Sudan University of Science and Technology

College of Graduate Studies

Thermodynamic Properties of *Azadirachta indica* (Neem) Gum

الخصائص الثيرموديناميكية لصمغ النيم

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of M.Sc in Chemistry

By

Abeer Abdallah Ali Salih

(B.Sc, Honors Chemistry)

Supervisor: Prof, Mohammed Elmubark Osman

June 2017

الإستهلال

قال تعالى:

﴿ وَقُل رَّبِّ زِدْنِي عِلْمًا ﴾

سورة طه، الآية (114)

صدق الله العظيم

Dedication

I dedicate this work to:

My Father,

Mother,

Brothers and Sisters.

ACKNOWLEDGEMENTS

First of all our Praise goes to Allah Almighty for giving me strength and helps to complete this work.

I would like to thank Prof, Mohamed Elmubark Osman for supervision and advice during the performance of this work. My appreciation extends to all teaching staff and to the Chemistry department, Sudan University of Science and Technology for their Technical Support.

Abstract

Some of the physiochemical properties of *Azadirachta indica* Gum (Neem) Gum were studied. They include: moisture, ash, nitrogen hence the protein, pH value and specific optical rotation.

The results show that: moisture content is 13.07%, ash content is 3.13%, Nitrogen content is 4.9%, protein is 32%, specific optical rotation is –65.5, and pH is 6.5.

The number molecular weight of the sample was estimated using osmotic pressure measurement and found to be 4.0×10^{6} g/mole.

Thermodynamic properties of *Azadirachta indica* (Neem) gum including, the partial specific volume of the solvent (water) and solute, and the volume fractions were estimated and found to be 1.000 $g^{-1}cm^{3}$, $0.947cm^{3}g^{-1}$ and 0.5136 $cm^{3}g^{-1,}$ 0.4863 $cm^{3}\,g^{-1}$respectively.

Chemical potential ranges of *Azadirachta indica* have been calculated from osmotic pressure measurement for different concentration of gum solution and were found to range from -0.444837×10^{-2} to -0.625968×10^{-2} Jg^{-1}, free energy of mixing between -0.12693×10^{-2} Jg^{-1} and -0.32145×10^{-2} Jg^{-1},and Second virial coefficient was $0.94x10^{-5}$.

مستخلص البحث

تمت في هذه الاطروحة دراسة الخواص الفيزيوكيميائية لصمغ النيم وتم تحديد محتوي كل من الرطوبة ،الرماد ،الرقم الهيدروجيني ،النيتروجين ،البروتين ،والدوران الضوئي النوعي .

الخواص الفيزيوكيميائية لصمغ النيم وجدت كالاتي (الرطوبة 13,07%،الرماد 3,13%،النتروجين 4,9%, الدوران الضوئي النوعي-65,5، والاس الهيدروجيني 6,5.

تم حساب الوزن الجزيئيئ عن طريق قياسات الضغط الاسموزي ووجد انه يساوي4×10^{6}جم/مول$^{-1}$

تم اجراء دراسة ثيرموديناميكية شملت الحجم النوعي الجزيئي، والكسر الحجمي للمذيب والصمغ التي وجدت كلاتي :1,000سم^{3} جم$^{-1}$، 0,947سم^{3} جم$^{-1}$، 0,5136سم^{3} جم$^{-1}$،0,4863سم^{3} جم$^{-1}$.

تم ايجاد الجهد الكيميائي -0,444837$\times10^{-2}$ الى -0,625968$\times10^{-2}$ جول.جم$^{-1}$ من قياسات الضغط الاسموزي لتراكيز مختلفة للمحاليل المائية للصمغ ثم حساب الطاقة الحرة للخليط -0,12693$\times10^{-2}$ الى

-0,32145$\times10^{-2}$جول.جم$^{-1}$ومعامل معدل طاقة الحركة الثاني 0,94$\times10^{-2}$.

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Chapter One

Introduction1

1.1 Gums

1.1.1 Definition of Gums

Gums are polysaccharides either hydrophobic or hydrophilic, of a high molecular weight, usually with colloidal properties, which in, an appropriate solvent or swelling agent produce gel, highly viscous suspension, or solutions at low dry, substance content (Anderson .al, 1968). Thus, the term gum is applied to a wide variety of substances of gummy characteristics and cannot be precisely defined. Hydrophobic substances which are often called gums are high molecular weight hydrocarbons and other substances which also considered petroleum products, rubbers, certain synthetic polymers, and the resinous saps which often exude from plants and which are sometimes tapped gum resin.

Most commonly, however, the term gum as technically employed in industry refers to plant polysaccharides or their derivatives which are dispersible in either cold or hot water to produce viscous solutions. Usage would classify as gums all polysaccharides or their derivatives which dispersed in water at

low, dry, substance content, swell to produce gels, highly viscous dispersions, or solutions.

1.1.2 Classification

It has been customary in the past to classify most of the gums as polysaccharides and to group them according to plant origin. Thus, the seaweed group comprise the extracts know as agar, alginates the tree exudates, and carrageenan; the tree exudates are gum Arabic, gum karaya, gum tragacanth, gum gatti, seed gums include locust bean and guar gum. Other gum like materials such as pectin and starch where treated as separate groups. While gelatin, being a protein was not included. In addition, synthetic gums such as cellulose derivatives which are carbohydrates gum, or for synthetic vinyl polymers such as poly vinyl pyroldinone (PVP) which form a completely new category. The use of botanical origin as a basis for the classification of important plant gums is valid and useful, since gums of similar origin and functionality, frequently, have similar properties and chemical structures, and can occasionally, be employed for the same purpose. Thus, locust been gum and guar gum, which are both derived from plant-seed sources, have the similar chemical structure of a neutral Glactomanans, and differ only in the ratio of Glactose and Mannose molecules. For a general classification to be useful, it should embrace all types of gums that are used in the

food industry, and it should leave for new gums that are certain to be developed in the future. Following this line of those it has been proposed that the following all inclusive classification composed of three main categories. Natural gums-those found in nature , modified natural or semi synthetic gums –those based on chemical modifications of a natural gum or gum like materials, synthetic gums –those produced by chemical synthesis. The specific gum comprising these categories is shown in Table 1.1. As a further aid to identification each category is desided into subgroups based, where possible, on the common origins, functions, or properties of particular gums.

Table 1.1 The Classification of Gums

Natural gums	**Modified (semi synthesis) gums**	**Synthetic gums**
Plant exudates: Arabic Tragacanth Karaya Ghatti	Cellulose derivatives: Carboxymethyl cellulose Methylethylpropyl cellulose Methyl ethyl cellulose Hydroxypropyl cellulose	Vinyl polymers: Polyvinylpyrrolidone (PVP) Polyvinyl alcohol(PVA) Carboxyvinyl polymer (carbopol)

Plant extracts: Pectin Arabinogalactan Plant seed flours: Locust bean Guar Psylium seed Quince seed Seaweed extracts: Agar Alginate Carageenan Furcellaran Cereal starches:	Low methoxy pectin Microbial fermentation gums: Dextran Xanthan gum Preglatinized starches Modified starches: Carboxymethyl starch Hydroxyethyl starch Hydroxypropyl starch	Ethylene oxide polymers : Polyox

Seed starches Com, Wheat Rice, Waxy maize Sorghum Waxy sorghum Tuber starch Potato Arrowroot Tapioca Animal: Gelatin Albumen Gasein Vegetable: Soy protein		

1.2*Azadirachta indica*Tree

1.2.1 Botanical Classfification

Kingdom: Plantae

Division: Magnoliophyta

Class: Magnoliopsida

Order: Sapindales

Family: Meliaceae

Genus: Azadirachta

Species: A. indica

Botanical Name: *Azadirachta indica*

Other Names of NeemTree: Miracle tree, Nimba, Arishtha, Margosa

Synonyms

Antelaeaazadirachta (L.)Adelb.

