	Pentanoic acid	$C_5H_{10}O_2$	102	21.058	15.91
2	9-hexadecenoic acid	$C_{16}H_{30}$	254	24.650	84.09

Table 4.7: Parameters deduced from GCMS spectrum of *FZ* gum

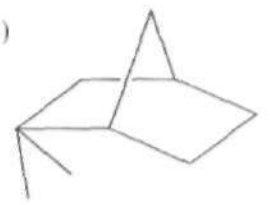
Line number	IUPAC name	Molecular formula	Molar mass (g/mol)	Retention time (m)	Concentration (%)
1	Alpha cubebene	$C_{15}H_{24}$	204	10.733	2.40
2	Alpha bourbinene	$C_{15}H_{24}$	204	11.492	6.59
3	5-mehoxy-thiophene-2-carboxamide	$C_6H_7NO_2$	157	14.775	1.80
4	(3-acetyl-2-oxo-imidazolidin-1-yl)-acetic acid	$C_8H_{12}O_4$	200	15.158	1.80
5	2,6-dimethyl-3,5,7-octatriene-2-ol	$C_{10}H_{16}O$	152	15.292	4.19
6	Caryophyllene oxide	$C_{15}H_{24}O$	220	15.558	6.59
7	Humulane-1,6-dien-3-ol	$C_{15}H_{26}O$	222	16.183	40.12
8	Cadalin	$C_{15}H_{18}$	198	17.042	4.79
9	1-phenyl-4-(1,2,2-trimethyl-cyclopentyl)-but-2-ene-1,4-dione	$C_{18}H_{22}O_2$	270	17.533	3.59
10	Cis-Z-alpha-bisabolene epoxide	$C_{15}H_{24}O$	220	18.558	25.15
11	Artemisia ketone	$C_{10}H_{16}O$	152	19.417	2.99

(1)



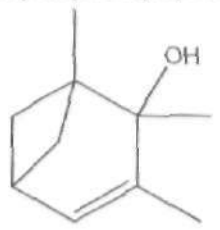
trimethylbicyclo[3.1.1]hept-2-ene

(2)



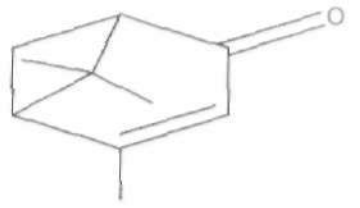
(1*S*,4*R*)-2,2-dimethylbicyclo[2.2.1]heptane

(3)



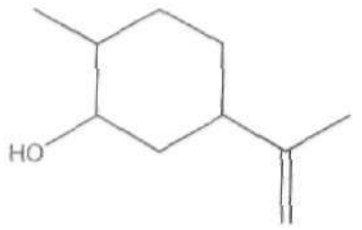
Trimethylbicyclo[3,1,1]hept-3-en-2-ol

(4)



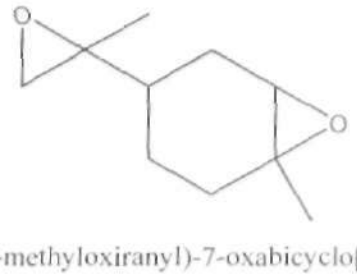
4,6,6-trimethylbicyclo[3.1.1]hept-3-en-2-one

(5)



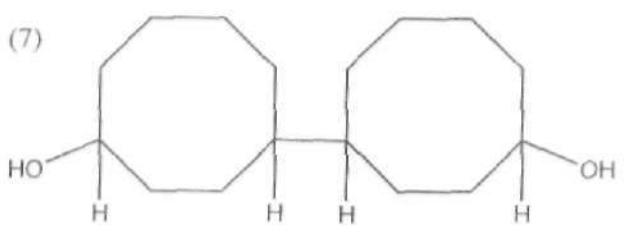
2-methyl-5-(1-methylethenyl) cyclohexanol

(6)



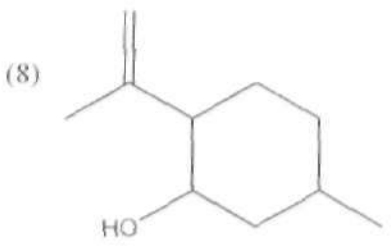
1-methyl-4-(2-methyloxiranyl)-7-oxabicyclo[4.1.0] heptane

(7)



bi(cyclooctane)-4,4'-diol

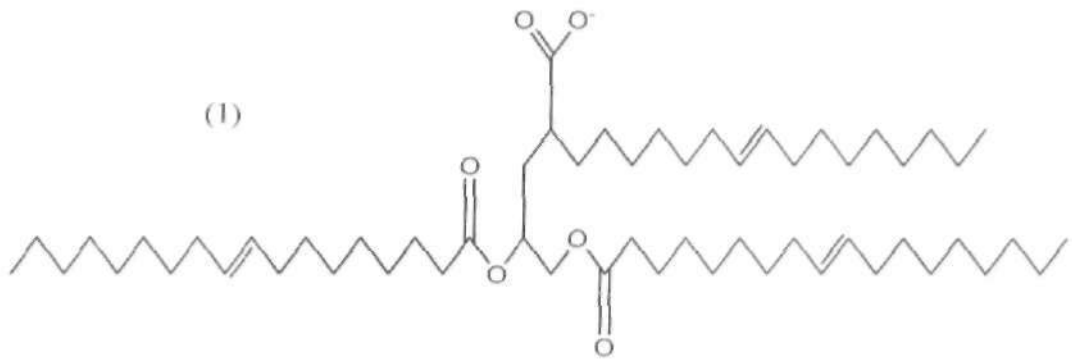
(8)



5-methyl-2-(1-methylethenyl)cyclohexanol

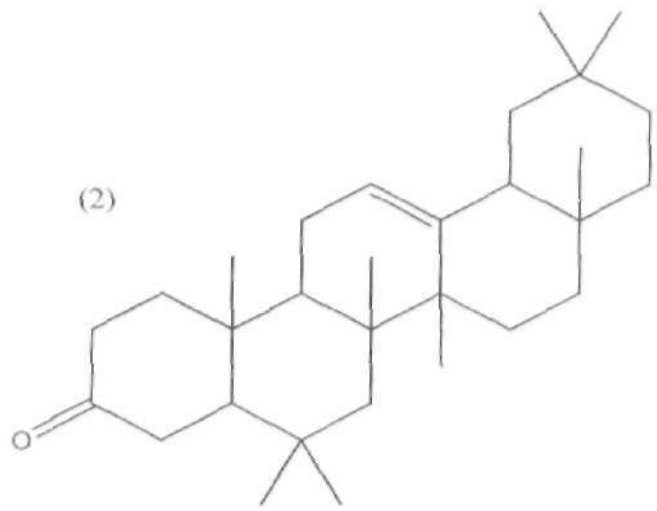
Figure 4.7: Chemical structures of compounds identified in GCMS spectrum of TR gum

(1)



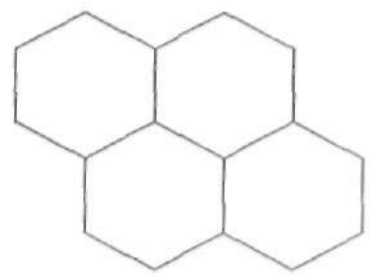
2,3-Bis[(9E)-9-octadecenoyloxy]propyl(9E)-9-octadecenoate

(2)



5,5,6a,6b,8a,11,11,14b-octamethyl-1,2,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,14,14a,14b-octadecahydropicen-3(4*H*)-one

(3)



hexadecahydropyrene

Figure 4.8: Chemical structures of compounds identified in GCMS spectrum of NL gum

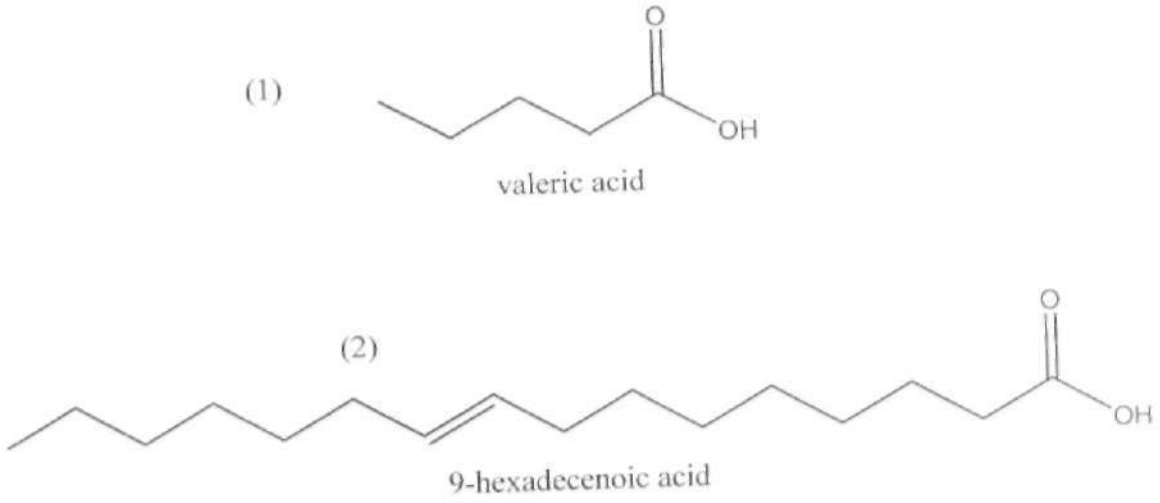


Figure 4.9: Chemical structures of compounds identified in GCMS spectrum of FS gum

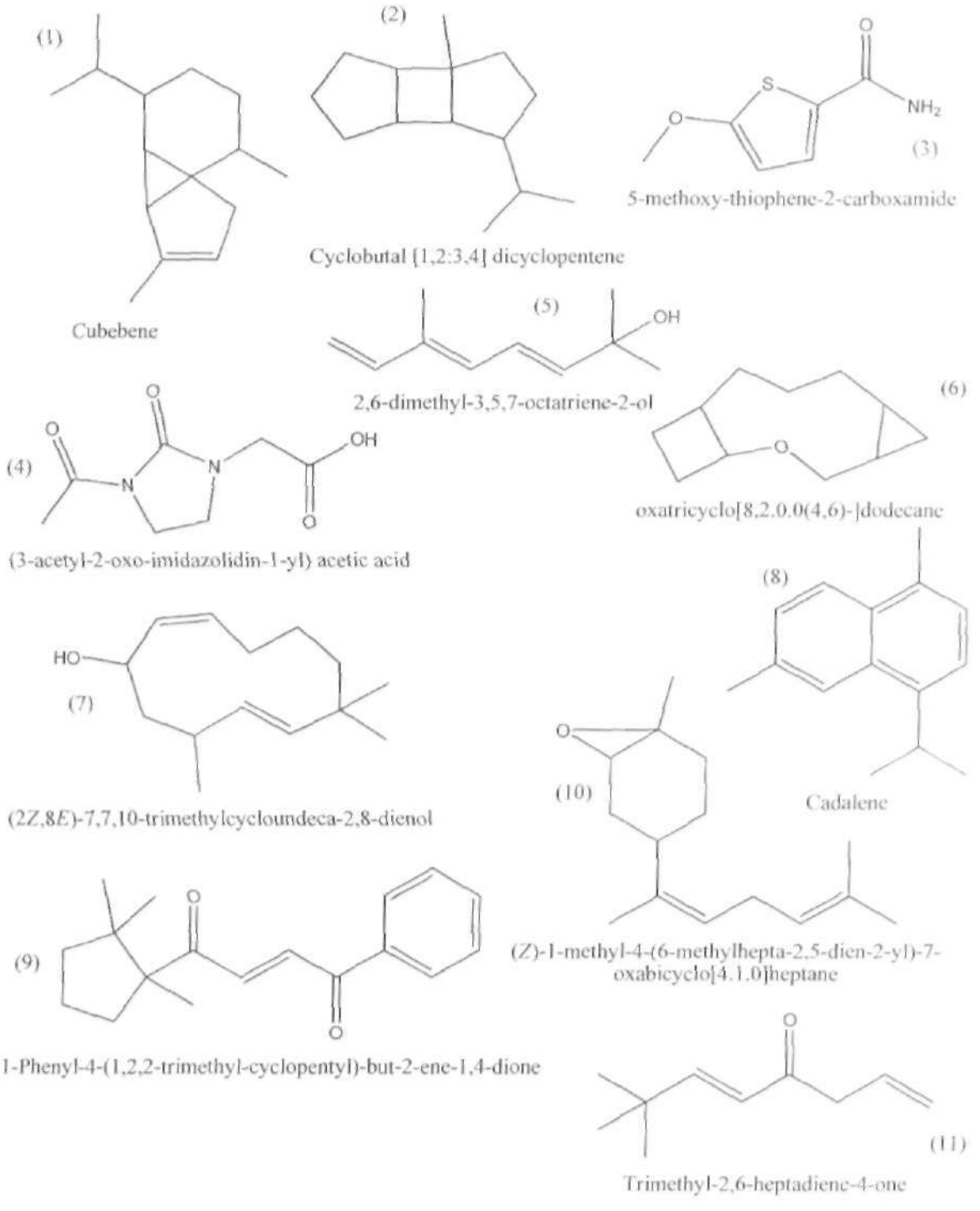


Figure 4.10: Chemical structures of compounds identified in GCMS spectrum of FZ gum

From the GCMS spectrum of TR gum (Figure 4.3), it can be seen that eight lines, corresponding to eight compounds were formed. Line 1 shows the presence of 40.12 % of alpha pinene, which is a bicycle compound (i.e bicycle (3.1.1) hept-2-ene. This compound was isolated at a retention time of 5.158 minutes. The molar mass of the compound is 136 g/mol. In line 2. 1.20 % of camphene, a bicycle compound (bicycle [2.2.1] heptane or 2,2-dimethyl-3-methylene) was identified at a retention time of 5.408 minutes. The molecular mass of the compound is 136 g/mol and its mass peak is 9.0. In line 3, another bicycle compound, 20.36 % of verbenol (i.e bicycle [3.1.1] hept-3-en-2-ol) was isolated at a retention time of 8.158 g/mol. The molecular weight of the compound is 152 g/mol while its mass peak is 52. Line 4 of the GCMS spectrum of *TR* gum shows the presence of 7.78 % of a bicycle compound, verbenone (bicycle [3.1.1] het-3-en-2-one or pinen-4-one) which was characterized by a retention time and mass peak of 8.950 minutes and 35 respectively. In line 5, the spectrum of *TR* gum revealed the presence of 1.20 % of neodihydrocarveol (i.e cyclohexanol) with characteristics retention time and mass peak of 24.917 minutes and 26 respectively. The most likely compound, identified in line 6 of the GCMS spectrum of *TR* gum is 14.97 % of limonene deproxide (ocobicyclo [4.1.0] heptane. The compound was identified when the retention time was 25. 142 minutes and its molar mass was 168 g/mol. 1.80 % of erythro(cis)(1',4')-4,4'-dihydroxybicyclooctyl was identified in line 7 of the GCMS spectrum of *TR* gum. The compound was characterized with a molar mass, retention time and mass peak of 254 g/mol, 26.092 minutes and 33 respectively. Finally, in line 8 of the GCMS spectrum of *TR* gum, 12.57 % of cyclohexanol derivative (5-methyl-2-(1-methylethenyl)-cyclohexanol), isopregol, was identified at a retention time and mass peak of 26.767 minutes and 61. The molar mass of this compound is 154 g/mol.

GCMS of *NL* gum yielded three major lines (Figure 4.3) and hence three major compounds were identified. Line 1 of the spectrum indicated the presence of 18.60 % of an ester, 2,3-bis[(9E)-9-octadecenoate, which had a characteristic retention time of 24.658 minutes and mass peak of 30. The molecular weight of the identified ester was found to be 884 g/mol. Line 2 of the spectrum indicated the presence of a ketone, 2.22 % of 4,4,11,11,14b-pentamethylicosahydropicen-3(4H)-one, which exhibited a molecular mass of 424 g/mol and was identified at a retention time of 25.692 minutes and mass peak of 28. Finally, line 3 of the GCMS spectrum of *NL* gum revealed the presence of 59.30 % of perhydropyrene (hexadecahydropyrene), which was found at a retention time and mass peak of 27.617 minutes and 59 respectively.

Figure 4.4 shows the GCMS spectrum of *FS* gum which revealed the presence of two compound. The first compound (15.91 %) which appears at a retention time of 21.058 minutes in line 1 is a pentanoic acid (i.e valeric acid or propylacetic acid). The molecular mass of this organic acid is 102 g/mol. The second compound that was identified in the GCMS spectrum of *FS* gum was 84.09 % of 9-hexadecenoic acid (molar mass = 254 g/mol). The compound was identified at a retention time of 24.650 minutes.

The GCMS spectrum of *FZ* gum (Figure 4.5) revealed the presence of 11 peaks and therefore, eleven compounds were identified. Line 1 of the spectrum indicated the presence of 2.40 % of alpha cubebene, a cyclo compound (1H-cyclopenta [1,3] cyclopropal [1,2] benzene. This compound has a molar mass of 204 g/mol and was characterized by a retention time of 10.733 minutes. In line 2, 6.59 % of alpha bourbonene was identified at a retention time of 11.492 minutes and its molar mass was found to be 204 g/mol. 1.80% of 5-methoxy-thiophene-2-carboxamide was identified in line 3 of the GCMS spectrum of *FZ* gum. The molar mass of

this compound is 157 g/mol and was identified at a retention time of 14.775 minutes. In line 4 of the GCMS spectrum of *FZ* gum, 1.80 % of (3-acetyl-2-oxo-imidazoline-1-yl)-acetic acid, a methyl ester was identified. The compound was identified at a retention time of 15.158 minutes and its molar mass is 200 g/mol. Line 5 of the GCMS spectrum of *FZ* gum revealed the presence of 4.19 % of 2,6-dimethyl-3,5,7-octatriene-2-ol which has a molar mass of 152 g/mol. The compound was identified under a retention time of 15.292 minutes. In line 6, 6.50 % of caryophyllene oxide (molar mass = 220 g/mol) was identified at a retention time of 15.558 minutes. Line 7 of the GCMS spectrum of *FZ* gum confirmed the presence of 40.12 % of humulane-1,6-diene-3-ol which has a molar mass of 222 g/mol and exhibited a retention time of 16.183 minutes.. In line 8, 4.79 % of cadalin, naphthalene derivative was identified. The identified compound has a molar mass of 198 g/mol and a characteristic retention time of 17.042 minutes. In line 9 of the GCMS spectrum of *FZ* gum, 3.59 % of 1-phenyl-4-(1,2,2-trimethyl-cyclopentyl)-but-2-ene-1,4-dione which has a molar mass of 270 g/mol. The retention time at which this compound was identified was 17.533 minutes. At a retention time of 18.558 minutes, line 10 of the GCMS spectrum of *FZ* gum showed the presence of –25.15 % of cis-*Z*-alpha-bisabolene epoxide, whose molar mass is 220 g/mol. Finally, line 11 of the GCMS spectrum of *FZ* gum revealed the presence of 2,99 % of 3,3,6-methylheptadien-4-one. This compound has a molar mass of 152 g/mol and was characterized by a retention time of 19.417 minutes.

4.5 Fourier transform infrared (FTIR) study

Figures 4.11 to 4.14 show FTIR spectra of TR, NL, FS and FZ gums while Tables 4.8 to 4.11 present frequencies and peaks of FTIR absorption for the various gums. From figure 4.7, it is evident that the FTIR spectrum of *TR* gum exhibited bands and peaks that are typical characteristics of polysaccharides.

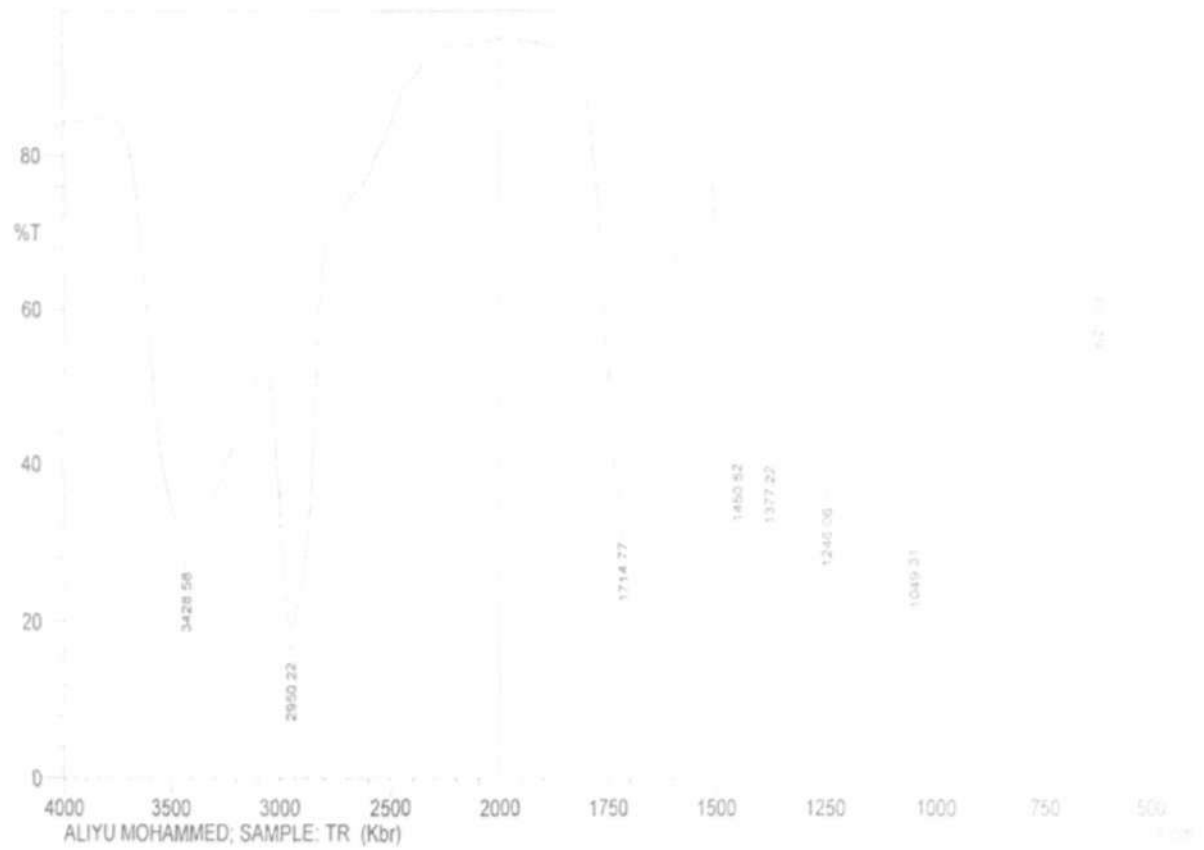


Figure 4.11: FTIR spectrum of TR gum exudate

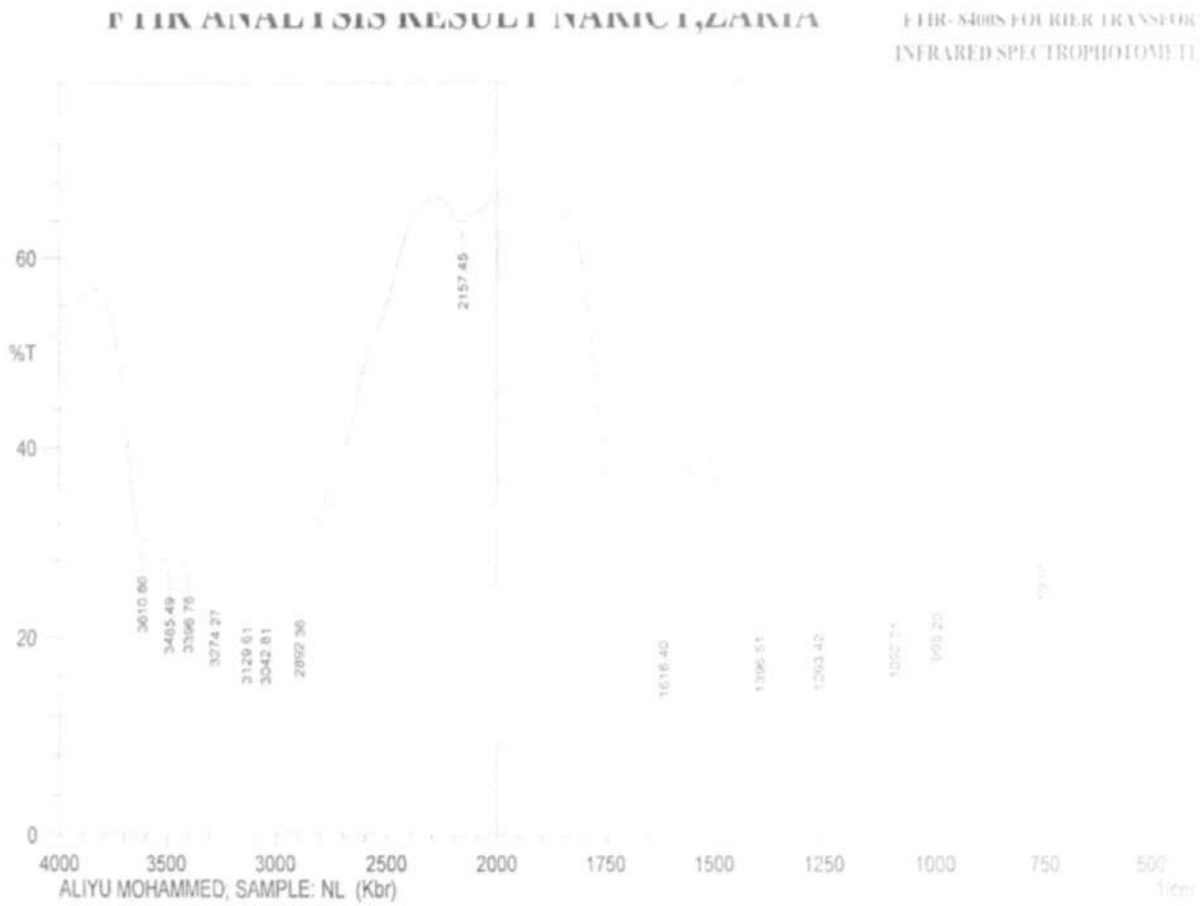


Figure 4.12: FTIR spectrum of NL gum exudate

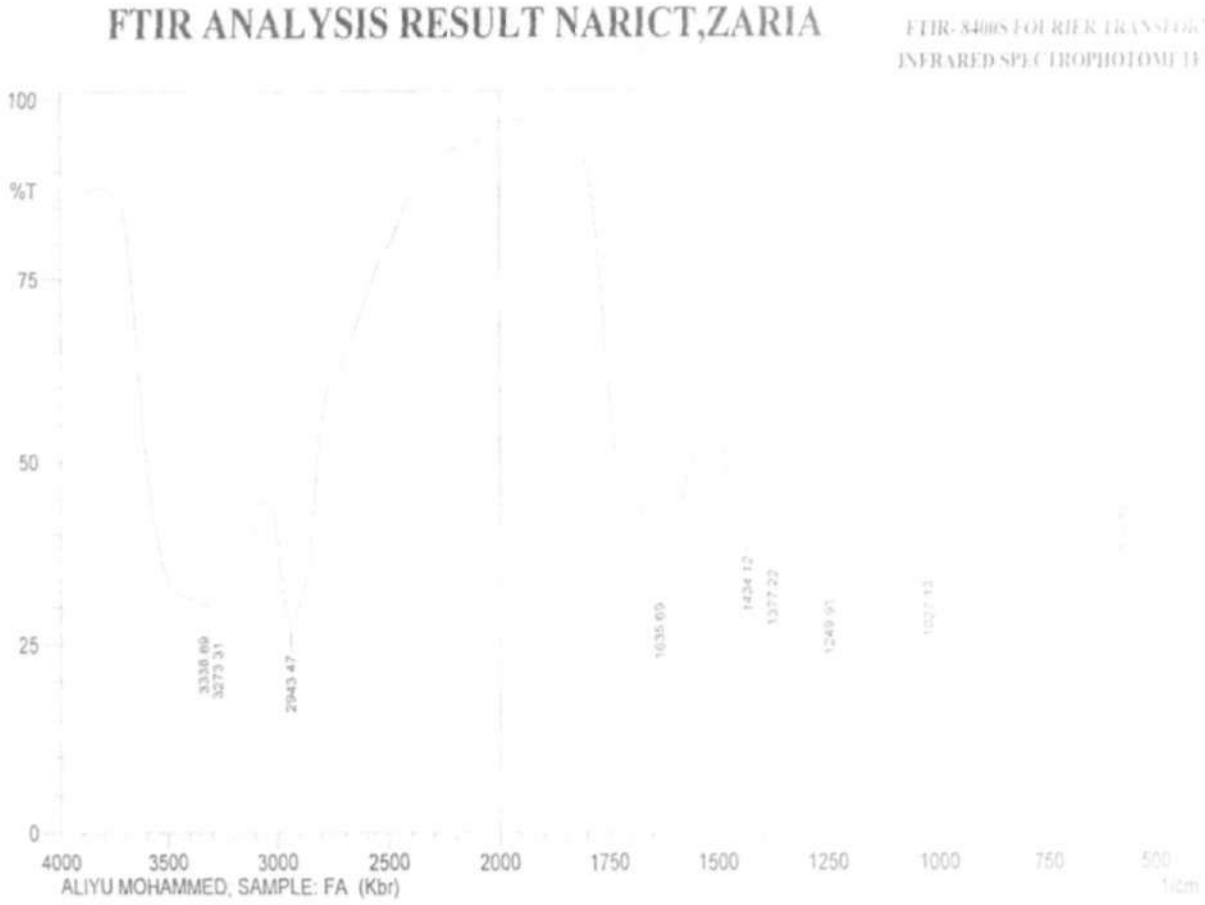


Figure 4.13: FTIR spectrum of FS gum exudate

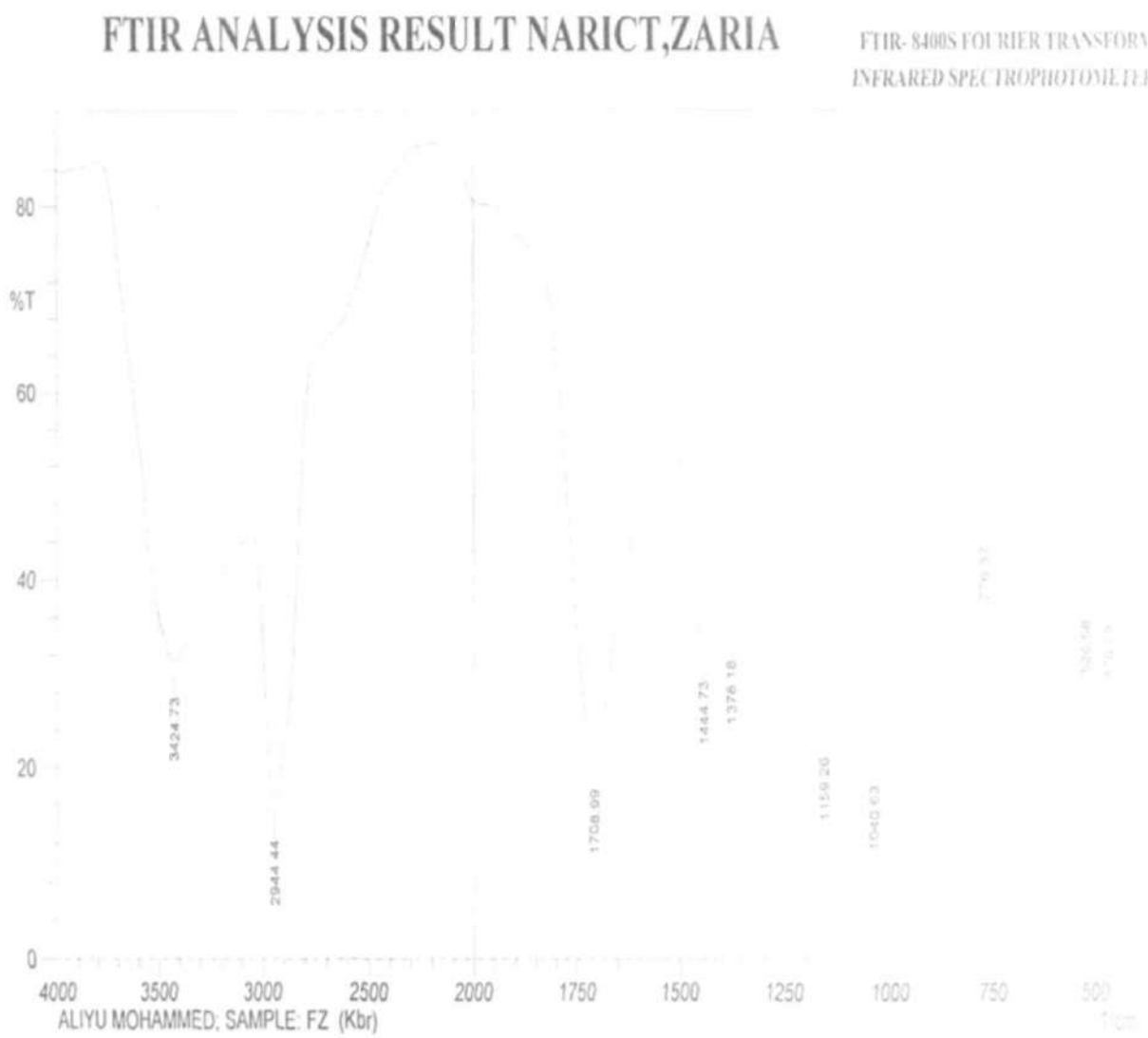


Figure 4.14: FTIR spectrum of FZ gum exudate

Table 4.8: Peak, frequency and assignment for FTIR absorption by *TR* gum

Peak	Intensity	Area	Assignment
621	65.66	27.88	C-H bending
1049	33.40	105.50	C-O stretch
1246	38.50	44.64	C-O stretch
1377	44.01	29.21	
1451	44.25	27.53	OH bend
1715	34.21	75.47	C=O stretch
2950	19.18	174.79	C-H stretch
3428	30.46	239.37	OH stretch