1.2.2 Definition

TheNeemtreis a tropical evergreen tree native to Indian sub-continent (Roxburgh, 1874);it has been used in Ayurvedic medicine for more than 4000 years due to its medicinal properties. Most of the plant parts such as fruits, seeds, leaves, bark and roots contain compounds with proven antiseptic, antiviral, antipyretic, anti-inflammatory, antiulcer and antifungal

uses. It has great potential in the fields of pest management, environment protection and medicine.Neemis a natural source of eco-friendly insecticides, pesticides and agrochemicals.The tree has adaptability to a wide range of climatic, topographic and edaphic factors. It thrives well in dry, stony shallow soils and even on soils having hard clay pan, at a shallow depth.Neemtree requires little water and plenty of sunlight (Sateesh, 1998). The tree grows naturally in areas where the rainfall is in the range of 450 to 1200 mm. However, it has been introduced successfully even in areas where the rainfall is as low as 150 to 250 mm.Neem grows on altitudes up to 1500 m (Jattan et al., 1995; Chari, 1996. It can grow well in wide temperature range of 0 to 49°C .It cannot withstand water-logged areas and poorly drained soils. The pH range for the growth of Neem tree lies in between 4 to 10.Neem trees have the ability to neutralize acidic soils by a unique property of calcium mining (Hegde, 1995).

Neem or Margosa is a botanical cousin of mahogany. It belongs to the family Meliaceae.The latinized name of Neem – *Azadirachta indica*– is derived from the Persian: Azad = Free, dirakht = Tree, i – Hind = of Indian.

Biologically active materials isolated from different parts of the plant include: azadirachtin, meliacin, gedunin, salanin, nimbin, valassin and many other derivatives of these principles. Meliacin

forms the bitter compnents of Neemseed oil; the seed also contain tignic acid (5-methyl-2-butanic acid) responsible for the distincitiveodour of the oil (Schmutterer, 1990; Uko and Kamalu, 2001; Lale, 2002). These compounds belong to natural products called triterpenoids (Limonoids). The active principles are slightly hydrophilic, but freely lipophilic and highly soluble in organic solvents like, hydrocarbon, alcohols, ketones and esters (Schmutterer and Singh, 1995).Therefore, this review will focus on the relevance ofNeemand its products in agriculture, industry, biomedicine and environment.

The Neem tree (*Azadirachta indica*A. Juss.) has been known as the wonder tree for centuries in the Indian subcontinent. It has become important in the global context today because it offers answers to the major concerns facing mankind. Neem Tree (*Azadirachta indica*) is versatile tree, it is considered to be one of the most promising trees of the 21 century. It has great potential in the pest management, environment protection and medicine. Also it has showing reappraise as potential fertilizer.

The history of the Neem tree is inextricably linked to the history of the Indian way of life. Although the antiquity of Neem is shrouded in the mists of time, this evergreen robust looking tree has long been cherished as a symbol of health in the country of its

origin. It has, for a very long time, been a friend and protector of the villager.(http://www.neemfoundation.org).

1.2.3 General Description

Neem is a fast growing tree that usually reaches a height of 15-20 m, and under very favorable conditions up to approximately 30-35 m. As rule it is an evergreen tree, but under extreme circumstances, such as extended dry periods, it may shed most of nearly all of its leaves. The branches spread widely. The fairly dense crown is roundish or oval and may reach a diameter 15-20 m in old free standing specimens.

The trunk is relatively short, straight and may reach a girth of 1.5-3.5 m. The bark is hard fissured or scaly and whitish-gray to reddish-brown. The sap wood is grayish-white and the heart wood reddish.

The root system consists of a strong taproot and well developed lateral roots. The lateral surface root may reach over 18 m. Vesicular-arbuscular mycorrhiza (VAM) is associated with the rootlets categorized Neem as a highly VAM dependant plant species.

The leaves are unpaired, pinnate, 20-30 cm long and the medium to dark green leaflets, which number up to 31, are approximately

3-8 cm long. The terminal leaf is often missing. The petioles are short. The shape of mature leaflets is more or less asymmetric.

Natural hybrids between *A.Indica* and *A. Siamensis*, found in Thailand on places where both species grow together, have an intermediate position regarding the shape and consistency of the leaflets.

The white, gragrant flowers are arranged in axillary, normally more or less drooping panicles which are up to 25 cm long.

The glabrous fruits are olive- like drupes which vary in shape from elongate ovea to nearly roundish and when ripe are 1.4-2.8 x 1.0-1.5 cm . They are green when young and yellowish-green to yellow, rarely reddish when mature. The fruit skin (exocarp) is thin and the bitter-sweet pulp (mesocarp) is yellowish-white and very fibrous. The mesocarp is 0.3-0.5 cm thick. The white hard ‘shell (endocarp) of the seed encloses one, rarely two and very rarely three elongated seed kernels having brown testa. (Ogbuewu, 2008).

1.2.4 Origin and Distribution of Neem

Two species of *Azadirachta* have been reported, *Azadirachta indica* A.Juss-native to Indian subcontinent and *Azadirachta excels* Kack. Confined to Philippines and Indonesia (Jattan*et al*., 1995; Hegde, 1995). The former grows as a wild tree in India,

Bangladesh, Burma, Pakistan, Sri Lanka, Malaysia, Thailand and Indonesia. Presently Neem trees can be seen growing successfully in about 72 countries worldwide, The Neem is native of Indian subcontinent; it is widely distributed by introduction, mainly in the drier (arid) tropical and subtropical zones of Asia, Africa, the Americas, Australia and the South Pacific islands. In India it is widely distributed in many states. In Myanmar it is very common in the central parts of the country. In the South Pacific Neem occurs in the Fiji Islands. In Australia it was first introduced about 60-70 years ago. In Indonesia, Neem exists mainly in the low-lying northern and eastern parts of Java and in the frier islands to the east (Bali, Lombok, and Sumbawa).In the Philippines it was introduced during the seventies and eighties of the last century. In China, *A.Indica* was planted on subtropical island of Hainan and southern china. In Nepal Neem trees are found in the southern, low-lying areas (Tarai region). In Sri Lanka it is wide spread in the drier northern parts of the island.

In Qatar and Abu Dhabi Neem was planted under irrigation using desalted seawater along avenues and parks. A large plantation was established on the Arafat plains near Makkah to provide shade for pilgrims (Ahmed et al, 1995).

1.2.5 Neemin Sudan

The Neem (*Azadirachta indica*A. Juss) trees have been grown successfully in all parts of Sudan. Neem has become a naturalized species in various parts of the Sudan. (Elteraifi et al, 2001). In the Sudan,Neemwhich was introduced in 1921 is frequent in Kassala, in threats in towns and village along the blue and the White Nile irrigated areas of central Sudan and rain fed regions in Kordofan and Darfur (Schmutterer, 1995). Neem tree occurs throughout Sudan; its performance is quite good even in the harshest conditions. Most of the original plantations were carried out by the colonial officers along the railway and the Nile banks. Then they spread all over the country. The Neem tree is noted for its drought resistance. Normally it thrives in areas with sub-humid conditions, with an annual rainfall between 400 and 1200 mm. It can grow in regions with an annual rainfall below 400 mm, but in such cases it depends largely on ground water. Neem can grow in many different types of soil, but it thrives best on well drained deep and sandy soils. It is a typical tropical/ subtropical tree and exists at annual mean temperatures between 21-32^0 C. It can tolerate temperatures below 40 C. Temperature is one of the most important factors affecting seeds. Water uptake, gas diffusion, respiration and other metabolic processes all proceed faster at

higher temperatures. Germination is dependent on all these processes and thus is, strongly, affected by temperature.

1.2.6 Chemistry of Neem

To give a brief background, chemical investigations of Neem were undertaken by Indian pharmaceutical chemists in 1919, whereby they isolated acidic principle in Neem oil, which they named as ‘margosic acid”. However, real chemical research originated in 1942 with isolation of three active constituents, viz, nimbin, nimbidin and nimbinene. In 1963 an Indian scientist, extensively, examined the chemistry of the active principles of Neem. Following the discovery ofNeemkernel as a locust feeding deterrent, its chemistry has grown considerably. Several compounds have been isolated and characterized. The main feature is that most of them are chemically similar and biogenetically derivable from a tetracyclicterpenes. These are also called liminoids (azadirachtin, meliantrol, salanin etc.) bitter principles and occur in other botanical species as well (Rutaceae and Simaroubaceae). The unraveling of high complex structural features (Figure 1.4) and biogenetic interrelationship represent classic piece of work on natural product chemistry. From the practical side these compounds also exhibit a wide variety of biological activity, for example, pesticides, antifeedants, and cytotoxic properties.