Table 4.9: Peak, frequency and assignment for FTIR absorption by *NL* gum

Peak	Intensity	Area	Assignment
759	31.46	175.97	=C-H rock
998	26.05	83.72	C-H 'oop'
1092	25.21	111.43	C-O stretch
1263	23.85	79.41	C-O stretch
1397	23.74	111.75	
1616	23.20	158.04	C-O stretch
2157	63.90	62.04	-C≡C-stretch
2892	25.24	258.40	C-H stretch
3043	24.53	62.88	C-H stretch
3130	24.61	72.63	OH stretch
3274	26.34	84.61	OH stretch
3397	27.75	44.25	OH stretch
3485	27.63	68.38	OH stretch
3611	29.87	96.93	OH stretch

Table 4.10: Peak, frequency and assignment for FTIR absorption by *FS* gum

Peak	Intensity	Area	Assignment
576	48.48	105.96	C-X stretch
1027	37.96	85.43	C-O stretch
1250	35.60	53.04	C-O stretch
1377	39.52	38.64	
1434	41.35	31.72	OH bend
1636	34.94	88.41	C-H stretch
2943	28.00	172.50	C-H stretch
3273	29.74	131.93	OH stretch
3339	30.52	149.98	OH stretch

Table 4.11: Peak, frequency and assignment for FTIR absorption by *FZ* gum

Peak	Intensity	Area	Assignment
471	39,06	36.32	
526	39.56	39.40	C-X stretch
776	47.32	33.09	C-X stretch
1041	22.11	138.58	C-O stretch
1159	25.08	111.24	C-O stretch
1378	35.33	46.91	
1445	33.17	46.91	OH bend
1709	21.69	149.66	C=O stretch
2944	16.25	149.66	C-H stretch
3425	31.43	256.48	OH stretch

The broad band occurring at 3429 cm^{-1} was due to the presence of hydroxyl group (i.e OH stretch). The peak obtained at 2950 cm^{-1} is due to stretching modes of C-H bonds of methyl group (CH_3). According to Nep and Conway (2010), natural gums usually contain fractions of sugar acid units which will usually impart a weakly anionic character to the gum macromolecule. A strong C=O stretch (absorption band) due to ketone or saturated aliphatic acid was found at 1715 cm^{-1}. Absorption bands around 1623 and 1421 cm^{-1} are typical of carboxylate groups of the galacturonic acid residues (Figueiro *et al.*, 2004). The medium absorption at 1450 cm^{-1} was due to C-C stretch in the ring. The strong C-O stretch absorption at 1049 cm^{-1} is attributed to the presence of carboxylic acid, alcohol, ester or ether. A medium absorption band due to C-H rock in alkane was observed at 1377 cm^{-1}. Finally, the weak vibration at 610 cm^{-1} indicates stretch due to alkyl halide.

The FTIR spectrum of *NL* gum also exhibited features that are common to other polysaccharides. OH stretches were found at 3611, 3485, 3397, 3274 and 3130 cm^{-1}. C-H stretch was found at 3043 cm^{-1} and a sharp C-H stretch obtained at 2892 cm^{-1} was due to stretching modes of C-H bonds of methyl group (CH_3). This vibration is capable of imparting weakly ionic character on the gum (Nep and Conway, 2010). The -C≡C-stretch at 2157 cm^{-1} indicated the presence of alkyne. According to Figueiro *et al.* (2004), adsorption bands between 1623 and 1421 cm^{-1} are typical of the carboxylare groups of the galacturonic acid. This justifies the presence of C-O stretch at 1616 cm^{-1}. The C=O stretch due to acetyl group was observed at 1263 cm^{-1} (Xiaodong and Marek, 2007). The C-O stretch was found at 1092 cm^{-1}while C-H oop and =C-H rock vibrations were observed at 998 and 759 cm^{-1} respectively.

The FTIR spectrum of *FS* gum revealed the occurrence of nine prominent peaks, which include those that are typical for polysaccharides. OH stretching vibrations were observed at

3339 and 3273 cm^{-1}. C-H stretch due to stretching bond of C-H in the methylene group was observed at 2943 cm^{-1}. C-H stretch was also found at 1636 while OH bending vibration was indicated at 1434 cm^{-1}. C-O stretching vibrations due to the presence of ketone, alcohol or carboxylic acid were found at 1250 and 1027 cm^{-1} respectively while alkyl halide stretch appeared at 576 cm^{-1}.

The FTIR spectrum of *FZ* gum indicated the presence of OH stretch at 3425 cm^{-1}, a strong C-H stretch due to C-H vibration in methylene group at 2944 cm^{-1} and a C=O stretch due to carboxylic acid group at 1709 cm^{-1}. OH bend at 1445 cm^{-1} and C-O stretches at 1159 and 1041 cm^{-1} respectively, were also observed. Finally, alkyl halide stretches were observed at 526 and 776 cm^{-1} respectively.

4.6 Water sorption study

Figure 4.15 shows the variation of %sorption with time for TR, NL, FS and FZ gum exudates. From the figure, it is evident that the four gums exhibit similar sorption trend. However the sorption capacity of the gums follows the trend FZ>NL>TR>FS indicating that FZ and FS gums have the highest and least sorption capacity. Generally, the %sorption first was found to increase up to the first four days, after which it decreases sharply to the sixth day and continue to decrease gradually. The maximum sorption capacity of TR (47 %), NL (48 %), FS (40%) and FZ (57 %) were observed in the fifth day. According to Eddy *et al.* (2013), adsorption capacity of a gum is an index that can be used to know the duration of time, within which a gum can be stable. From the results obtained, it is evident that FS gum which had the least adsorption capacity is the most stable while FZ gum is the least stable, when exposed to moisture.

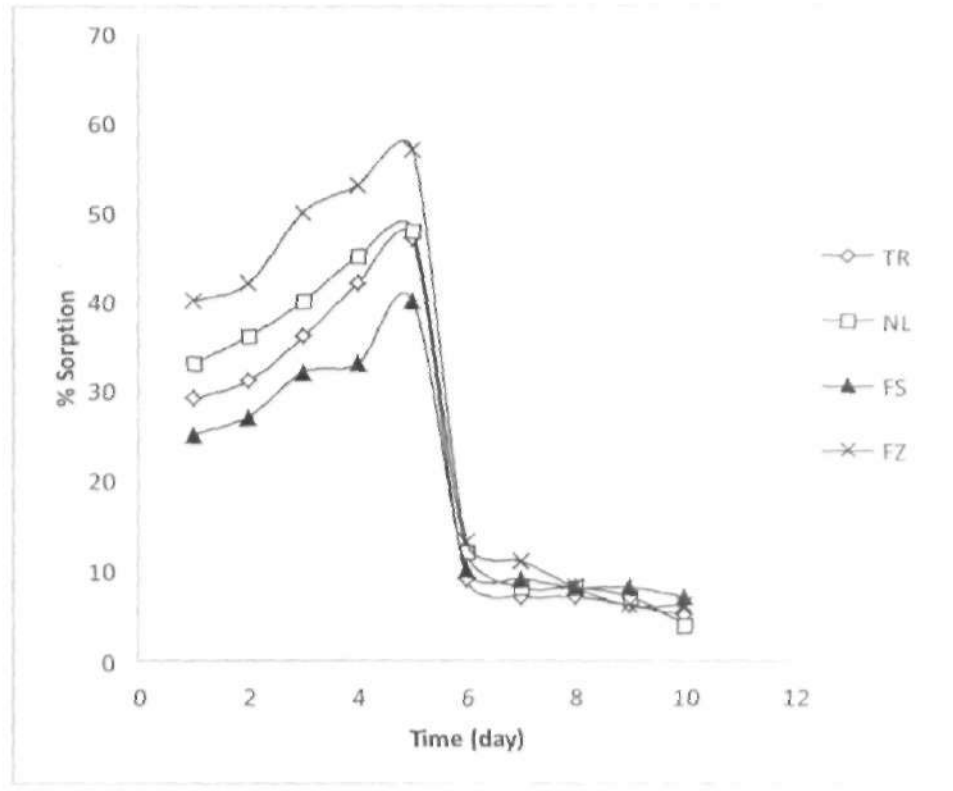


Figure 4.15: Variation of %sorption of water with time for TR, NL, FS and FZ gum exudates

4.7 Rheological study

Rheology is defined as the study of the deformation and flow of materials. In this study, the effect of concentration, pH, electrolytes, temperature and speed of rotation on the viscosity of TR, NL, FS and FZ gum exudates were studied using a viscometer.

Figure 4.16 shows plots for the variation of viscosity of TR, NL, FS and FZ gums with pH. From the Figure, it is evident that the viscosity of the various gums increases linearly with increase in pH. The increase of viscosity with temperature can be attributed to a decrease in the degree of association of the gum particles due to electrostatic repulsion between the gum particles.

4.7.1 Intrinsic viscosity

The intrinsic viscosity [η] is a measure of the hydrodynamic volume occupied by a macromolecule and is closely related to the size and conformation of the macromolecular chains in a particular solvent (Higiro *et al.*, 2007). It has been found that for a macromolecule, such as gum, several viscosity terms can be outlined. These include relative viscosity, specific viscosity and intrinsic viscosity. These viscosity terms are related according to the following equations,

$$Relative\ viscosity: \eta_{rel} = \frac{t - t_0}{t_0} \qquad 4.4$$

$$Specific\ viscosity: \eta_{sp} = \eta_{rel} - 1 \qquad 4.5$$

$$Intrinsic\ viscosity: [\eta] = \lim_{c \to 0} \frac{\eta_{sp}}{C} \qquad 4.6$$

Equation 4.6 reveals that the intrinsic viscosity of a macromolecule can be obtained by measuring specific viscosities at different concentrations at the same shear rate, and extrapolating specific viscosity to infinite dilution. This can be achieved by using a linear regression called the graphic double extrapolation procedure (GDEP). Equation 4.6 has also been

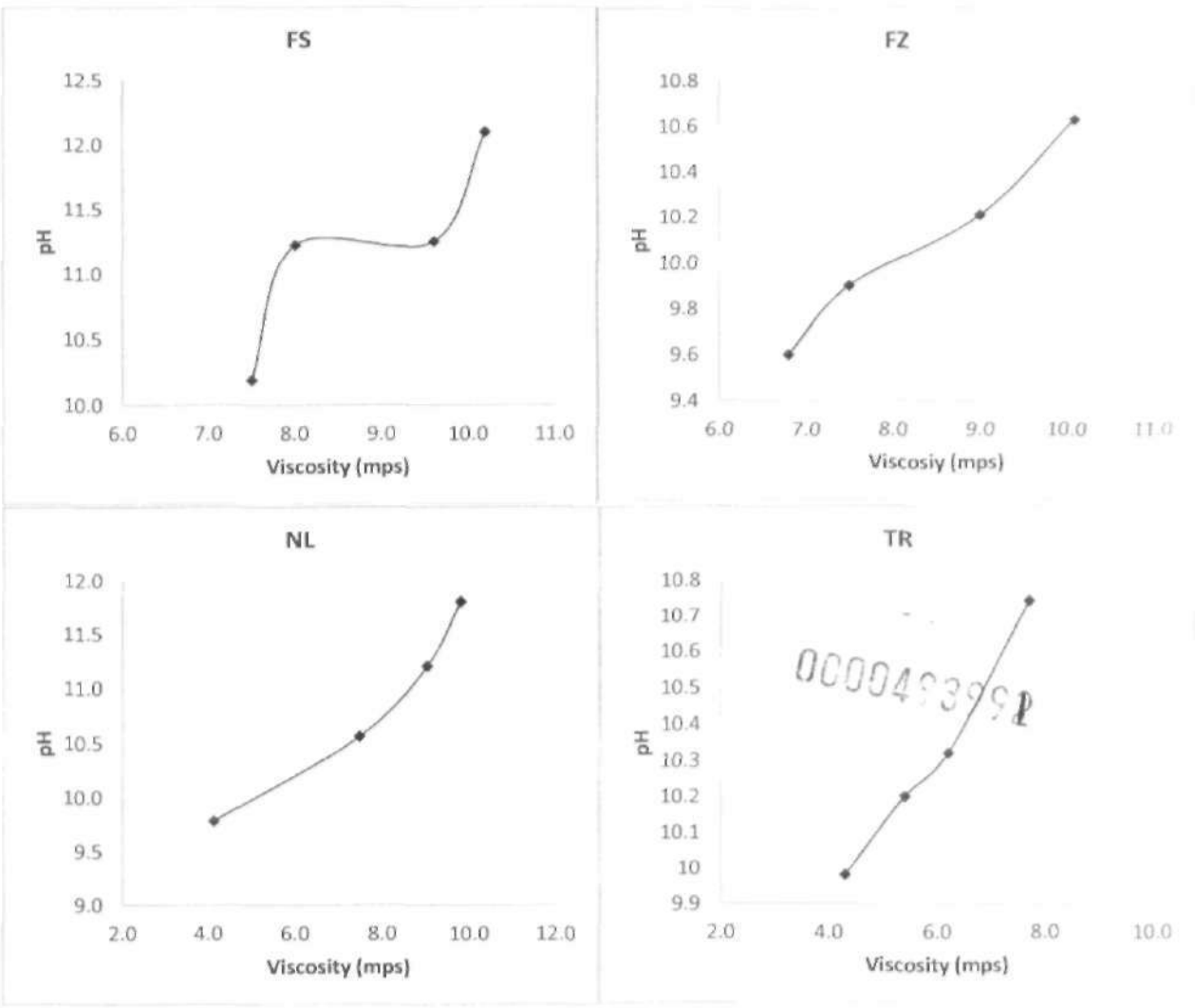


Figure 4.16: Variation of pH with the viscosity of FS, FZ, NL and TR gum exudates

found to be closely related to the Huggins equation and can be written as equation 4.7

$$\frac{\eta_{sp}}{C} = [\eta] + k'[\eta]^2 C \qquad 4.7$$

From equation 4.7, a plot of $\frac{\eta_{sp}}{C}$ versus C should be linear with intercept equals to the intrinsic viscosity. Figure 4.17 presents plots for the variation of $\frac{\eta_{sp}}{C}$ versus C (Huggins' plots). The intrinsic viscosities, Huggins constants and degree of linearity (R^2) were deduced from the plots and are presented in Table 4.12. The results obtained indicate that the values of R^2 were close to unity indicating excellent correlation and hence better fitness of the data to the Huggins model. The Huggins constants deduced from the plots were found to range from 0.061 to 0.084 while calculated values of $[\eta]$ were in the range of 6.13 to 8.57. According to Higiro *et al.* (2007), theoretical values of k' are expected to be between 0.3 and 0.8 and that values larger than unity imply polymer-polymer aggregation. Values from this study fall within the range, meaning molecular association was absent.

McMillan (1974) had reported that the intrinsic viscosity of a macromolecule can also be obtained from the Kraemer equation, which is expressed as equation 4.8

$$\frac{\eta_{rel}}{C} = [\eta] + k''[\eta]^2 C \qquad 4.8$$

where k'' is the Kraemer constant. From equation 4.8, $[\eta]$ is obtained by extrapolation of the plots of $\frac{\eta_{rel}}{C}$ versus C to zero concentration. Kraemer plots for TR, NL, FS and FZ gums are also presented in Figure 4.17 and Kraemer parameters deduced from the plots are also presented in Table 4.12. Correlation between intrinsic viscosities obtained from Huggins and Kraemer plots were excellent ($R^2 = 0.9987$) indicating that there is a strong agreement between Huggins and

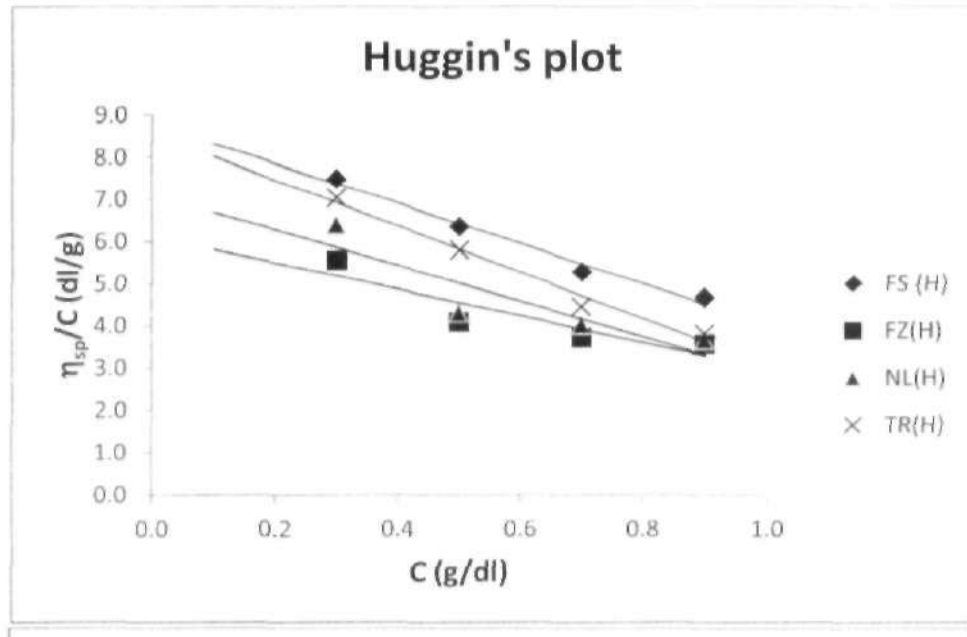


Figure 4.17: Huggins and Kraemer plots for TR, NL, FS and FZ

Table 4.12: Huggins and Kraemer parameters for TR, NL, FS and FZ gum exudates

	Huggins				Kraemer				
	slope	[η]	K'	R^2	slope	[η]	K''	R^2	K'+K''
TR	5.4945	8.57	0.0749	0.9807	3.5415	4.67	0.1625	0.9546	0.2374
NL	4.2345	7.13	0.0833	0.7923	3.0605	4.18	0.1756	0.8800	0.2589
FS	4.7635	8.81	0.0614	0.9830	3.4655	4.79	0.1513	0.9520	0.2127
FZ	3.1615	6.13	0.0840	0.8100	2.7040	3.85	0.1820	0.8931	0.2660

Kraemer plots. Kraemer constants were also found to display similar relationship with those of Huggins constant. Generally, the sum of the Huggins and Kraemer constants is expected to be equal to 0.5 ± 10 % and larger or smaller values are attributed to molecule association (Higiro *et al*, 2007). The results obtained from the present study indicate that the sum of the Huggins and Kraemer constants are within the range of 0.21 to 0.27. Therefore, molecular association is absent in the gums studied.

One of the major criticisms surrounding the use of Huggins and Kraemer constant in the determination of intrinsic viscosity is that in the models, intrinsic viscosity is deduced from the intercept of the respective plots. McMilan (1974) stated that the methods of determination of the intrinsic viscosity that were based on slopes of plots had higher correlation coefficients and lower standard errors, compared to those based on intercepts of plots. On the basis of such findings, Tanglertpaibul and Rao (1987) proposed the following equations,

$$\eta_{rel} = 1 + [\eta]C \qquad 4.9$$

$$\eta_{rel} = e^{C[\eta]} \qquad 4.10$$

$$\eta_{rel} = \frac{1}{1 - [\eta]C} \qquad 4.11$$

From equation 4.9, the intrinsic viscosity is the slope of a plot of η_{rel} versus C. From equation 4.10, the intrinsic viscosity is the slope of the plot of $\ln(\eta_{rel})$ versus C and from equation 4.11, the intrinsic viscosity is a slope obtained from the plot of $1 - 1/\eta_{rel}$ versus C. Figure 4.18 shows Tanglertpaibul and Rao plots based on equations 4.9 to 4.11. Values of intrinsic viscosity and degree of linearity deduced from the plots are presented in Table 4.13. The results obtained revealed high degree of linearity but values of $[\eta]$ were relatively low compared to those obtained from Higgins and Kraemer plots. However, good correlations were obtained for both

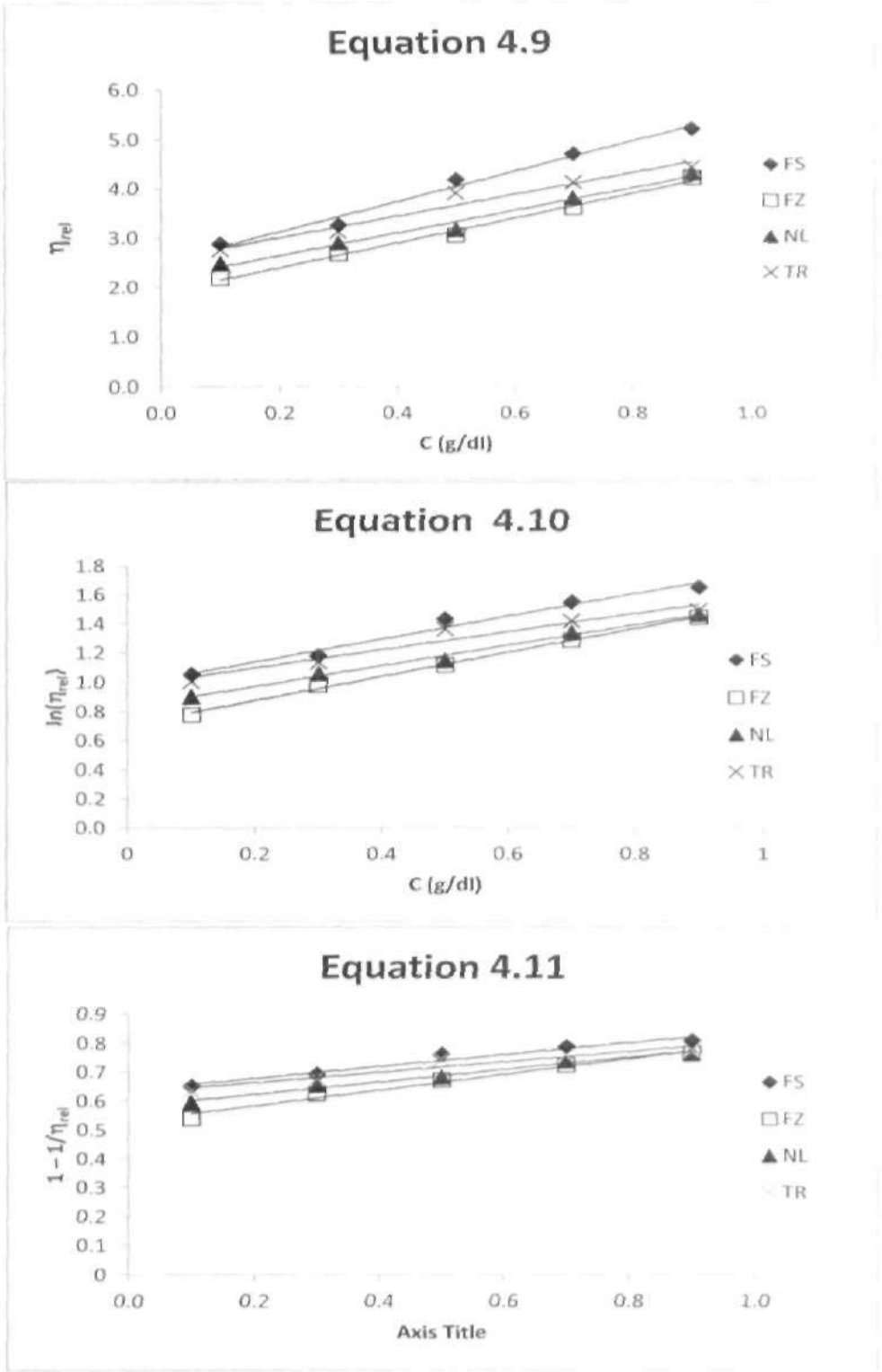


Figure 4.18: Tanglertpaibul and Rao plots for TR, NL, FS and FZ gum exudates

Table 4.13: Tanglertpaibul and Rao parameters for TR, NL, FS and FZ gum exudates

	Equation 4.9			Equation 4.10			Equation 4.11		
Gum	$[\eta]$	**intercept**	R^2	$[\eta]$	**intercept**	R^2	$[\eta]$	**intercept**	R^2
TR	2.194	2.5597	0.9584	0.6205	0.9704	0.943	0.1785	0.6282	0.9256
NL	2.2875	2.1771	0.9817	0.781	0.9807	0.9751	0.2135	0.5803	0.9867
FS	3.062	2.507	0.9845	0.812	0.713	0.9966	0.271	0.5293	0.9794
FZ	2.5075	1.8891	0.993	0.6935	0.8341	0.9905	0.2045	0.6376	0.956

the Huggin's, Kraemer's as well as the Tanglerpaibul and Rao plots. Hence the intrinsic viscosity of the various gums studied can be assumed to lie between the range of values obtained from Huggins/Kraemer plots to those obtained from Tanglertpaibul and Rao plots.

4.7.2 Molecular conformation, polymer interaction and coil overlap parameter

The power law equation (equation 4.11) can be used to study the molecular conformation and level of interaction between the molecules of the gums (Eddy *et al.*, 2012a)

$$\eta_{sp} = aC^b \qquad 4.11$$

where a and b are the power law constants. Equation 4.11 can be simplified by taking the logarithm of both sides of the equation to obtain equation 4.12.

$$\ln(\eta_{sp}) = \ln(a) + b\ln(C) \qquad 4.12$$

Figure 4.19 shows the power law plot for TR, NL, FS and FZ gum exudates while the constants deduced from the plots are presented in Table 4.14. The results obtained indicate high degree of linearity (values of R^2 ranged from 0.9180 to 0.9540) indicating that the power law model is obeyed by all the gum studied. Also, values of 'a' were found to range from 1.1121 to 1.4184 while those of 'b' ranged from 0.3201 to 0.4383. It has been found that the value of 'b' greater than unity is associated with random coil conformation while the value of 'b' less than unity is associated with rod like conformation. From the results of the present study, it can be stated that the studied gums are more rod like.

In dilute solutions, the individual polymer coils are separated from each other and are free to move independently. However, with increasing concentrations, the coil starts to overlap and interpenetrate one another. The transition from dilute solutions to concentrated solutions is usually accompanied by a pronounced change in the concentration dependence of solution viscosity (Morris *et al*, 1981; Khouryieh *et al*, 2007). The concentration that corresponds to the

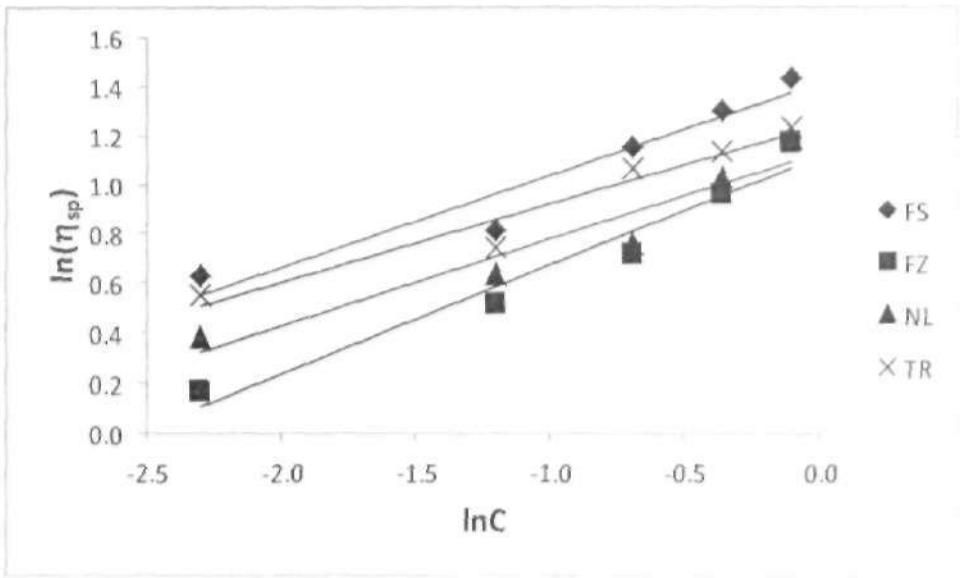


Figure 4.19: Variation of $\ln(\eta_{sp})$ with ln(C) for TR, NL, FS and FZ gum exudates

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Table 4.14: Power law constants for TR, NL, FS and FZ gum exudates

Gum	b	a	R^2
TR	0.3201	1.2442	0.9478
NL	0.3521	1.1297	0.9150
FS	0.3774	1.4184	0.9282
FZ	0.4383	1.1121	0.954

change in the conformation of the polymer is called critical or coil overlap concentration (C*). Coil overlap parameter can be tested using the slopes obtained from the plot of logarithm of η_{sp} against C[η] as shown in Figure 4.20. In this study, the slopes of the logarithm plots were relatively low for both dilute and concentrated solutions (Table 4.15). The highest slope of 0.7449 was obtained for FZ gum in dilute solutions. In TR gum, the slope changed from 0.2855 to 0.4133; in NL gum, the slope changed from 0.6871 to 0.4323; in FS gum, the slope changed from 0.4620 to 0.4220 and for FZ gum, the change in slope was from 0.7449 to 0.2882. In TR, NL, FS and FZ gums. C* transition occurred at values of C[η] of 2.1471, 2.1472, 2.896 and 3.695 for TR, NL, FS and FZ gums. These values are slightly different compared to those expected for plant gums. Morris *et al*. (1981) reported that for most plant gums, the slope of double logarithm plots of η_{sp} against C[η] should be close to 1.4 in a dilute regime, whereas in a concentrated regime, the slope should increase to 3.3. However, decrease in slope was noticed for NL gum exudate while other gums exhibited an increase in slope. Deviations from the range proposed by Morris *et al*. (1981) is not strange since the same researchers also found that Guar gum exhibited a coil overlap parameter of 2.5 and the viscosity showed a higher dependence on the slope, which was recorded as 5.5 instead of 3.3.

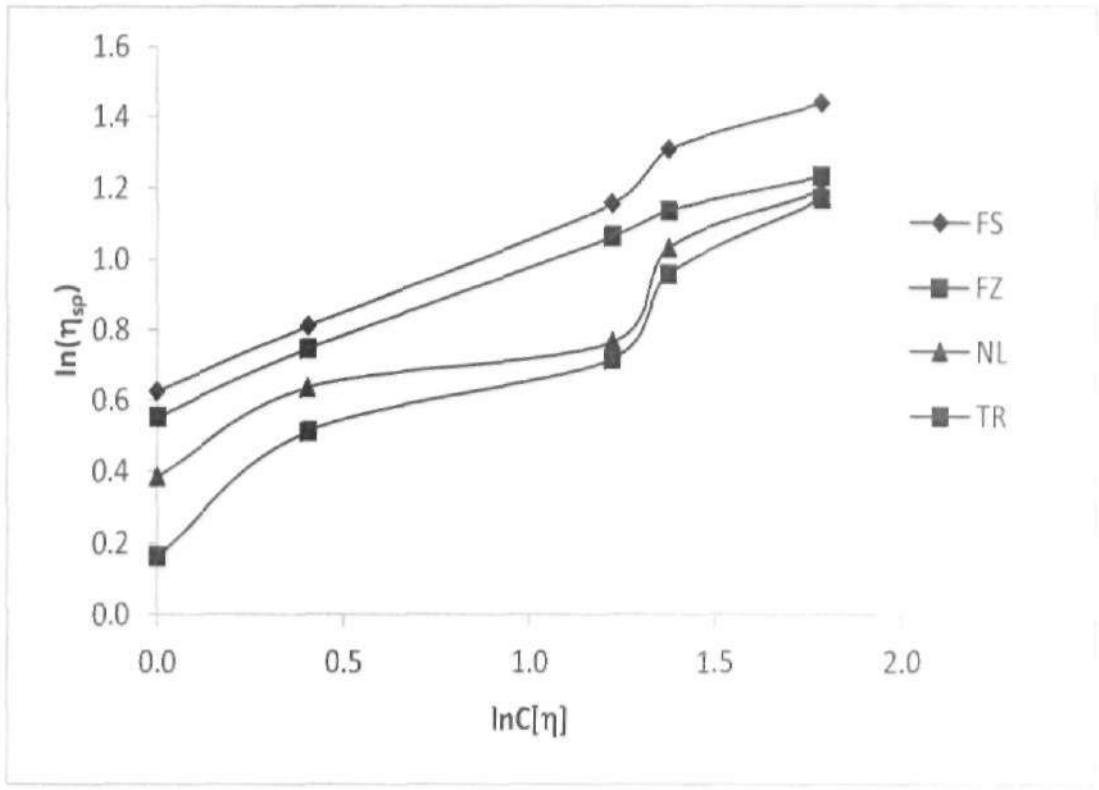


Figure 4.20: Variation of specific viscosity versus coil overlap parameters

Table 4.15: Slope and R^2 values for the logarithm plots of η versus $C[\eta]$ in dilute and concentrated regimes for TR, NL, FS and FZ gum exudates

Gum	Dilute regime		Concentrated regime		$C[\eta]$
	slope	R^2	slope	R^2	
TR	0.2855	0.9664	0.4133	0.9971	2.1471
NL	0.6871	0.6871	0.4323	0.9995	2.1471
FS	0.4620	0.9105	0.4220	0.8879	2.8960
FZ	0.7449	0.9437	0.2882	0.8642	3.6950

4.7.3 The effect of temperature and thermodynamic parameters on viscous flow

The effect of temperature on the viscous flow of the various gums was studied using the Arrhenius-Frenkel-Eyring equation (equation 4.13) (Menon, 2003)

$$\eta = A\exp\left(\frac{E_F}{RT}\right) \qquad 4.13$$

where A is the pre-exponential factor, E_F is the activation energy of flow, R is the universal gas constant and T is the absolute temperature in Kelvin. From the logarithm of both sides of equation 4.13, equation 4.14 is obtained.

$$ln(\eta) = lnA + \frac{E_F}{RT} \qquad 4.14$$

Equation 4.14 shows that a plot of $ln(\eta)$ versus 1/T should be linear with a slope and intercept equal to E_F/R and $(ln(\eta)$ respectively. Figure 4.21 shows the Arrhenius-Frenkel-Eyring plots for TR, NL, FS and FZ gum exudates. The Arrhenius-Frenkel-Eyring parameters deduced from the plots are presented in Table 4.16. The results obtained indicated excellent degree of linearity through R^2. Calculated values of E_F ranged from 12.42 to 17.93 J/mol. These values are within the range of values reported for some plant gums including *Albezia lebbeck* gum by de Paula *et al.* (2011), gum Arabic (15 kJ/mol: *Varfolomeeva et al*, 1980); *A. occidentale* gum (16.2 kJ/mol) by de Paula and Rodrigues (1995) and that of *A. macrocarpa* gum (16. 8 kJ/mol) by Silva *et al.* (1998). Generally, low activation energy of flow indicates few inter and intra-interactions between polysaccharide chains in the concentration range investigated while higher values of E_F indicate that the polymer is less sensitive to change in temperature (Shaikh *et al*, 2011; Nair *et al*, 2002). Hence there are few inter and intra molecular interactions in the gums studied.