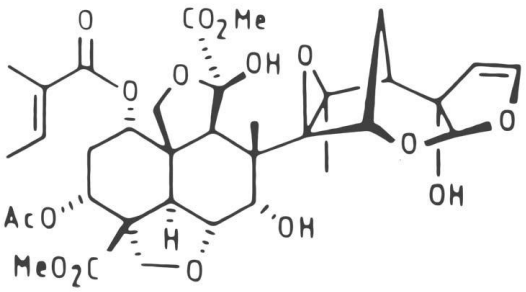

Figure 1.1 Chemical Structure OfAzadirachtin

1.2.7Applications of Neem

Products made from Neem have been used in India for over two millennia for their medicinal properties. They are said to be antifungal, antidiabetic, antibacterial, antiviral, contraceptive and sedative. Neem products are also used in selectively controlling pests in plants. Neemis considered a part of Ayurvedic medicine.

- All parts of Neem are used for preparing many different medicines, especially for skin disease.
- Part of the Neem tree can be used as a spermicide .
- Neem oil is used for preparing cosmetics (soap and shampoo, as well as lotions and others), and is useful for skin care such as acne treatment. Neem oil has been used effectively as a mosquito repellent.
- Neem is useful for damaging over 500 types of insects, mites, ticks, and nematodes, by changing the way they grow and act.

Neem does not normally kill pests right away, rather it slows their growth and drives them away. As Neem products are cheap and not poisonous to animals and friendly insects, they are good for pest control

- In the UK, plant protection products that contain azadirachtin, the active ingredient ofNeemoil, are illegal.

1.2.7.1 Neem use in Pharmaceutical drugs

- Digestive system drugs.
- Circulatory system drugs.
- Skin treatment drugs.
- Dental treatment drugs.
- Diabetic and blood pressure treatment drugs.

Leading global pharmaceutical companies are entering into partnerships or joint ventures with the natural medicine manufacturers to tap the growing herbal medicine market. Therefore Neem will be in great demand in the coming future as it is multi functional and multipurpose product and it does not have any side effects unlike other allopathic medicines.

External medicinal uses of Neemis for the treatment of dermatological disorders like psoriasis, herpes, eczema, purities, and acne vulgaris, inflammatory condition, infected wounds,

abscesses and ulcer, ophthalmic care, ear infection and sinusitis, alopecia and hair care, snake bite and scorpion sting, rheumatic pain, gout, etc. InternallyNeemis used for dental hygiene, for treating malaria and filaria, typhoid, digestive disorders, liver disorders, intestinal worms, hepatitis, spleenomeglay, respiratory disorders, tuberculosis, urinary disorders, gynecological problems, diabetes, hypertension, cancer, leprosy, leucoderma, allergies, etc., infectious diseases such as smallpox, chicken pox, and measles, vaginal disorders, sexually transmitted infection, and AIDS.(www.neem-products.com)

1.2.7.2 Industrial Uses

In 2002, at the World Neem conference, idea of promoting Neem as an Industrial Plant was put forward. Several industries including pharmaceuticals, cosmetics and textile industries use Neem oil (Jattan et al., 1995). Many such neem-based commercial preparations are currently available. In India Neem is highly exploited by many Ayurvedic drug industries. Neem oil and powdered Neem leaves are employed in various cosmetic preparations such as face creams, nail polish, nail oils, shampoos, conditioners (Jattan et al., 1995). A new shampoo, based on seed extract of Neemwas highly effective, more than permethrin-based product, against head lice under in vitro conditions. Neem cake a by-product of Neem oil industry is used as livestock feed,

fertilizer and natural pesticide. Neem oil is commonly used in soap production. Medicated Neem soaps are gaining popularity.

Neem based toothpaste is widely used in India and European countries. Neem is a source for many oral-hygiene preparations and dental care products. Neem bark yields gum and tannins which are used in tanning, dyeing etc. Neem seed pulp is used as a rich source of carbohydrate in fermentation industries and for methane gas production. Cultivation of Neem and processing of Neem products provides employment and income generation opportunities.

1.2.8 TheFuture with Neem

Today's exploding growth in human population is seriously depleting the world's natural reserves and economic resources. Unless the run-away human population growth rate is slowed down, there would be little hope for raising everyone out of poverty in the developing world. Besides educational constraints, the non-availability of inexpensive methods of contraception, which do not cause trauma or aesthetic, cultural, and religious sensitivities of people, limit the success of birth regulation programmed. However, recent findings indicate that some Neem derivatives may serve as affordable and widely available contraceptives. A recent controlled study in the Indian army proved the efficacy of Neem as a contraceptive.

According to a recent report by the Washington based International Food Policy Research Institute, by 2020, the world will be an even more unfair place than it is at present, with food surpluses in the industrialized world and with chronic instability and food shortages in the south, particularly in African countries.

The US Academy of Sciences currently attaches very high importance to the Neem tree. The United Nations declared Neem as the “Tree of the 21st Century.

Figure 1.2 *Azdirachta indica* Gum

1.2.9 *AzadirachtaIndica*Gum

1.2.9.1 Definition

Azadirachta indica gum, which belongs to the Family of galactan gums, it is a very complex condensate of hetero polysaccharides and proteins. The Proteins are tightly linked to the polysaccharides, which constitute the major component. Drastic degradation of a smaller gum complex component shows that it contains D-glucose, D-glucuronic acid, L-arabinose, L-fucose, mannose and xylose. Investigation of the amino acid composition of the gum shows a aspartic acid as the most abundant, aspartic acid in *Azadirachta indica* gum were reported by few authors (Anderson DMW, Hendrie A,1971). In addition to that it also found to contain organic fatty acids(Zechmeister,1999)**.***Acacia gum* (gum Arabic) consists of a group of macro molecule characterized by a high proportion of carbohydrates (approximately about 97%), which are predominantly composed of D-galactose and L- arabinose units and a low proportion of proteins (< 3%). However, Neem gum has unusual structural features in that it contains appreciable amount of D-glucosamine and proteins unlike other plant gums .*Azadirachta indica (Neem)* gum occupies a special position among plant gums in that, it contains about one-third of its weight as proteins (Anderson and Henrie, 1971), the highest concentration reported for any plant

gum. Thus, Neem gum is an excellent experimental material for the study of the biological activities of proteins in exudates gums. (Anderson et, al, 1968).

1.2.9.2 Origin

Many plants exude viscous, gummy, liquids, which exposed to air and allowed to dry, from clear, glassy masses. The shapes of these masses vary from spherical, tear-drop balls typical of gum producing by *Azadirachta indica* trees. The colours of these exudates also vary widely from almost clear white to dark brown, depending on the species, climate, soil, and adsorbed impurities.

1.2.9.3 Description

Gum is a byproduct obtained as a result of certain metabolic mechanism of plants and trees.

Neem Gum is a natural exudate from Neem Tree by induced or natural injury. TheNeembark, due to some internal activity discharges clear, bright and brown-coloured gum material non-bitter in taste and is soluble in cold water. The gum is a multipurpose by product. Natural gums obtained from plants are either water soluble or absorb water to form viscous solutions. Neem has been commercially tapped for using its gum which is of use in large number of industries. It is being grown on a large scale basis for using all its parts, no wonder it is called a

'Universal Tree' having a cure for almost everything. It has been used, traditionally, as an adhesive for paintings. It is used as a bulking agent and for the preparation of special purpose food (those for diabetics). (Anderson and Hendrie, 1971)

1.2.9.4ChemicalCharacteristic

Neem gum gives on hydrolysis L-arabinose, L-fucose, D-galactose, and D-glucuronicacid. The oldobiuronic acid component of the gum obtained by graded hydrolysis is shown be 4-0-(D- glucopyranosyluronic acid) D-galactopyranose. Information on the structure of the gum has also been obtained by periodate oxidation studies. Neem gum atypical plant gum is the salt of a complex polysaccharide acid (K.M.NadKarni, 1927).The gum acid, obtained from acidified aqueous solutions of the gum by precipitation with alcohol, and is a white amorphous powder which has an equivalent weight of 1080. This communication is concern with the composition of the Neem gum and with the determination of the structure of an aldobiuronic (I) produced when the gum is hydrolyzed with acid. Complete hydrolysis of the gum followed by partition chromatography and the preparation of the crystalline derivatives has shown that the gum contains L-arabiose, L-fucose, D-galactose, D-glucuronic acid and traces of D-xylose. The ratio of D-galactose to L-arabinose proved to 3:2. By mild acid hydrolysis, the arabinose and fucose

units were removed first. The eases of removal of the arabinose units indicate that they were present in the gum in the furanose form**.**

More drastic hydrolysis of the gum affords D-galactose and an aldobiuronic acid (I) composed of a unit of D-glucuronic acid and one of D-galactose, Fig 1.2. The structure of the aldobiuronic acid (I) was established as follows, upon methylation of the barium salt of (I), an octa- o-methyl –D galactose and 2,-3,4-tri-o-methyl –Dglucuronic acid, the former being identified as crystalline γ-Lactone and the later as 1,5-Lactone6-methyl ester(J,K,N, Jones and F. Smith1949). These fact prove that the structure (I)assigned to the aldobiuronic acid is correct, a view supported by the further observation that oxidation with periodate result in formation of 2-3 moles of formic acid and 0.5 mole of formaldehyde per mole of aldobiuronic acid,(Gill,. Hirst and Jsones, 1025). When the gum its self was oxidized with periodate , 2moles of formic acid were produced by equivalent weight of the gum and chromatographic analysis of the oxidized gum, after hydrolysis, showed that certain galactose units had survived periodate oxidation. This evidence demonstrated the, highly, branched chain character of the gum and that the branching in the molecular, complex is located at those galactose units of the gum which are not affected during periodate oxidation.