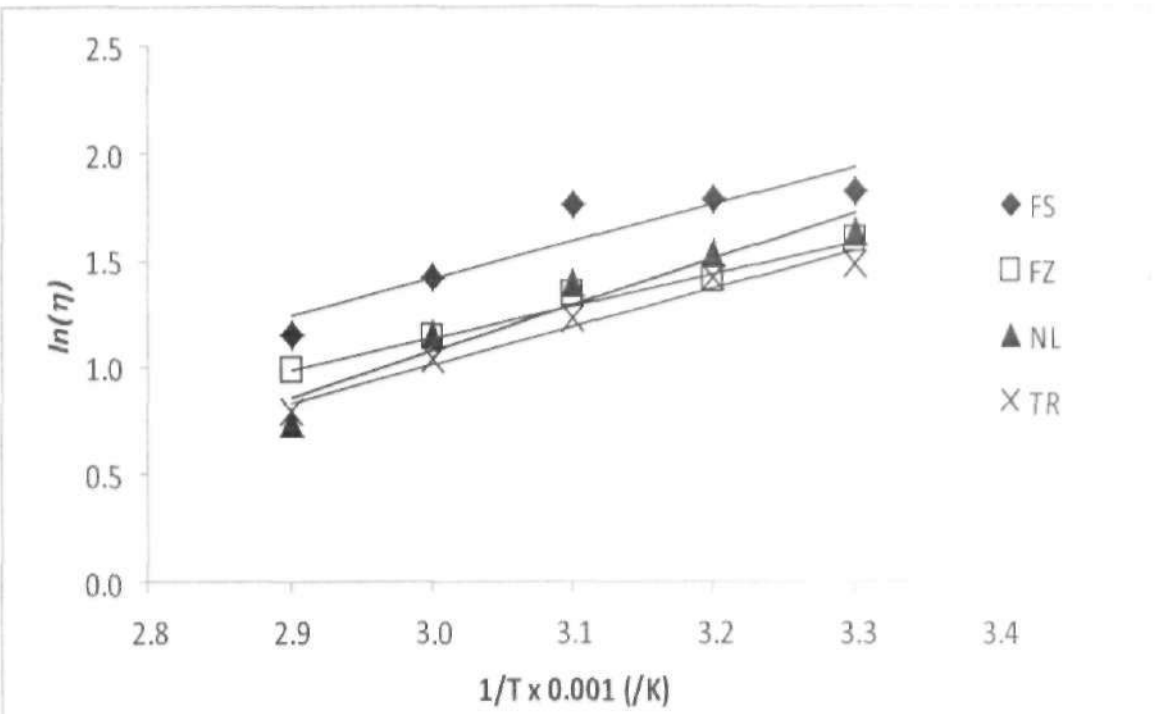


Figure 4.21: Variation of $ln(\eta)$ with 1/T for TR, NL, FS and FZ gum

Table 4.16: Arrhenius-Frenkel-Eyring parameters for TR, NL, FS and FZ gum exudates

Gum	slope	ln(A)	A	E_F (J/mol)	R^2
TR	1.769	-4.2969	0.0136	14.7075	0.9706
NL	2.157	-5.3991	0.0045	17.9333	0.9265
FS	1.745	-3.8205	0.0219	14.5079	0.8525
FZ	1.494	-3.3446	0.0353	12.4211	0.9829

Thermodynamic parameters for TR, NL, FS and FZ gums were studied using the Frenkel-Eyring transition state equation (Acevedo and Katz, 1990; Eissa, 2013)

$$\ln\left(\frac{\eta}{T}\right) = ln\left(\frac{R}{Nh}\right) + \frac{\Delta S_V}{R} - \frac{\Delta H_V}{RT} \qquad 4.15$$

where ΔS_V and ΔH_V are changes in entropy and enthalpy of flow. From equation 4.15, a plot of $\ln(\eta)$ versus 1/T is expected to be linear with slope and intercept equal to $\frac{\Delta H_V}{R}$ and $\left(lnA - \frac{\Delta S_V}{R}\right)$ respectively. Figure 4.22 shows the variation of $\ln\left(\frac{\eta}{T}\right)$ with 1/T for TR, NL, FS and FZ gum exudates. Values of thermodynamic parameters deduced from slopes and intercepts of the plots are presented in Table 4.17. The results obtained indicated a high degree of fitness for the plots indicating the application of equation 4.15 to the various gums. Changes in enthalpy and entropy of flow were found to be positive and negative indicating that the attainment of transition.

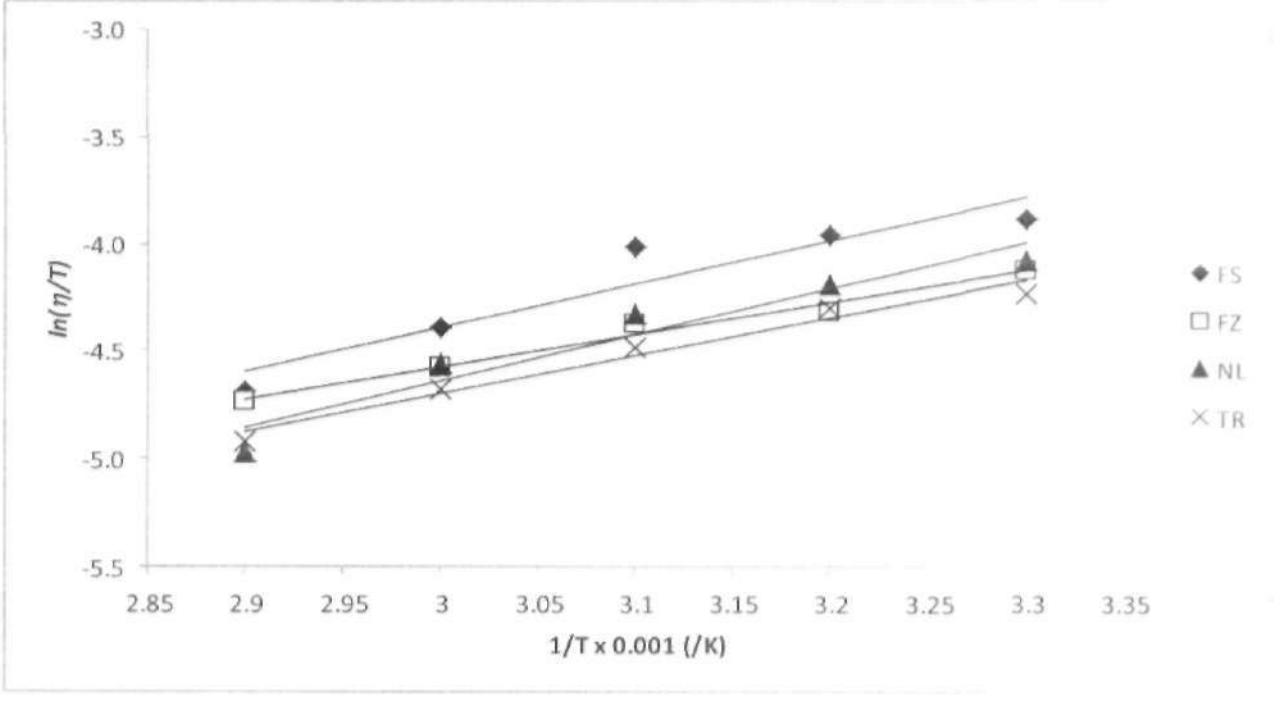


Figure 4.22: Variation of *ln(η/T)* with 1/T for TR, NL, FS and FZ gum

Table 4.17: Thermodynamic parameters of flow for TR, NL, FS and FZ gum exudates

Gum	slope	Intercept	ΔH_v (J/mol)	ln A	ΔS_v (J/mol)	ΔG_v (J/mol)	R^2
TR	1.7690	-10.011	14.71	2439896	-280.77	99.78	0.9706
NL	2.1570	-11.113	17.93	61423189	-289.93	105.78	0.9265
FS	2.0549	-10.558	17.08	26283150	-285.32	103.54	0.8905
FZ	1.4940	-9.0583	12.42	247983.1	-272.85	95.09	0.9829

state for viscous flow is accompanied by bond breaking. On the other hand, negative values of entropy change are associated with uncoiling and orientation of the polymer molecules and the system becomes more ordered in the course of flow (Ahmed *et al.*, 1994).

The free energy of activation of flow was calculated by substituting values of entropy and enthalpy changes into equation 4.16.

$$\Delta G_V = \Delta H_V - T\Delta S_V \qquad 4.16$$

Values of ΔG_V calculated from equation 4.16 are also presented in Table 4.17. ΔG_V values ranged from 99.78 to 105.78 J/mol. These values are relatively low and point towards the existence of few inter and intra molecular interactions.

4.7.4 Steady shear properties

Macromolecules such as exudate gums can be classified as Newtonian and non-Newtonian. Newtonian fluids exhibit constant viscosity at various shear rates. One of the methods that can be used to classify exudate gum as Newtonian or non-Newtonian involves the plotting of graphs of viscosity against speed of rotation. If a linear plot is obtained, then the gum is a Newtonian fluid and vice versa. Figure 4.23 shows plots for the variation of viscosity with speed of rotation for TR, NL, FS and FZ gums. The degree of linearity of the plots measured by R^2 values is excellent hence the various gums studied are Newtonian. The intercept of the plot is an index for measuring the yield stress of the gum (i.e the amount of force needed to be applied to the gum before it can flow) while the angle formed between the straight line and y-axis is an index that can be used to classify the gum as pseudoplastic (if the angle is less than 45°) or dilatant (if the angle is greater than 45°). Estimated values for the power law index and angles obtained through Figure 4.23 are presented in Table 4.18. From the results obtained, it can be

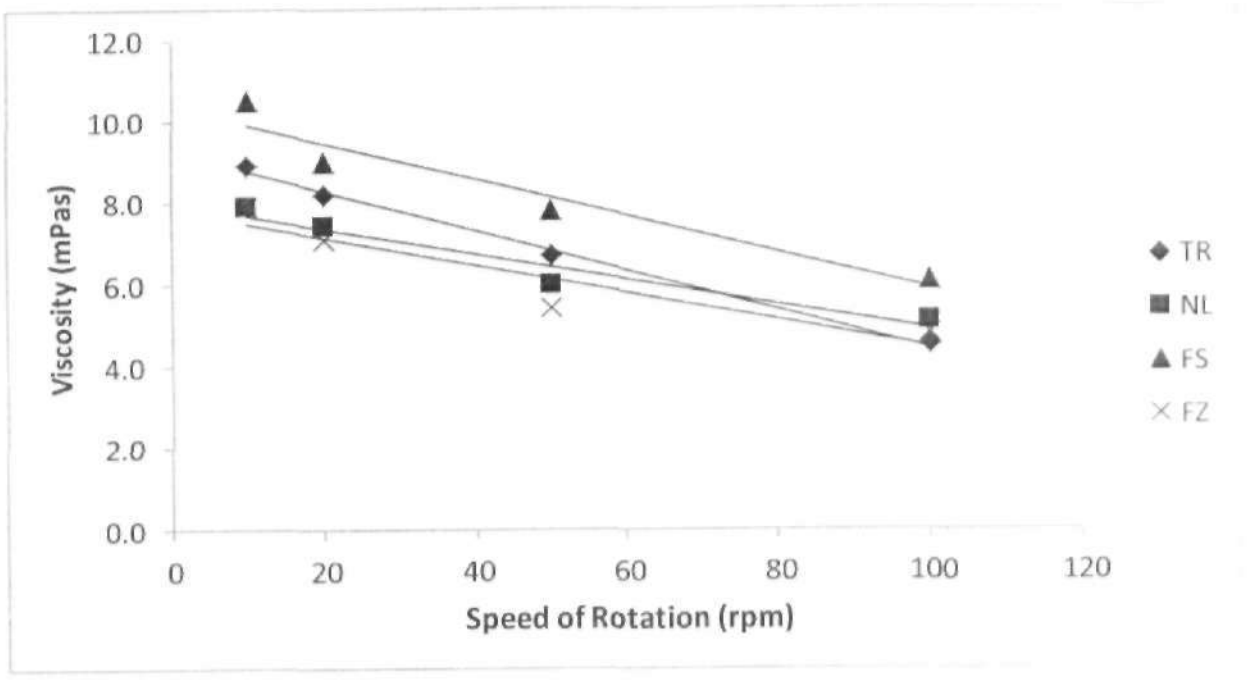


Figure 4.23: Variation of viscosity with speed of rotation for TR, NL, FS and FZ exudate gums

Table 4.18: Values of yield stress, tanθ and θ for TR, NL, FS and FZ

Gum	Yield stress	tanθ	θ	90-θ	R^2
TR	9.2378	0.0481	2.7538	87.25	0.9957
NL	7.7969	0.0308	1.7642	88.24	0.9420
FS	10.352	0.0445	2.5480	87.45	0.9317
FZ	7.7969	0.0333	1.9072	88.09	0.8662

power law index is greater than 45° hence the various gums studied are dilatant. The yield stress of the gums was highest for FS gum and least for NL and FZ gums which had similar values.

4.7.5 Effect of electrolyte on the viscosity of the gums

Examination of the results obtained for the composition of cations and fractions eluted from GCMS analysis of the various gums studied revealed that these gums are acid polysaccharides containing various metal ions as neutralized cations. This inference agrees with the findings of de Paula *et al*. (2001), who stated that exudate gums behave as polyelectrolytes and that the solution viscosity of the gums can be affected by addition of other electrolytes. In this study, the effects of strong electrolytes (i.e, monovalent: KCl, divalent: $CaCl_2$ and trivalent: $AlCl_3$) and a weak electrolytes (i.e urea) on the viscosity of the gums studied were investigated under constant electrolyte and gum concentration respectively.