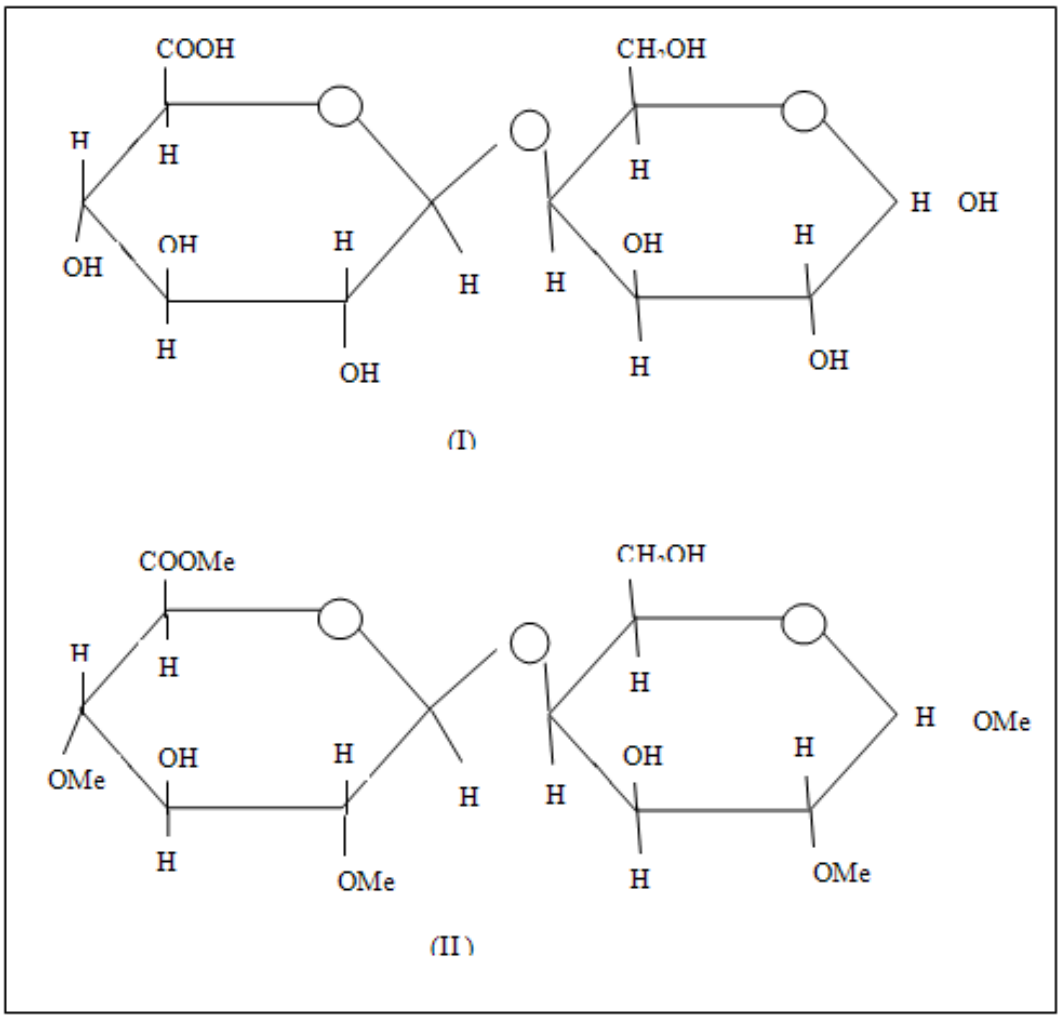

Figure 1.3Chemical Characteristic of Neem Gum

1.2.9.5 Applications of Neem Gum

Cosmetic Industry: Used in facial masks, lotions, face powder, protective creams.

Paper Industry: Used as an adhesive and strengthening the paper.

Pharmaceutical Industry: Used in antiseptic creams, tablet binder, and coater.

Textile Industry: Used in dyeing and printing of fabrics.

Personal Hygiene Industry: Used in soaps, tooth paste, tooth powders.

Food Industry: Used as a stabilizing agent, gels and thickening agent.

Bakery: *Azadirachta indica* gum used in the baking industry for its low water absorption properties, its cold water soluble and has adhesive properties.

1.3 Physiochemical Properties f Gums

The physiochemical properties of *Azadirachta indica* gums are important in specification, characterization and quality indication of the gum, and also assist to differentiate between different Neem gums. These properties vary with gums of different botanical sources, and even substantial differences in gum from the same species when collected from the plant at different season of the year, different places and different ages of the same plant.

Several parameters can be used in this study but the most important are:

1.3.1Moisture Content

The moisture content express the amount of water present in a moist sample. Moisture content gives indication about the hardness of the gum and microbial counts and helps calculation of the dry gum sample. It can be determined by measuring the weight lost after evaporation of water. Mohammed kashif and shafatvllah in (2013) reported the moisture of Neem gum to be 10.30%, Eman awad in (2016) reported the moisture content in the Neem gum to be 10.6%.

1.3.2 Ash Content

In analytical chemistry, ashing is the process of mineralization for pre concentration of trace substances prior to chemical analysis. The residues after a sample is completely burnt - in contrast to the ashes remaining after incomplete combustion - consist mostly of metal oxides.

Ash is one of the components in the proximate analysis of biological materials, consisting mainly of salty, inorganic constituents. Ash content is the measure of inorganic residue remaining after removal of organic matter; it is generally affected by the type of soil.

Mohammed kashif and shaftvvllah in (2013) reported the ash content in Neem gum to be8.31%. Eman awad in 2016 reported the ash content in Neem gum to be 3.45 %.

1.3.3 Optical Rotation

Many substances possess the inherent property to rotate the plane of the incident polarized light; this property is called optical activity. In chemistry, specific rotation (α) is a property of a chiral chemical compound. It is defined as the change in orientation of monochromatic plane-polarized light, per unit distance–concentration product, as the light passes through a sample of a compound in solution.

The measurement of optical activity is used for establishing the identity of the substances, it may also be employed to test the purity of the substance, the optical rotation is angle through which the plane of polarization rotates when polarized light passes through a layer of a solution Compounds which rotate light clockwise are said to be dextrorotary, and correspond with positive specific rotation values (+ve), while compounds which rotate light counterclockwise are said to be levorotary, and correspond with negative values (–ve). If a compound is able to rotate plane-polarized light, it is said to be "optically active". (Makka. H.A, 2011)

In principle the rotation produced by molecule is equal in magnitude but opposite in sign to that produced by its mirror image .an assembly with freedom of rotation, such as that which occurs in solution, will produce an observable net effect only if the individual molecules are optically asymmetric .the direction and magnitude of rotation are sensitive to the detailed structure in the vicinity of asymmetric center of the molecule (Iph).In practice the angle of rotation (α) is measured in degrees. However α depends on the number and nature of the molecules, the distance through which light travels and varies only slightly with temperature and solvent. The parameter determined from rotation measurements is the specific rotation (α) is given by:

$$[\alpha]_D = \frac{100\ \alpha}{L\ .C}$$

Where:

α is the measured rotation in degrees.

D is the wavelength of the light (sodium line, 589 nm).

C is the concentration of solution in g/100ml.

L is the path length in decimeters.

The specific rotation was determined for 1% aqueous solution on a dry weight basis using digital optical ADP220 polarimeter fitted with a sodium lamp and with cell path length of 20 cm .The solution was passing through NO-42 filter paper. Eman awad in 2016 reported the specific optical rotation of Neem gum to be + 65.35.

1.3.4 Nitrogen and Protein Content

Protein as a part of gum molecule was established by (Anderson and Henrie, 1971; Anderson et al., 1972; Usha Lakshmi and

Pattabiraman, 1967).It has been suggested that the gum proteins may arise as contaminants when the exuding gums come into contact with the stem of the tree (Jones and Smith, 1949). An alternate suggestion (Jones and Smith, 1949) that the proteins might be integral components of the gum as enzymes involved in

Polysaccharide formation has not been verified. Neem (*Azadirachta indica*) gum occupies a special position among plant gums in that, it contains about one-third of its weight as proteins (Anderson and Henrie, 1971), the highest concentration reported for any plant gum. Thus, Neem gum is an excellent experimental material for the study of the biological activities of proteins in exudates gums. There is strong correlation between the proportion of the protein in the gum and its emulsifying stability .so it's important to determine the nitrogen and protein content of the gum by using a micro Kjeldahl method.

Anderson and Henrie, (1971) reported protein content in Neem gum to be 35 %.

Mohammed kashif and shaftvvllah in (2013) reported the protein content in Neem gum to be 8.93 %;

Eman awad in 2016 reported the Nitrogen content and protein content of Neem gum to be 4.6% and 30% respectively.

1.4 Thermodynamic Properties

1.4.1 Introduction

Chemical and physical processes are almost invariability accompanied by energy changes. Chemistry can be viewed as being based on the interrelated physics factors of energetic, structure, and dynamics. In some ways, energetic can be considered as the most fundamental parameter, since the energetic behavior of molecule determines their structure and reactivity.

Thermodynamics has immense predictive power and the thermodynamic laws can be used to predict the direction in which the process would proceed.

To understand the behavior of gum molecules in solution it is necessary to measure some of their thermodynamic parameters and functions. Thermodynamic of polymer solution can be applicable to gum solutions since gum molecules are classified as biopolymer molecules. Solutions are characterized by thermodynamic parameters like the volume, internal energy, Gibbs free energy, entropy and enthalpy. However, one usually makes use of the differences of these quantities in two specified states of the system. In the case of solution processes it is customary to refer to the difference between thermodynamic functions of the solution and the same functions of the

Components before dissolving, the properties of the real solutions are non additive for example:

$$V_{sol} \neq \sum V_{comp} \quad \ldots\ldots\ldots (1.4.1.1)$$

$$G_{sol} \neq \sum C_{comp} \quad \ldots\ldots\ldots (1.4.1.2)$$

Hence the volume, enthalpy, entropy, etc, of components in solution differ from their values before dissolving. This made it necessary to introduce the concept of partial molar (specific) functions to characterize the thermodynamic behavior of the components in solution. (Tager, 1978).

1.4.2 Weight Fraction (W)

The weight fraction of a component is the ratio of it is weight to the sum of weights of all components.

$$W_1 = \frac{g_1}{g_1+g_2} \quad \ldots\ldots\ldots (1.4.2.1)$$

$$= \frac{g2}{g_1+g_2} \quad \ldots\ldots\ldots (1.4.2.2)$$

$$W_2$$

Where g_1 and g_2 the weights of components 1 and 2 respectively.

1. 4.3 The Molar Fraction (N)

It is the most useful concentration variable for theoretical understanding of solutions of like size molecules. The mole

fraction of a component (N_i) of a binary solution is calculated from the following equation:

$$N_1 = \frac{n_1}{n_1+n_2} \quad \ldots\ldots\ldots (1.4.3.1)$$

$$N_2 = \frac{n_2}{n_1+n_2} \quad \ldots\ldots\ldots (1.4.3.2)$$

Where n_1 and n_2 are number of moles of component involved.

1.4.4 Volume Fraction (ϕ)

The volume fraction of the component (ϕ) is the ratio of its partial molar (specific) volume to the total volume of the solution. For the binary system for instance (ϕ_i)is given as (Tager, 1978).

$$(\phi_1) = \frac{\bar{v}_1}{\bar{v}_1+\bar{v}_2} \quad \ldots\ldots\ldots (1.4.4.1)$$

$$(\phi_2) = \frac{\bar{v}_2}{\bar{v}_1+\bar{v}_2} \quad \ldots\ldots\ldots (1.4.4.2)$$

Where: $\bar{v}_1$ is partial molar (specific) volume of the solvent.

$\bar{v}_2$ is partial molar (specific) volume of the solute.

1.4. 5 Partial Molar (Specific) Volume ($\bar{v}$)

In general the partial molar volume of a substance A in a mixture is the change in volume per mole added to a large volume of the mixture. If the molecular mass of the components are not exactly known, so that their mole fractions cannot be calculated, its more

convenient to use specific partial functions, i.e., function referred to one gram rather than to one mole of the component.

A partial specific function ($Z_{i\ sp}$) equal the partial molar function ($Z_{i\ mol}$) divided by the molecular mass (M_i) of the component:

$$Z_i\ sp\ =\ Z_i\ mol/M_i \quad \ldots\ldots\ldots\ldots (1.4.5.1)$$

To discuss the determination of partial molar volume of liquid solution, it is convenient to write the molar volume (V_m) of a binary solution as a function of the partial molar volumes of the two components and their mole fractions (N_1, N_2)

$$\bar{V}_M\ =\ N_1\bar{V}_1\ +\ N_2\bar{V}_2 \ldots\ldots\ldots (1.4.5.2)$$

The molar volume of a solution can be calculated from it is density and composition. For binary solution the molar volume at constant temperature and pressurecan is calculated by graphical method. There two graphical methods for calculating partial molar (specific) volume (Tagger, 1978).

(I) Tangent Method

The volume of the solution (V) is plotted against the number of moles (n) grams (g) of one of its components.

Evidently, the derivative $\frac{\partial V}{\partial n}$ or $\frac{\partial V}{\partial g}$ determined at any point of the curve, equal the partial molar (specific) volume of the component in a solution of the corresponding concentration (Tager, 1978).

(II)Intercept Method

The intercept method, consist in plotting the value of volume (V) or its change (ΔV) referred to one mole of solution $\{V_{total}$ $(n_1+n_2)\}$. If the volume referred to one gram of solution (V/g_1+g_2) are plotted along the ordinate against composition in weight fractions (w),the tangent intercepts on the ordinate will be numerically equal to the partial specific functions (Tager,1978)

Paijk, et al (1990) studied the density of aqueous solutions of some monosaccharide's (D-pentose's and D-hexoses). The mean molar volumes of the solutions were found to be linearly dependent on the mole fraction of the solute .Thus, the partial molar volumes of solvent and solute, respectively, are concentration- independent; i.e., the partial molar volume of the solvent equal the molar volume of the pure solvent, and the partial molar volume of the solute is equal to it is value at infinite dilution.

The graphical methods described by Lewis and Randall (1923) are used in the determination of the apparent molal volume ϕ which defined by the relation

$$\phi = \frac{V - n_1 v^0}{n_2}$$ (T, P constant) ……. (1.4.5.3)

1.4.6 Chemical Potential (μ)

One of the most function characteristic in the behavior of each component in a solution is the chemical potential of the component .The chemical potential equals the change in eternal energy of a solution on addition of an infinitely small number of moles of its component, referred to that amount of substance at constant volume, entropy, and quantity of each of the other component.

$$\mu_1 = \left(\frac{\partial u}{\partial n_i}\right)_{v, s, n_j (j \neq 1)} \quad \ldots\ldots (1.4.6.1)$$

$$\Delta G = \Delta\mu \ldots\ldots\ldots\ldots\ldots\ldots (1.4.6.2)$$

Since

$$\Delta G = \Delta H - T\Delta S \quad \ldots\ldots\ldots (1.4.6.3)$$

$$\Delta\mu = \Delta H - T\Delta S \quad \ldots\ldots\ldots (1.4.6.4)$$

The change in chemical potential of solvent with environmental pressure at constant temperature is given by the equation:

$$\left(\frac{\partial \mu}{\partial p}\right)_r = \bar{V} \ldots\ldots\ldots\ldots\ldots (1.4.6.5)$$

Or

$$d\mu_i = \bar{V}\, dp \ldots\ldots\ldots\ldots (1.4.6.6)$$

Hence

$$d\mu_i = -\int_{\mu 1}^{\mathring{\mu}_1} d\mu 1 = \int_{p0}^{p} v dp \quad \ldots\ldots\ldots (1.4.6.7)$$

Assuming v to be constant, we obtain after integration:

$$\mu_{10} - \mu_1 = v\,(p - p^0) = \bar{\bar{v}}_1 \pi \ldots\ldots\ldots (1.4.6.8)$$

$$\mu_{10} - \mu_1 = \bar{\bar{v}} \pi \ldots\ldots\ldots\ldots\ldots\ldots (1.4.6.9)$$

Where π = Osmotic Pressure.