Figures 4.24 to 4.27 respectively show the plots for the variation of viscosities of TR, NL, FS and FZ gums with concentrations of the gums in the presence of 1 % of KCl, $CaCl_2$, $AlCl_3$ and urea. The Figures reveal that the viscosity of TR gum is increased by the presence 1% of urea and KCl while the presence of 1% $AlCl_3$ and $CaCl_3$ decreases the viscosity of the gum. Similarly, 1% solutions of urea, KCl and $AlCl_3$ were found to increase the viscosity of NL gum. On the other hand, 1% of KCl, $AlCl_3$, $CaCl_3$ and urea increased the viscosities of FS and FZ gums. The observed decrease in viscosities of TR and NL gums may be due to the existence of fewer intermolecular interactions through charge screening and the contraction of the macromolecular interaction in the presence of the counter ions (de Paula *et al*, 2001). On the other hand, several reasons may be advanced for the increase in viscosity of the gums by the various electrolytes. Firstly, some metal ions such as Al^{3+} have a tendency of establishing a strong interaction with

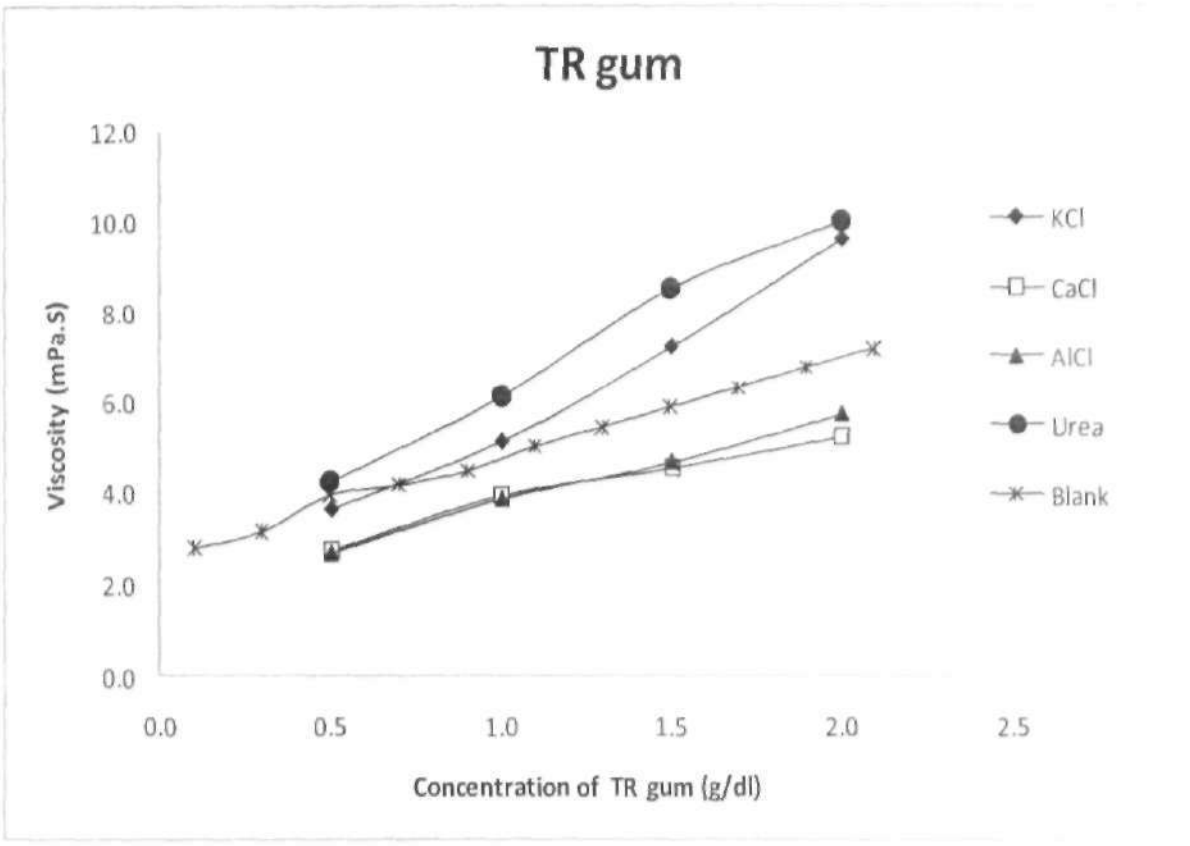
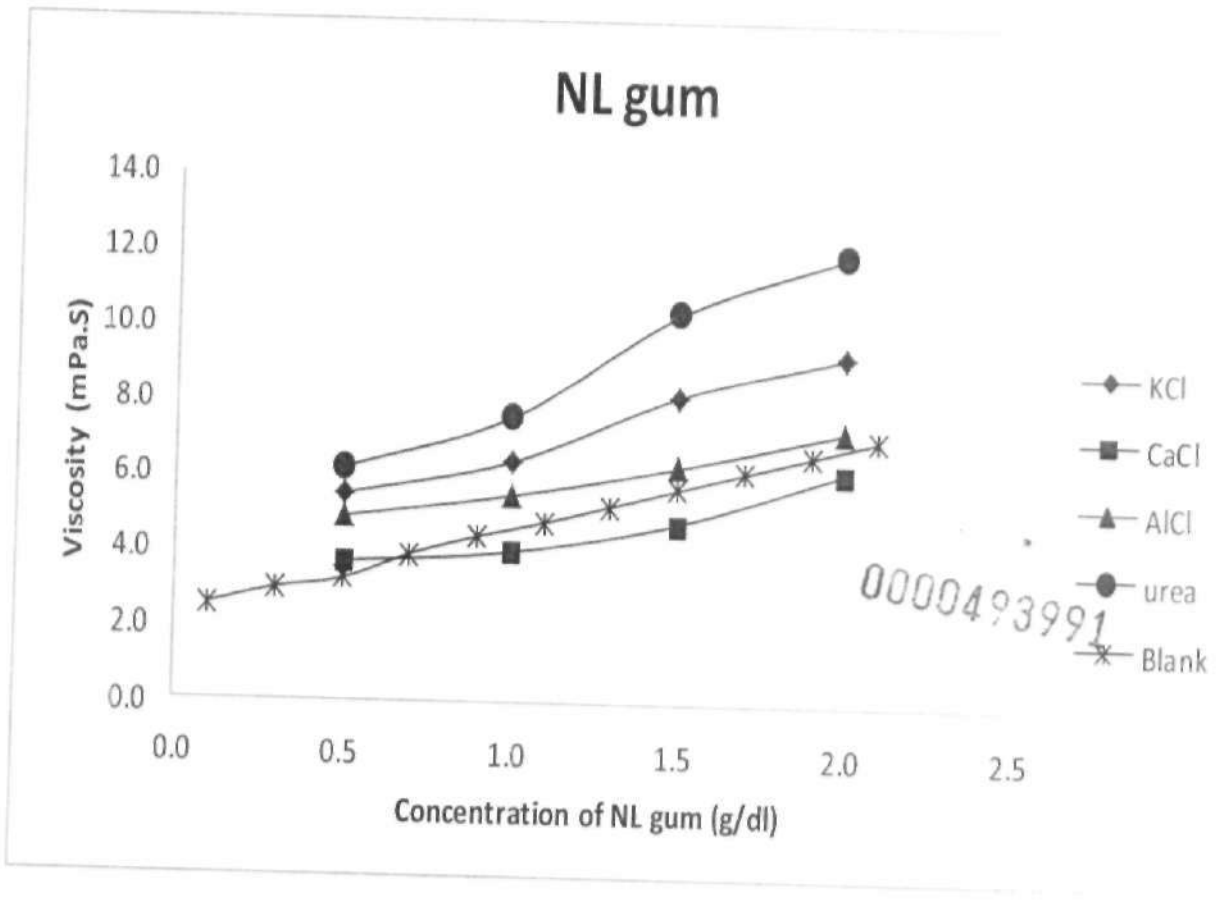


Figure 4.24: Variation of viscosity of TR gum with concentration in the presence of 1% KCl, $CaCl_2$, $AlCl_3$ and urea solution



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Figure 4.25: Variation of viscosity of NL gum with concentration in the presence of 1% KCl, $CaCl_2$, $AlCl_3$ and urea solution

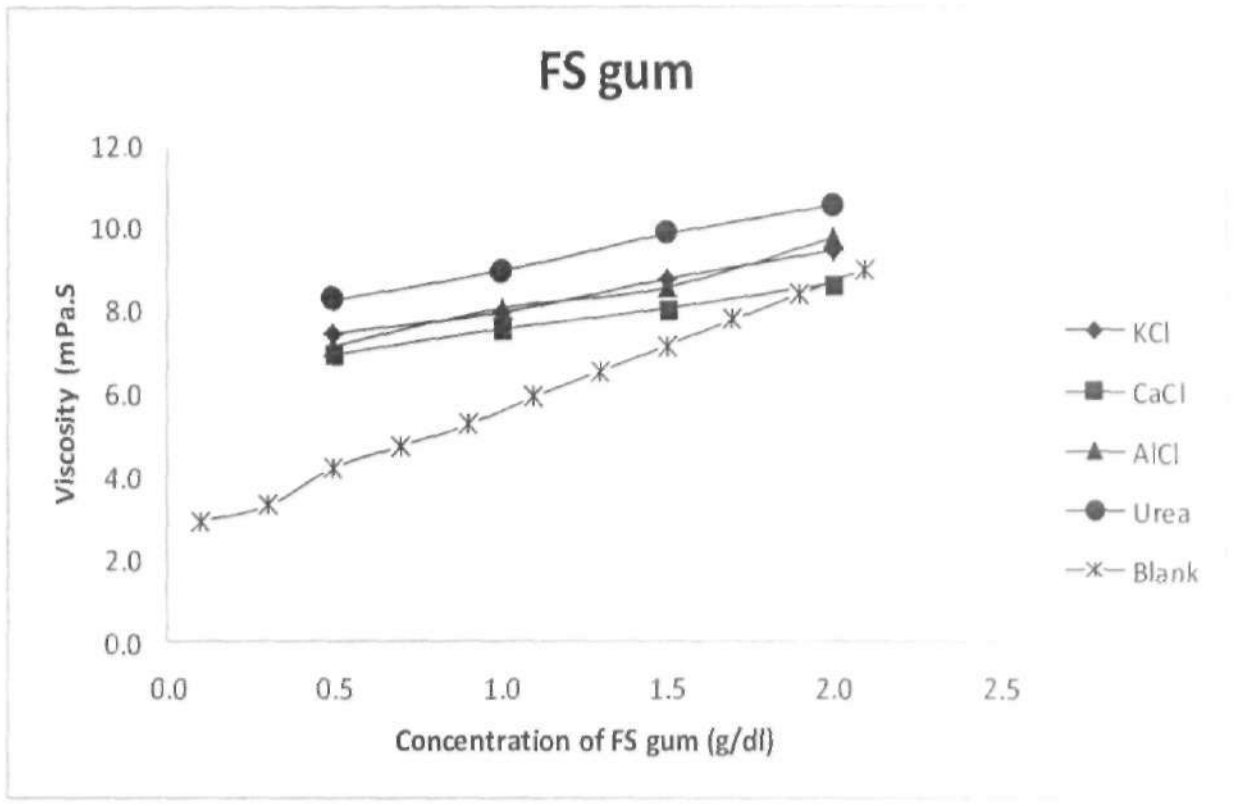


Figure 4.26: Variation of viscosity of FS gum with concentration in the presence of 1% KCl, $CaCl_2$, $AlCl_3$ and urea solution

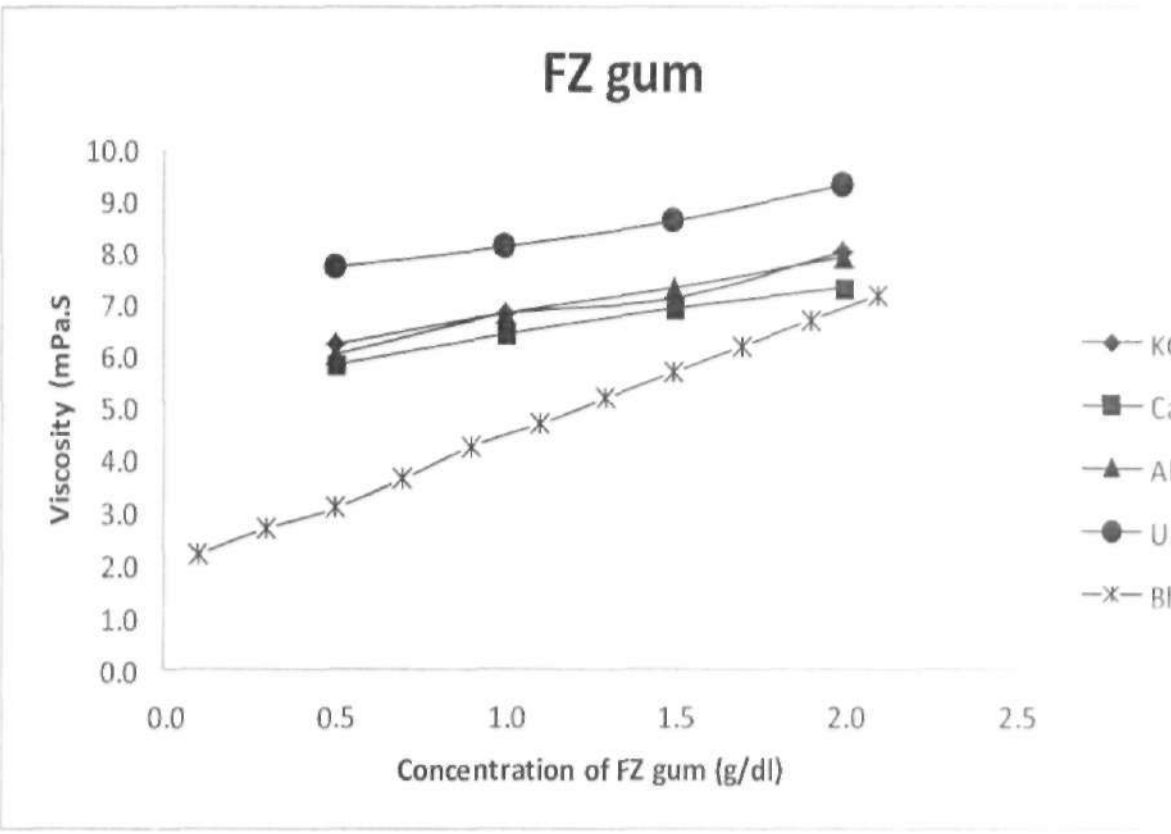


Figure 4.27: Variation of viscosity of FZ gum with concentration in the presence of 1% KCl, $CaCl_2$, $AlCl_3$ and urea solution

macromolecules through intermolecular crosslinking effect. Secondly, other metal ions such as K^+ and Ca^{2+} can alter the viscosity of a macromolecule through steric ability of gelling the gum and lastly the turbidity of dilute electrolyte increases with increase in the charge of the ions hence its viscosity can vary with the degree of charge interaction between the gum molecules (Ahmed *et al.*, 1994). Urea is an organic compound and it has been found that it has the tendency to form a porous framework and could alter the viscosity of a gum, depending on the strength of the framework.

The viscosity of many macro systems has been found to be strongly influenced by ionic strength. In order to investigate the effect of ionic strength on the viscosities of TR, NL, FS and FZ gums, plots of viscosity with log[concentration of salt] were obtained as shown in Figure 4.28. From Figure 4.28, it is evident that the viscosity of the various gums decreases with increase in ionic strength. The decrease in viscosity of the gums with increasing ionic strength may be attributed to the repulsions by the counter ions or neutralization by the added salt on the backbone of the macromolecule (Sanin, 2002). This effect may buildup charges on the macromolecules of the gums. According to Sanin (2002), this variation is associated with suppression of the charge atmosphere of the polyelectrolyte molecules, which become less rod like and hence more flexible.

According to Rey *et al.* (1996), the decrease in viscosity with ionic strength of can also be attributed to the compression of the electrical double layer at high ionic strengths, which will lead to particles and flocs assuming closer localities with each other. In addition, the surface polymers of gums may assume a coiled conformation rather than a stretched conformation when the ionic strength of the medium is high. This makes the flocs more compact. In addition, smaller amounts of polymers will be extending out into the solution since their charges are screened out.