V = Partial molar (specific) volume of solvent.

Hence

$$\mu_1 - \mu_1^0 = \Delta \mu_1 \ldots\ldots (1.4.6.10)$$

$$\mu_1 - \mu_{10} = - \bar{v} \pi \ldots\ldots\ldots$$

(1.4.6.11)

1.4.7 Ideal and Non Ideal Solution:

Ideal solutions are those which form with a zero heat effect ($\Delta H = 0$) and ideal entropy of mixing equal ($-R \ln N$), consequently, in accordance with equation (1.4.6.4), the change in chemical potential of the component in an ideal solution equals:

$$\Delta \mu_i = -T \Delta S_i = RT \ln N_i \ldots\ldots\ldots (1.4.7.1)$$

i.e., depends only on the mole traction of that component in the solution. In this case of a real solution

$$\Delta \mu_i = \Delta G = RT \ln \left(\frac{pi}{pi□} \right) \ldots\ldots\ldots\ldots (1.4.7.2)$$

Where piand p_i are the partial vapour pressures of the component above the solution and above the pure component respectively.

1.4.8 Osmotic Pressure: (π)

Osmotic is the phenomenon of penetration of a solvent into a solution through a semi permeable membrane. The tendency of solvent molecules to pass spontaneously into a solution, due to the inequality of chemical Potential of the pure solvent and solution estimated quantitatively by osmotic pressure, which has the dimension of pressure (atm). The osmotic pressure of the solution is equal to the additional pressure which must be applied to the solution to make the chemical potential of the component in solution equal to the chemical potential of the pure solvent.

$$\pi = p - p^0 \ldots\ldots\ldots \text{(1.4.8.1)}$$

Comparison for equation(1.4.6.11) and equation (1.4.7.1) show that the osmotic pressure of an ideal solution can be given by the relation:

$$\Pi = -\left(\frac{RT}{V1}\right) \ln N_1 \ldots\ldots\ldots\ldots \text{(1.4.8.2)}$$

$$\Pi = -\left(\frac{RT}{V1}\right) \ln (1\text{-}N_{2)} \ldots\ldots\ldots \text{(1.4.8.3)}$$

Expanding ln (1-N_2) in a series, and using the first term of this series for high dilution, we obtain

$$\text{In } N_1 = \ln (1-N_2) = -N_2 - \frac{N_2^2}{2} \ldots\ldots\ldots \text{(1.4.8.4)}$$

$$\Pi = \left(\frac{RT}{V1}\right) N_2 \ldots\ldots\ldots\ldots (1.4.8.5)$$

The mole fraction of a component is

$$N_2 = \frac{n_2}{n_1+n_2} \ldots\ldots\ldots\ldots (1.4.8.6)$$

When n_1 and n_2 are the numbers of moles of the components. If $n_1 >> n_2$ then $N2 \approx \frac{n2}{n1}$ .Substituting this expression into equation (1.4.8.5), we get

$$\Pi = \left(\frac{RT}{V}\right) n_2 = C_2RT \ldots\ldots\ldots (1.4.8.7)$$

Where v is the volume of solution, equal to $n_1 v_1^0$.

$C = n_2/v$ = concentration of a solute in units of mole/liter.

Equation (1.4.8.7), was first derived empirically by vant Hoff, and is known as Vant Hoff equation.

The vant Hoff equation $\Pi = CRT$ does not apply to polymer solutions, even though they are very dilute. The concentration dependence of osmotic pressure is expressed by a more complex equation which results if concentration C is replaced by power series (Flory, 1953)

$$\Pi = RT (A_1C+A_2C^2+A_3C^3\ldots.) \ldots\ldots\ldots (1.4.8.8)$$

Or

$$\frac{\pi}{C} = RT\,(A_1 + A_2 + A_3C\ldots) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1.4.8.9)$$

Where C = concentration of a polymer in a solution (g/cm^3)

A_1, A2, A3 are first, second and third virial coefficients. The first virial coefficient A_1 is related directly to the molecular mass of a polymer by the relation

$$A_1 = \frac{1}{Mn} \qquad \text{(Tager, 1978)}$$

Hence, equation 1.4.8.9may written in the following form,

$$\frac{\pi}{C} = RT\left(\frac{1}{Mn} + A_2c + A_3c^2\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1.4.8.10)$$

Equation (1.4.8.10) can be written in thefollowing form (Billmeyer,1971, Krigbaum and Flory, 1953).

$$\frac{\pi}{C} = RT\frac{1}{Mn}\,(1 + \Gamma^2 c + g\,\Gamma^2 c^2\ldots) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1.4.8.11)$$

Where $\Gamma = A_2/A_1$, and g is a slowly varying function of the polymer – solvent interaction with values near zero for poor solvents and near 0.25 for good solvents (Krigbaum, 1952; Stockmayer, 1952).

In most cases, the term c^2 may be neglected; when dependence on c^2 is significant, it may be convenient to take g=0.25 and equation (1.4.8.11) Becomes:

$$\frac{\pi}{C} = \frac{RT}{M^n}\left(1 + \frac{\Gamma}{2}C\right)^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.4.8.12)$$

In terms of the polymer – solvent interaction constant $X_1$of the Flory Huggins theory, the osmotic pressure is given by,

$$\frac{\pi}{C} = \frac{RT}{M^n} + \left(\frac{p}{MC} P_2^2\right)\left(\frac{1}{2} - \chi C\right) \ldots\ldots\ldots (1.4.8.13)$$

Where subscript 1indicate to the solvent, and 2 to the gum.

As equation (1.4.8.11) it is usual to plot $\frac{\pi}{C}$ vs C .in general straight line result whose intercept at C = 0 is $A_1 = \frac{RT}{M^n}$ and whose slope is the second virial coefficient A_2 that allows evaluation of the polymer –solvent interaction constant χ_2 .if the solvent is good enough or the concentration is high enough then C^2 terms is significant of the point may deviate from straight line. In such cases it is useful to plot $\left(\frac{\pi}{C}\right)^{0.5}$versus C as suggested by equation(1.4.9.12) which can be written as follow:

$$\left(\frac{\pi}{C}\right)^{0.5} = \left(\frac{RT}{M^n}\right)^{0.5}\left(1+\frac{\Gamma}{2}C\right) \ldots\ldots\ldots\ldots\ldots (1.4.8.14)$$

Since

$$\Gamma = \left(\frac{A_2}{A1}\right) \qquad \text{and } A_1 = \frac{1}{M^n}$$

We can write

$$\left(\frac{\pi}{C}\right)^{0.5} = \left(\frac{RT}{M^n}\right)^{0.5} + \left(\frac{RT}{M^n}\right)^{0.5}\left(\frac{A_2 Mn}{2}\right) C \ldots\ldots\ldots\ldots\ldots (1.4.8.15)$$

The intercept = $\left(\frac{RT}{M^n}\right)^{0.5}$…… (1.4.8.16)

$$\text{The slope} = \left(\frac{RT}{M^n}\right)^{0.5} \left(\frac{A_2 Mn}{2}\right) \ldots\ldots\ldots (1.4.8.17)$$

If the second virial coefficients equal zero, the solvent is called ideal solvent.

The better solvent has a higher value of A_2 (Figure 1.4).

For an ideal solvent, $A_2 = 0$.

For good solvent, $A_2 > 0$.

For poor solvent, $A_2 < 0$.

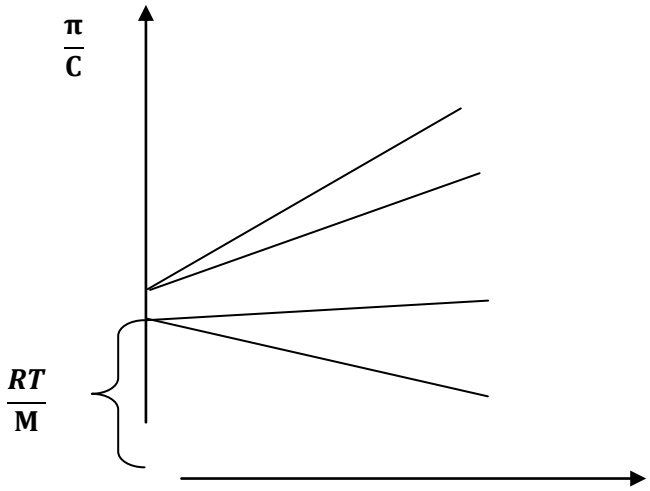

Figure 1.4 Dependence of on concentration of polymer solution in Various solvents.