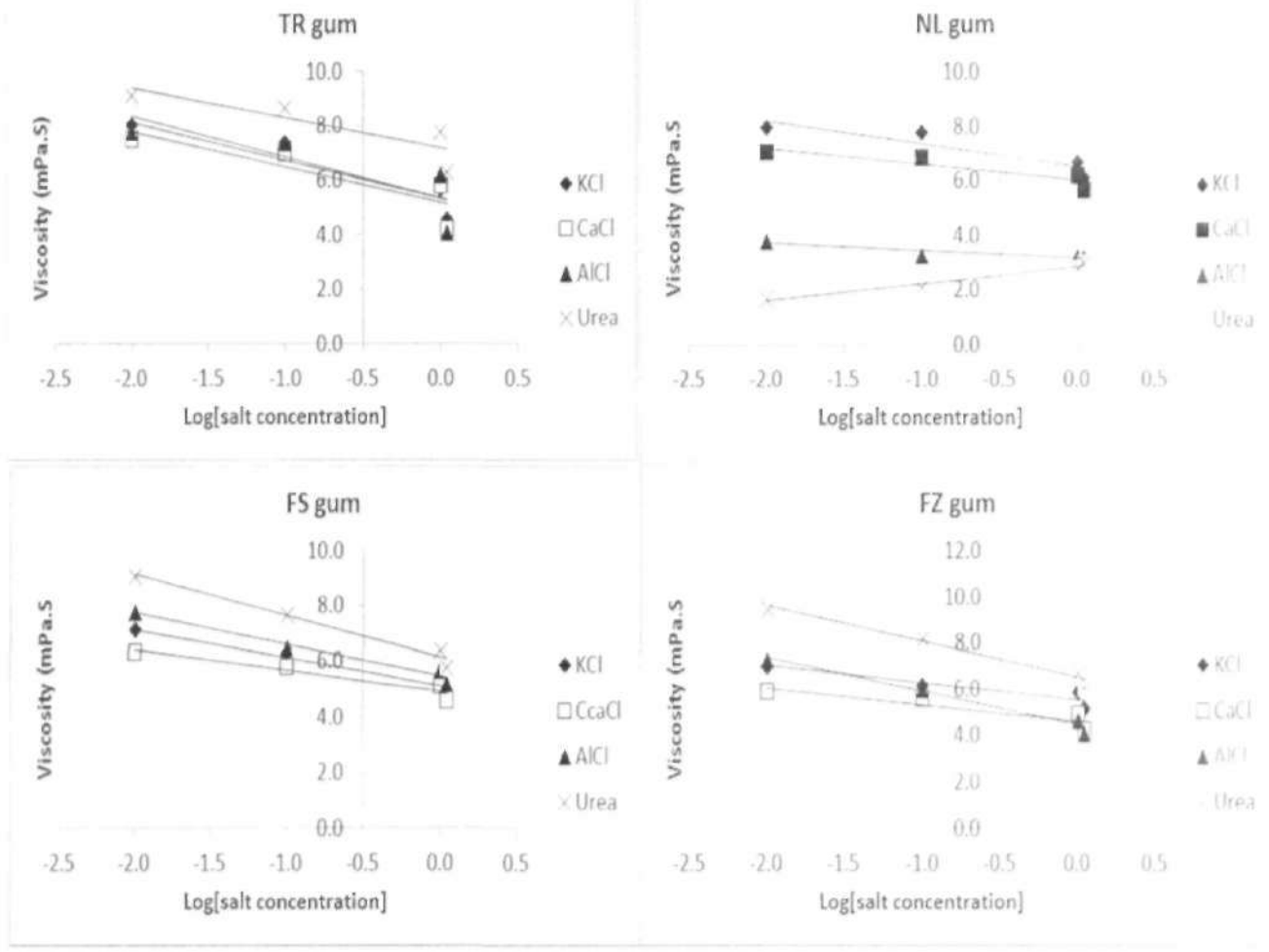


Figure 4.28: variation of viscosity with log[salt concentration] for TR, NL, FS and FZ gums

On the contrary, at low ionic strengths, the floc structure is expanded; the charged polymers are stretched far out into the solution since their charges are not screened out. Furthermore, when high salt concentrations are added, the bound water content of the gum decreases. Therefore, the mechanism of the effect of increasing ionic strength on the viscosity may also be through a decrease in the amount of bound water content which further causes a decrease in viscosity.

4.8 Corrosion inhibition study

An insight into the chemical composition of TR, NL, FS and FZ gums reveals that they may be good corrosion inhibitors because of the following reasons,

i They have aromatic, cyclic or long carbon chains

ii. They are rich in hetero atoms

iii. They contain long carbon chains

iv. They are less toxic

In view of the above, the corrosion inhibition potentials of the gums studied were investigated and are reported as below

4.8.1 Effect of concentration

Figures 4.29 to 4.32 show the variation of weight loss with time for the corrosion of aluminium in 0.1 M HCl containing various concentrations of TR, NL, FS and FZ gums inhibitors at 303 and 333 K. From the figures, it is evident that the weight loss of aluminium increases with increase in the period of contact and with increasing temperature indicating that the rate of corrosion of aluminium in solution of HCl increases with increase in the period of contact and with increase in temperature. It is also obvious from the figures that the weight loss of aluminium in the presence of various concentrations of the inhibitors are lower than the corresponding weight loss.

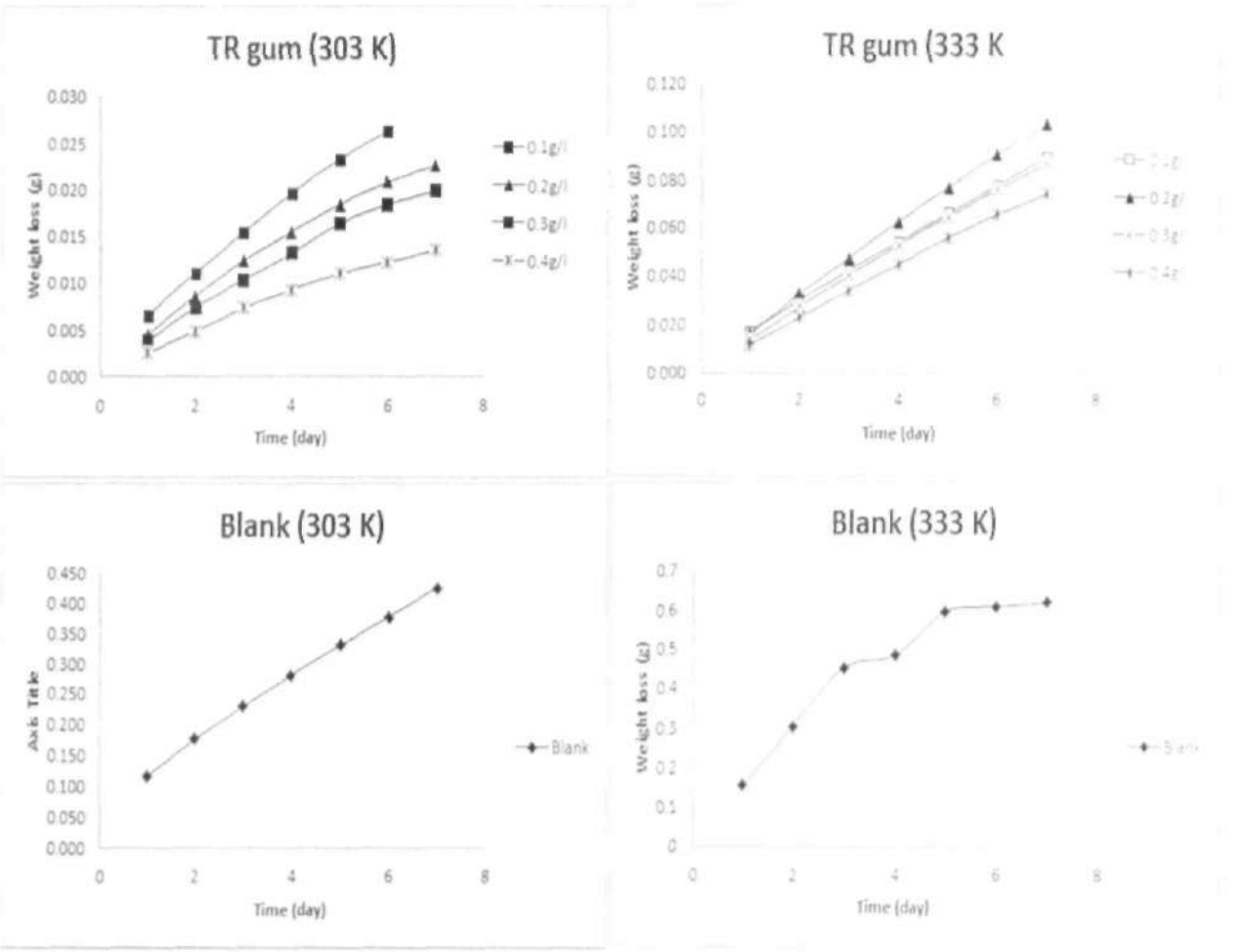


Figure 4.29: Variation of weight loss with time for the corrosion of aluminium in 0.1 M HCl containing various concentrations of TR gum

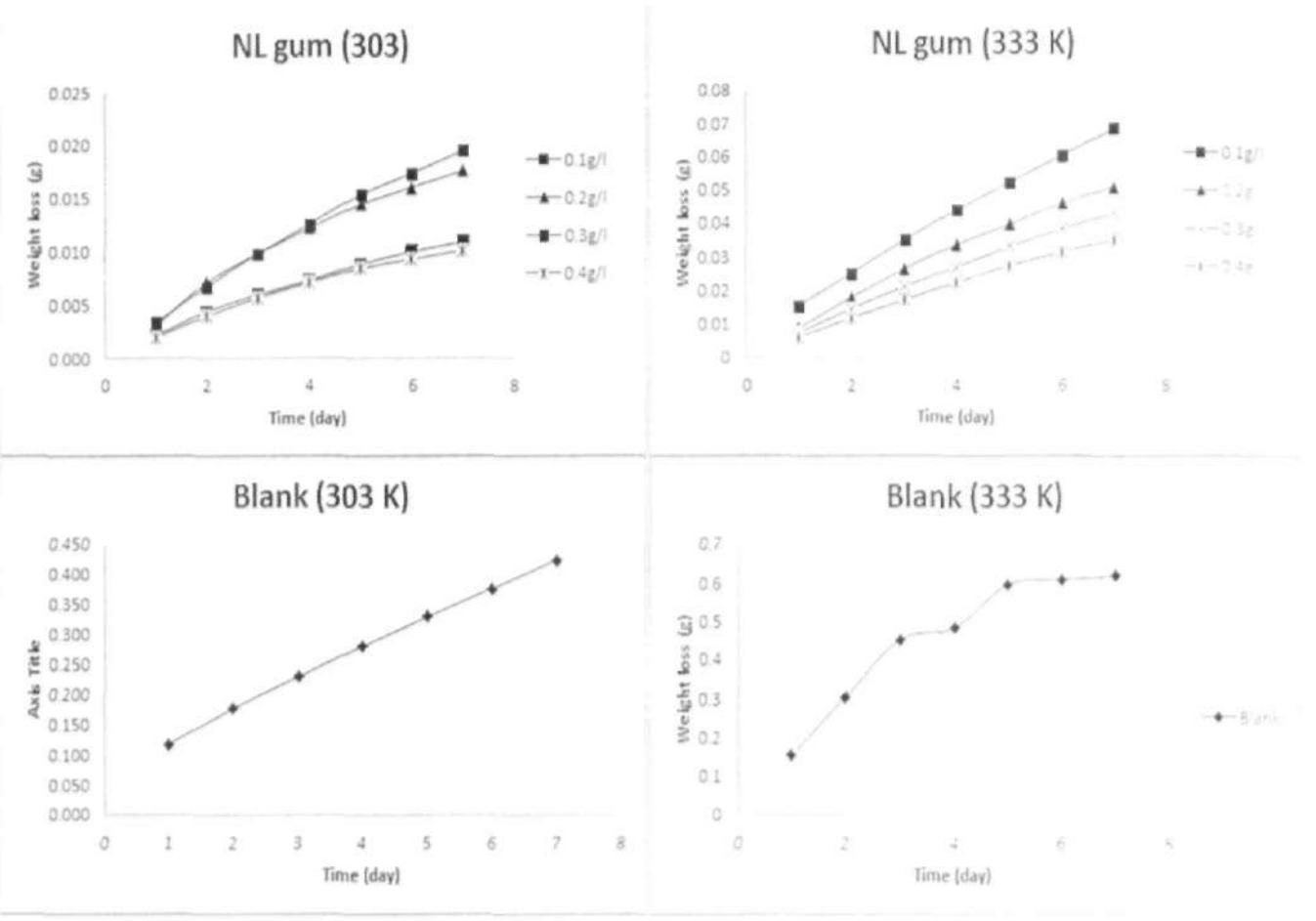


Figure 4.30: Variation of weight loss with time for the corrosion of aluminium in 0.1 M HCl containing various concentrations of NL gum

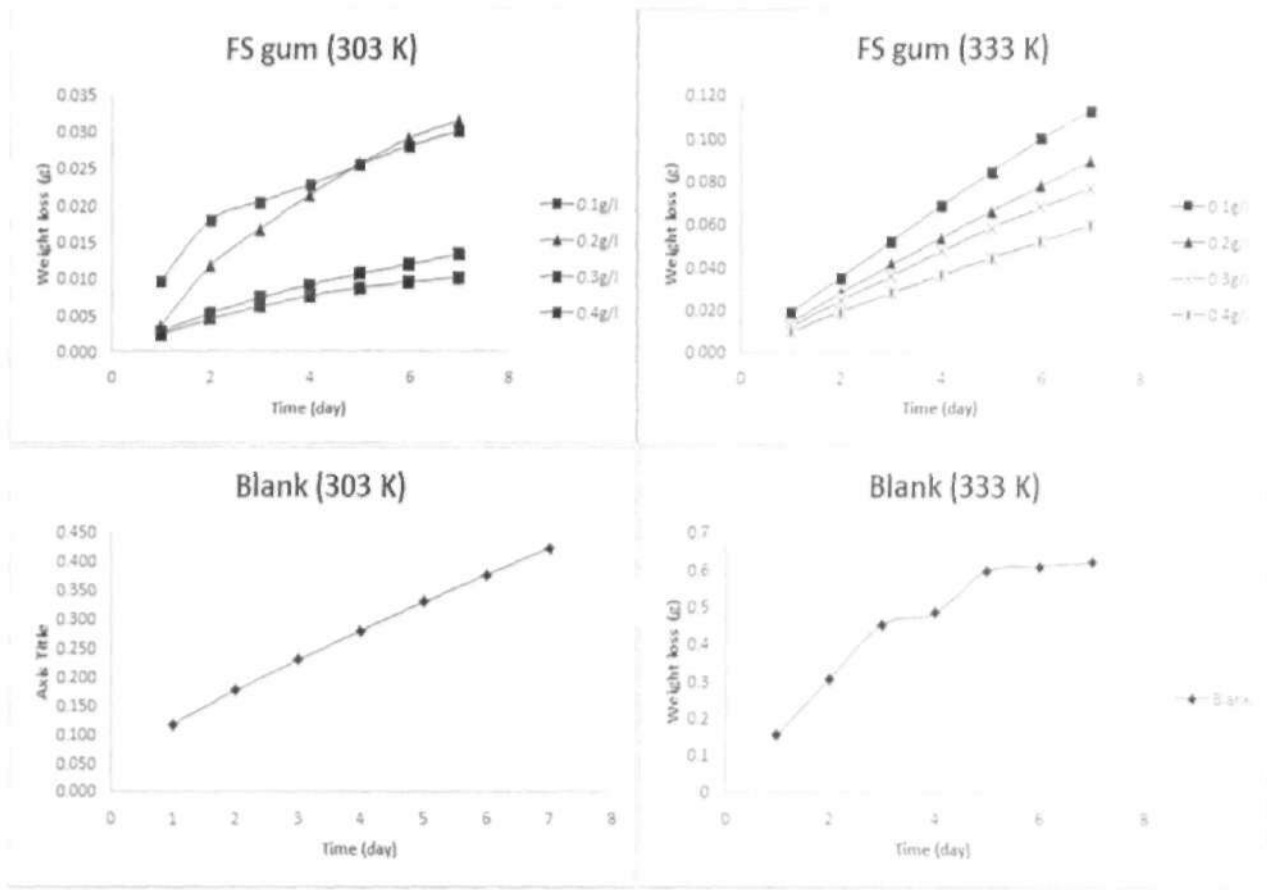


Figure 4.31: Variation of weight loss with time for the corrosion of aluminium in 0.1 M HCl containing various concentrations of FS gum