1.4.9 Free energy of mixing of polymer with solvent

To calculate the free energy of mixing ΔG^m, it is necessary to know the chemical potential of polymer or to be more exact, the quantity $\Delta\mu_2$ it is value is calculated by using the Gibbs,-Duhem equation for specific quantities (Tiger, 1978)

$$\omega_2 d\,\Delta\mu_2 = -\omega_1 d\,\Delta\mu \ldots\ldots\ldots\ldots (1.4.9.1)$$

Where ω_1 and ω_2 are weight fractions of component 1 and 2.

Hence,

$$\Delta\mu_2 = -\int \left(\frac{\omega_1}{\omega_2}\right) d\Delta\mu_1 + C \ldots\ldots\ldots\ldots\ldots (1.4.9.2)$$

To solve this equation, it is necessary to plot the graph of dependence of $\left(\frac{\omega_1}{\omega_2}\right)$ on $\Delta\mu_1$ (Figure1.5)

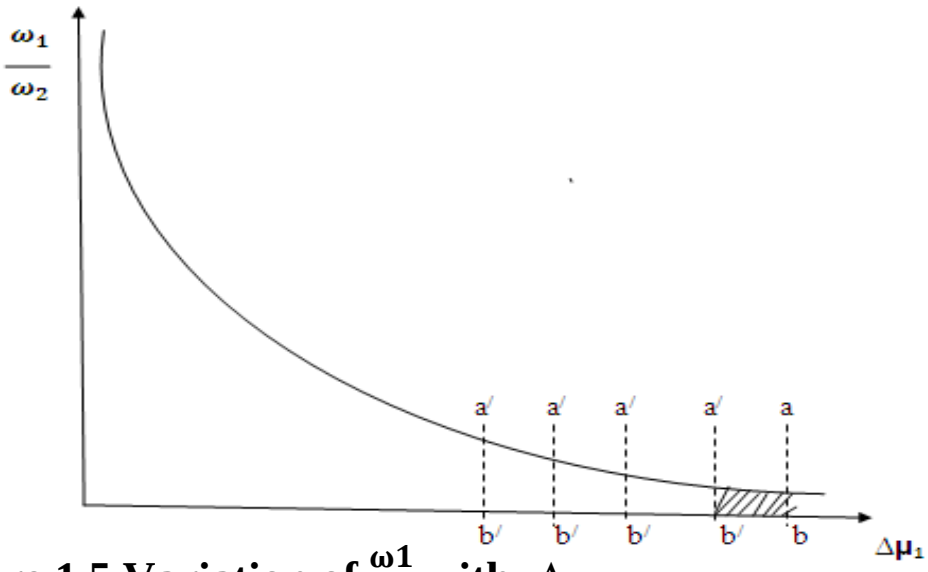

Figure 1.5 Variation of $\frac{\omega 1}{\omega 2}$ with$\mu\Delta_1$

For $\omega_2 = 1$ ($\omega_1 = 0$), the ratio $(\frac{\omega_1}{\omega_2}) = 0$ and $\Delta\mu_1 \rightarrow -\infty$.

For $\omega_1 = 1$ ($\omega_2 = 0$), the ratio $(\frac{\omega_1}{\omega_2}) = \infty$ and $\Delta\mu_1 = 0$

Hence the curve goes with both ends into infinity and the integral may be determined in the limits range from $-\infty$ to a certain value of $\Delta\mu_1$ which corresponds to the concentration of a solution

$$\Delta\mu_2 = \int_{-\infty}^{\Delta\mu} \left(\frac{\omega_1}{\omega_2}\right) d(\Delta\mu 1) \ldots\ldots\ldots (1.4.9.3)$$

Such an improper integral is replaced with a proper integral which is analogous to it; in this case the finite value $\Delta\mu_1'$ which conforms to concentration ω_2' less than one is taken as the lower limit.Thus the areas under the curve that are bounded by ordinates corresponding to $\Delta\mu_1'$at $\omega_2'$and$\Delta\mu_1$ at different values of ω_2, are calculated (figure 1.5) the calculated areas for $\Delta\mu_2'$are less than the true values obtained of $\Delta\mu_2$,a graph of dependence $\Delta\mu_2 = f(\omega_2)$ is plotted ;in the region of concentration close to $\omega_2' = 1$, it is rectilinear .in extrapolating the straight line to $\omega_2 \rightarrow 1$,we obtain segment A. However, at $\omega_2 = 1$, $\Delta\mu_2 = 0$ it follows that the true values of $\Delta\mu_2$ different from, $\Delta\mu_2'$by the length of segment A (Figure 1.6).

$$\Delta\mu_2 = \Delta\mu_2^{/} + A \quad \ldots\ldots\ldots (1.4.9.4)$$

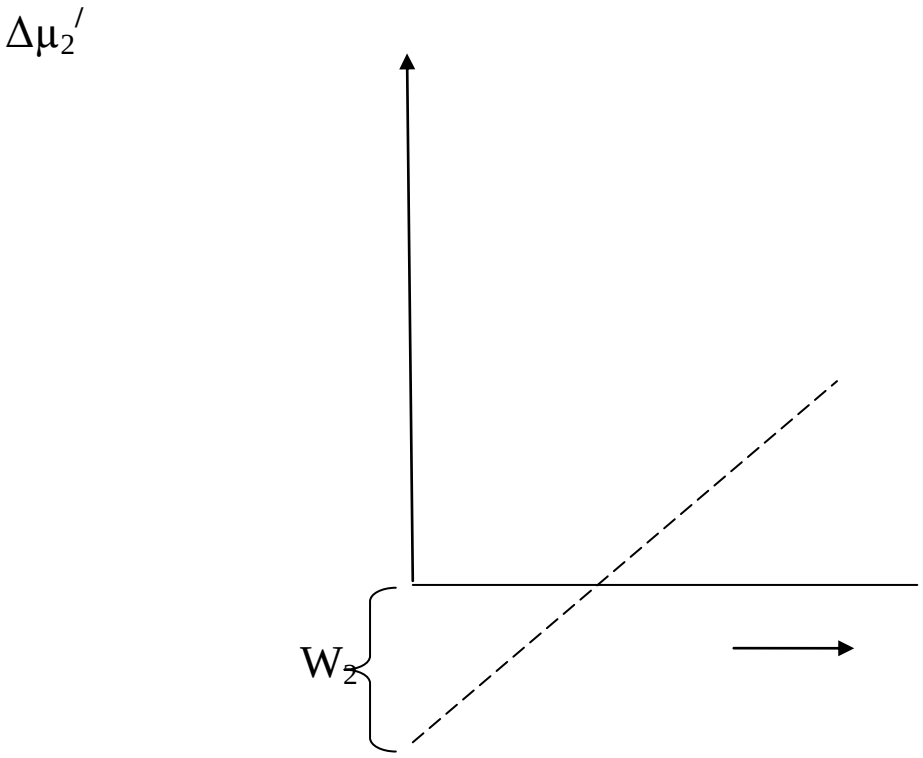

Figure 1.6 Correction of $\Delta\mu_2$

This is an ordinary way of approximately calculating $\Delta\mu_2$.
Knowing $\Delta\mu_1$ and$\Delta\mu_2$ the average free energy of mixing per grams of a solution can be calculated.

$$\Delta G^m = \omega_1 \Delta\mu_1 + \omega_1 \Delta\mu_2 \ldots\ldots\ldots (1.4.9.5)$$

Good solvents are liquids whose mixing with polymers is accompanied with great change in the chemical potentials of components and the free energy of the entire system, and with large values of osmotic pressure and positive value of the second virial coefficient.

1.5 Objectives

- To authenticate the gum for *Azadirachta indica* (Neem) Gum.
- To study of the thermodynamic properties of the *Azadirachta indica* gum.
- To calculate the virial coefficient, chemical potential and free energy of *Azdirachta indica* gum Solution.

Chapter Tow

2. Materials and Methods

2.1 Materials

The Sample of Neem gum which was nodules and lumps were obtained from Sudan University for Science and Technology (SUST).