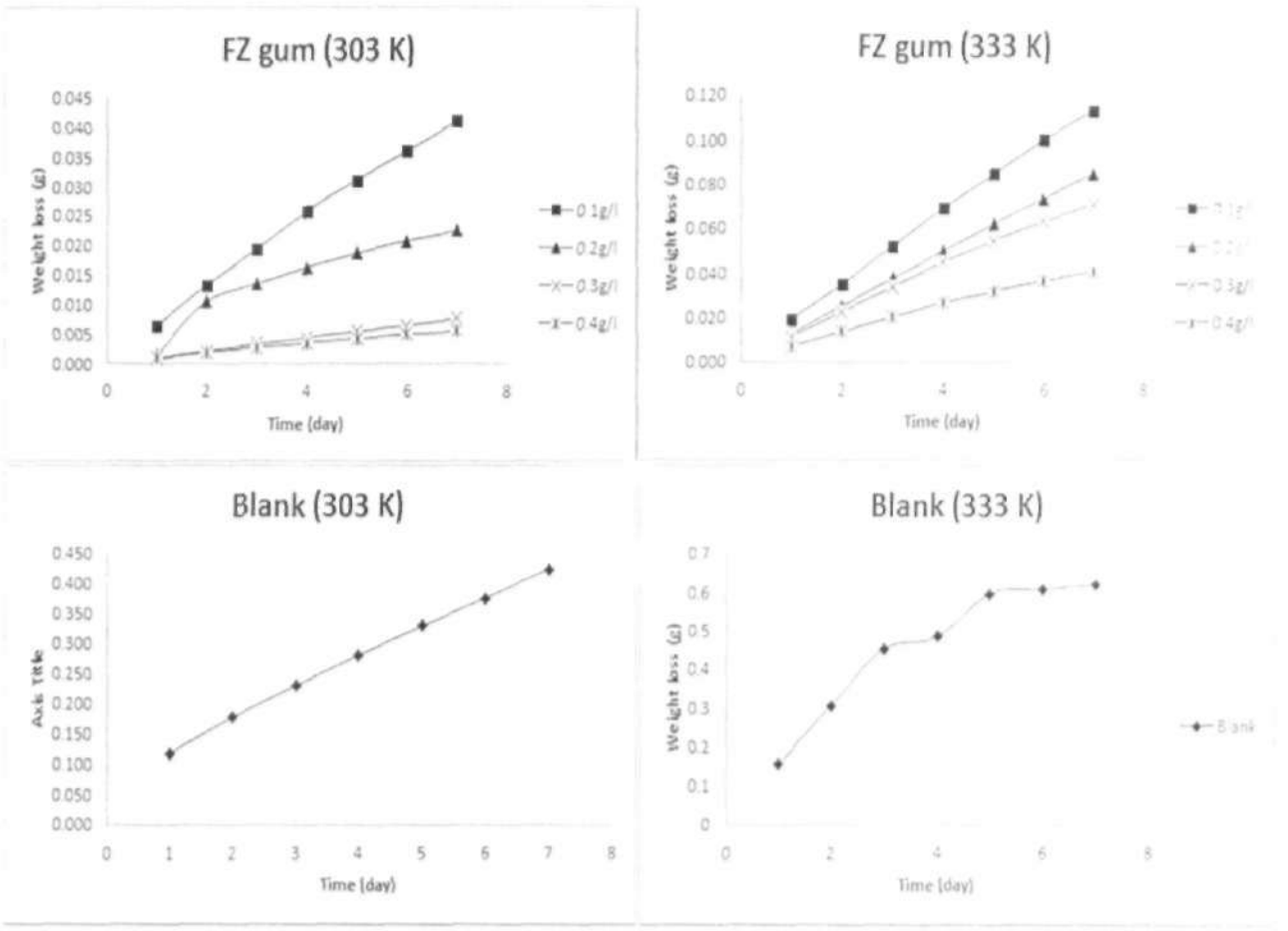


Figure 4.32: Variation of weight loss with time for the corrosion of aluminium in 0.1 M HCl containing various concentrations of FZ gum

obtained for the blank indicating that the various gums studied inhibited the corrosion of aluminium in solution of HCl. Also, the weight loss of aluminium was found to decrease with increase in the concentration of the respective inhibitors indicating that the inhibition efficiencies of the various gums increase with increasing concentration and decrease with increase in temperature. Hence TR, NL, FS and FZ gums are inhibitors for the corrosion of aluminium in solutions of HCl (Ameh and Eddy, 2013). The inhibition efficiencies of TR, NL, FS and FZ gums calculated using equation 3.9 are presented in Table 4.19. The results obtained indicated that the inhibition efficiencies of the gums increase with increase in concentration but decrease with increasing temperature hence the various gums are adsorption inhibitors and their adsorption on the surface of aluminium favours the mechanism of physical adsorption.

4.8.2 Effect of temperature

The effect of temperature on the corrosion of aluminium in the absence and presence of various concentrations of TR, NL, FS and FZ gums was studied using the logarithm form of the Arrhenius equation, which can be written as equation 4.17

$$\frac{CR_2}{CR_1} \quad \frac{E_a}{2.303RT}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad 4.17$$

where CR_1 and CR_2 are the corrosion rates of aluminium at temperatures, T_1 and T_2 respectively ($T_1<T_2$), E_a is the activation energy and R is the universal gas constant. Calculated values of E_a are recorded in Table 4.19. E_a values ranged from 32.17 to 47.86 kJ/mol, 29.96 to 38.94 kJ/mol, 29.17 to 49.61 kJ/mol and from 28.60 to 62.79 kJ/mol for TR, NL, FS and FZ gums. These values are less than the threshold values expected for the mechanism of chemical adsorption (80kJ/mol) hence the adsorption of the various gums on aluminium surface is

Table 4.19: Corrosion rates of aluminium, inhibition efficiencies of gums, activation energy and heat of absorption for the inhibition of the corrosion of aluminium by TR, NL, FS and FZ gums

System	CR (303 K)	CR (333 K)	% I (303 K)	% I (333 K)	E_a (kJ/mol)	Q_{abs} (kJ/mol)
Blank	0.00013	0.000123	-	-	1.55	
0.5 g/l TR gum	8.4E-06	2.65E-05	91.62	78.40	32.17	-23.13
1.0 g/l TR gum	6.7E-06	3.06E-05	93.34	75.11	42.53	-32.21
1.5 g/l TR gum	5.9E-06	2.58E-05	94.14	79.01	41.31	-30.44
2.0 g/l TR gum	4E-06	2.21E-05	96.03	82.03	47.86	-34.98
0.5 g/l NL gum	5.74E-06	2.03E-05	94.29	83.46	35.37	-24.87
1.0 g/l NL gum	5.18E-06	1.51E-05	94.85	87.70	29.96	-19.91
1.5 g/l NL gum	3.21E-06	1.29E-05	96.80	89.54	38.94	-26.48
2.0 g/l NL gum	2.98E-06	1.04E-05	97.04	91.50	34.99	-23.36
0.5 g/l FS gum	8.9E-06	3.36E-05	91.15	72.69	37.20	-28.38
1.0 g/l FS gum	9.35E-06	2.65E-05	90.71	78.43	29.17	-20.72
1.5 g/l FS gum	3.96E-06	2.29E-05	96.06	81.36	49.13	-36.08
2.0 g/l FS gum	3.01E-06	1.77E-05	97.01	85.57	49.60	-35.65
0.5 g/l FZ gum	1.21E-05	3.36E-05	87.93	72.69	28.60	-21.12
1.0 g/l FZ gum	6.64E-06	2.52E-05	93.40	79.52	37.34	-27.13
1.5 g/l FZ gum	2.23E-06	2.1E-05	97.78	82.88	62.79	-46.32
2.0 g/l FZ gum	1.61E-06	1.21E-05	98.40	90.17	56.47	-39.91

consistent with the mechanism of physical adsorption. The activation energies were also found to increase with increase in the concentration of the inhibitors (in most cases) indicating increasing strength of retardation of the corrosion of aluminium with increase in the concentration of the gums. The activation energy for the blank was significantly lower than those obtained for systems containing the respective inhibitors, which also indicates that the corrosion of aluminium is retarded by the presence of the inhibitors.

4.8.3 Thermodynamic/adsorption considerations

The heat of absorption of the inhibitors on the surface of aluminium was estimated using equation 4.18

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] x\left(\frac{T_1 T_2}{T_2 - T_1}\right) kJmol^{-1} \qquad 4.18$$

where Q_{ads} is the heat of absorption, R is the gas constant and θ_1 and θ_2 are the degrees of absorption of the inhibitor at temperatures, T_1 and T_2 respectively. Calculated values of Q_{ads} are also presented in Table 4.19. From the results obtained, the values are negative indicating that the inhibition of the corrosion of aluminium in solutions of HCl by TR, NL, FS and FZ gums is exothermic.

The adsorption characteristics of the inhibitors was studied by fitting data obtained for the degree of surface coverage into different adsorption isotherms including Langmuir, Freundlich, Temkin, El awardy, Flory Huggins and Brokris Swinkel adsorption isotherms. The tests revealed that the adsorption of TR, NL, FS and FZ gums best fitted the Langmuir adsorption isotherm, which can be expressed as equations 4.19 and 4.20

$$\frac{C}{\theta} = C + \frac{1}{b_{ads}} \qquad 4.19$$

$$log\left(\frac{C}{\theta}\right) = logC - logb_{ads} \qquad 4.20$$

where C is the concentration of the inhibitor in the bulk electrolyte, b is the adsorption equilibrium constant and θ is the degree of surface coverage of the inhibitor. Figure 4.33 shows the Langmuir plots for the adsorption of TR, NL, FS and FZ gums on aluminium surface. Adsorption parameters deduced from the plots are presented in Table 4.20. From the results obtained, calculated R^2 values and the slopes of the plots were very close to unity indicating the fitness of the data to the Langmuir adsorption model. Therefore, there is no interaction between the adsorbed molecules.

The equilibrium constant of adsorption obtained from the Langmuir adsorption plots is related to the free energy of adsorption according to equation 4.21

$$logb_{ads} = -\frac{1}{1.744}\left(\frac{\Delta G^0_{ads}}{2.303RT}\right) \qquad 4.21$$

Values of ΔG^0_{ads} calculated from equation 4.21 are also presented in Table 4.20. The free energies are negative and are within the range of values expected for the mechanism of physical adsorption hence the adsorption of TR, NL, FS and FZ gums on aluminium surface is spontaneous and supports the mechanism of physical adsorption.

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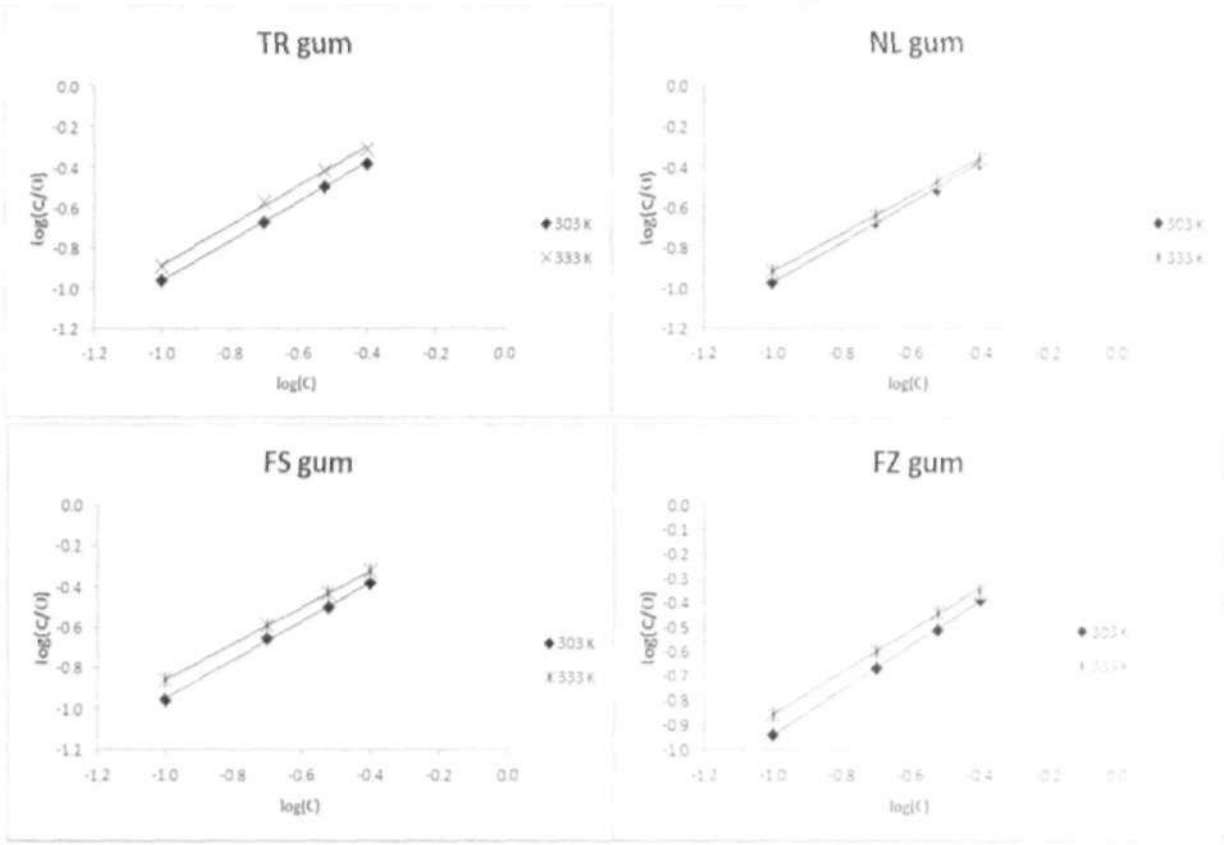


Figure 4.33: Langmuir isotherm for the adsorption of TR, NL, FS and FZ gums on aluminium surface

Table 4.20: Langmuir adsorption parameters for the adsorption of TR, NL, FS and FZ gums on aluminium surface

Inhibitor	T (K)	Slope	$logb_{ads}$	ΔG^{0}_{ads} (kJ/mol)	R^2
TR	**303 K**	0.9685	0.0073	-10.16	0.9999
	333 K	0.9691	0.0844	-10.61	0.9972
NL	**303 K**	0.9775	0.0042	-10.14	0.9999
	333 K	0.9347	0.0128	-10.19	1.0000
FS	**303 K**	0.9508	-0.0039	-10.10	0.9999
	333 K	0.8865	0.0260	-10.27	0.9998
FZ	**303 K**	0.9145	-0.0305	-09.94	0.9998
	333 K	0.8540	-0.0045	-10.09	0.9988

CHAPTER FIVE

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

5.1 Summary

GC-MS (Gas chromatography mass spectrometry), FTIR (fourier transformed infrared spectrometry), AAS (Atomic adsorption spectroscopy), physicochemical/rheological analysis and corrosion inhibition studies have been carried out on purified samples of *Trichilia roka* (TR), *Newbouldia laevis* (NL), *Ficus sycomorus* (FS) and *Fagara zanthoxyloides* (FZ) gum exudates. The gums were found to be mild acidic, ionic and soluble in water but insoluble in organic solvents. The colours of the gums were found to be whitish-yellow, yellowish-red, reddish-brown and black for TR, NL, FS and FZ gums respectively. They all had a bland taste except FZ gum which had a sour taste. NL and FS gums were odourless while TR and FZ gums had the floral and camphor-like odour. NL gum had the highest yield after purification while FZ gum had the least. On the other hand, TR gum had the highest capacity to absorb moisture while FZ gum had the least capacity.

Rheological properties of the gums have been adequately studied using Huggins, Kraemer, Arrhenius, Frenkel-Eyring, Tanglertpaibul and Rao parameters, power Law, and Newtonian theories. Plots were obtained from by each of these theories and master curves were also developed. From the results obtained, it was found that the gums are non-Newtonian and dilatant with characteristic shear thickening properties. The molecular conformations of the gums are more rod like than random like. The existence of few inter and intra-interactions between the molecules of the gums was also affirmed.

Polysaccharides, acetates, alcohol and other cosmetics, pharmaceutical and food viable chemicals were also found to be present in the gums. From FTIR analysis, the functional groups

associated with the gums were found to be diverse. From the AAS analysis, the trend for the concentration of elements in the various gum samples decreased in the order Ca>Na>Mg>K>Fe>Pb>Ni>Al>Zn>Mn>Cd.

The gums have also been found to be good corrosion inhibitors for aluminum in solutions of HCl. The inhibition process was found to be first order, exothermic, spontaneous and from calculated values of the activation energy (Ea), enthalpy of adsorption (Q_{ads}) and free energies of adsorption, the mechanism of physical adsorption (consistent with the Langmuir adsorption model) has been proposed for the various gums studied. The results obtained indicate that the inhibition efficiencies of the gums increase with increase in concentration but decrease with increasing temperature hence the various gums studied are adsorption inhibitors and their adsorption on the surface of aluminium favours the mechanism of physical adsorption.

5.2 Conclusions

From the results obtained from the present study, the following conclusions have been made:

i. TR, NL, FS and FZ gums are macromolecules whose viscosity depends on temperature, concentration, electrolytes and shear rate.

ii. The viscosity of the various gums studied can be adequately modeled using Kraemer, Huggins, power law, and Tanglerpaibul and Rao equations.

iii. The various gums displayed non-Newtonian features. They are dilatants having shear thickening properties.

iv. Physicochemical properties of the gums reveal that the gums may have some food value.

v. From GC-MS study, it is evident that the gums have some potential for use in the food, polymer and pharmaceutical industries as well as intermediates for other chemicals.

vi. The FTIR spectra of the gums closely resemble those of polysaccharides and show major adsorption bands typical of C=O, C-O, O-H and C-H vibrations. The spectra also reveal that the gums have dissociating carboxylic group.

vii. TR, NL, FS and FZ gums are good adsorption inhibitors for the corrosion of aluminium. The adsorption characteristics of the inhibitors favour physical adsorption and are consistent with Langmuir adsorption model. The gums are adsorbed on the surface of aluminium through some functional groups via the formation of multiple adsorption layers.

5.3 Recommendations

i. Studies on uses of gums from TR, NL, FS and FZ for pharmaceutical, cosmetics, polymer, food and other industries are hereby also recommended.

ii. The uses of the various gums as inhibitors for the corrosion of aluminium are advocate for this work. Extension of corrosion studies to other exudates gum is also recommended for the further study.

iii There is a need to invest in the plantations of gum producing trees since the gums are biodegradable and cost effective since most of the drug excipients used in Nigeria for example, methyl cellulose, magnesium stearate are costly.

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