The sample was dried at room temperature, then cleaned by hand ground using mortor and pestle, sieved and kept in labeled plastic container for analysis.

2.2 Analytical Methods

2.2.1 Determination of Moisture Content

Accurately (2.0 g a triplicate)of the gum sample were weighed in pre-weighed evaporation dish and placed in the oven for 6 hours at 105 ^{0}Cto a constant weight .the percentage weight loss compared to the original weight was obtained according to the following equation (JECFA / FAO., 1990).

$$\text{Moisture \%} = \frac{W_1 - W_2}{W_1} \times 100 \qquad \text{..... (2.2.1.1)}$$

Where

w_1= weight of the sample after heating.

W_2= weight of the sample before heating.

2.2.2 Determination of Ash Content

The total ash was determined according to FAO paper NO, (44), (1990) .A crucible was heated at 550^0C, cooled in desiccators and weighed (w_1), two grams of gum sample (including moisture) was accurately weighed in the crucible (w_2) and ignited at 550^0C in a furnace until free from carbon, cooled in desiccators' and weighed (w_3) .then the total ash % was calculated as follow:

$$\text{Total ash \%} = \frac{w_3 - w_1}{w_2 - w_1} \text{x}100 \quad \ldots\ldots\ldots\ldots (2.2.2.1)$$

2.2.3 Determination of pH Value

PH was determined in 1% aqueous solution at room temperature using PH meter (SSSPH Ion meter).

2.2.4 Determination of the Specific Optical Rotation

The specific rotation was determined for 1%aqueous solution on a dry weight basis using digital optical ADP220polarimeter fitted with a sodium lamp and with cell path length of 20 cm .the solution was passed through NO-42 filter paper.

2.2.5 Determination of the Total Nitrogen and Protein Content

Kjeldal method was used to determine the total nitrogen in Neem gum sample. The procedure used (Bradstreet,1965) is two stages , process in which the gum sample is digested in hot concentrated sulphuric acid and the ammonia released using sodium hydroxide is neutralized using standard acid.

The reactions involved in these steps can be shown as follow:

* Sample $+H_2SO_4$ (conc.) catalyst+ Heat $\rightarrow (NH_4)_2SO_4$

* $(NH_4)_2SO_4 + 2NaOH \rightarrow 2NH_3 + Na_2SO_4 + 2H_2O$

* $NH_3 + H_3BO_3 \rightarrow NH_4^+ + H_2BO_3^-$

* $H_2BO_3 + HCL \rightarrow H_3BO_3 + CL^-$

0.5 gram of the sample was weighed and transferred to Kgeldahl digestion flask and Kjeldahl tablet (copper sulphate, potassium sulphatecatalyst) was added to the sample. 10 cm^3 of concentrated nitrogen free ,sulphuric acid was added .The tube was then mounted in the digestion heating system which was previously set to 240^0c and capped with an aerated manifold .the solution was then heated at the above temperature until a clear pale yellow – wish green colour was observed which indicates the completion

of the digestion .the tube was then allowed to attain room temperature .their contents were quantitatively transferred to two separate Kjeldahl distillation apparatus followed by addition of distilled water and 80% (w\v)sodium hydroxide .steam distillation was then started and the released ammonia was absorbed in 25 cm^3 of 2% boric acid . back titration of the generation of borate was then carried out versus , 0.02M, hydrochloric acid using methyl red as an indicator . Blank titration was carried in the same way.

$$N\% = \frac{14.01 \text{ x M x (volume of titrant – volume of blank) x 100}}{\text{weight of sample (grams)}} \quad (2.2.5.1)$$

Where M : is the molarity of hydrochloric acid.

Protein content was calculated using nitrogen conversion factor (NCF) of 6.51 (Anderson, 1986) as follow:

$$\text{Protein\%} = N\% \text{ x } 6.51 \ldots\ldots\ldots (2.2.5.2)$$

2.2.6 Partial specific Volume of the Solvent

Tangent method was used (Tager, 1978) by dissolving a constant weight of gum sample in different weights of water (Table 3.2).The density of solution was determined by a pyknometer and then the total volume of the solution was calculated.Then volume of solution was plotted against weight of solutions. The partial

specific volume of water is equal to the $\frac{\partial v}{\partial g}$ was then found from the slope of the graph shown in Fig (3.1).

2.2.7 Partial Specific Volume of the Gum

Tangent method was used in different weights of gum were dissolved in a constant weight of water, Table (3.3) the density of solution was determined by a pyknometer and then the total volume of gum was calculated. A graph of the volume of solution versus the weight of gum was plotted, where the partial specific volume of the gum sample is equal to the $\frac{\partial v}{\partial g}$ which can be calculated from the slope of the graph shown in Fig (3.2)

2.2.8 Osmotic Pressure

Osmotic pressure of gum solution was measured using osmomat^{R}050 colloidal osmometer at 25^{0}c.

Chapter Three

3. Results and Discussion

3.1 Physiochemical Properties of *Azadiracht indica* Gum

Table (3.1) shows the physiochemical properties of *Azadirachta indica* gum which was found by (Mohammed Kashif and Shatvllah 2013), (Eman Awad 2016), and the result of this study, 2016), They include; moisture content ,ash content, nitrogen, protein, pH value, molecular weight and optical rotation .

Results for this study indicated that the moisture content differ significantly from that reported by (Mohammed Kashif and Shatvllah2013), and (Eman Awad2016). The result also showed that the moisture content of Neem Gum is higher than that of *Acacia*11.01 % (Malik 2008), which might have resulted from the appreciable amount of polysaccharide and proteins present in Neem gum unlike in *acacia* gum. It could also be due to the tightlink between the polysaccharides and the protein.

The ash content is smalller than that obtained by (Mohammed Kashif and Shatvllah2013) and similar to that obtained by (Eman Awad2016).

The PH value of *Azadirachta indica* gum was (significantly has) near to the value that obtained by (Eman Awad 2016), and higher than that reported by (Mohammed Kashif and Shatvllah2013), all in acidic range.

The nitrogen and protein content were closely to that reported by (EmanAwad2016) and higher than that tested by (Mohammed Kashif and Shatvllah2013) but they had near values to that reported by (Anderson and Henrie, 1971).

The specific optical rotation of *Azadirachta indica* gum was agreed with that reported by (Eman Awad 2016).

The molecular weight of *azadirachta india* gum calculated from osmotic pressure, the result was similar to that obtained by (Eman Awad 2016).

Table (3.1): Analytical data for *Azadirachta indica* gum.

Property	**Mohammed Kashif and Shatvllah(2013)**	**EmanAwad(2016)**	**This study(2017)**
Moisture (%)	10.30%	9.50%	13.07%
Ash (%)	8.31%	3.20%	3.13%
Nitrogen (%)	1.37%	4.6%	4.9%
Protein (%)	8.93%	30%	32%
pH	5.84	6.8	6.5
Optical rotation	–	– 67.7	– 65.5
Number average molecular weight(g/mole)	–	2.9×10^{6}	4.08×10^{6}

3.2 Thermodynamic Properties of *Azadirachta indica* Gum

The partial specific volume of the solvent and solute were calculated using the tangent method. From the results in the Table

3.2**,** 3.3, it's possible to obtain Figures 3.1**,** 3.2 and from the slope of these figures partial specific volume of the solvent and solute are obtained .The partial specific volume of water and *Azadirachta indica* gum in *Azadirachta indica* gum solution was obtained from the slopes**,** which were found to be 1.0000 cm^3g^{-1} and 0.947cm^3g^{-1} respectively.

Table 3.2: Partial Specific Volume of Water in *Azadirachta indica* Gum Solution

Gum concentration w/w %	**Weight of gum W_2 (g)**	**Weight of water W_1 (g)**	**Solution volume V(cm^3)**
1	1.847	197.9900	199.8310
2	1.847	97.9980	99.8240
3	1.847	71.9985	73.8219
4	1.847	68.9986	70.7322
5	1.847	61.0000	62.7333
6	1.847	55.0000	56.7331

Table 3.3Partial Specific volume of *Azadirachta indica* gum solution

Gum concentration w/w %	Weight of gum W_2 (g)	Weight of water W_1(g)	Solution volume V (cm^3)
1.1	0.4370	55	55.434
2.2	0.9290	55	55.917
4.6	2.1740	55	57.076
6.4	3.4801	55	58.3296
8.3	4.7921	55	59.585
12.0	5.4181	55	60.142

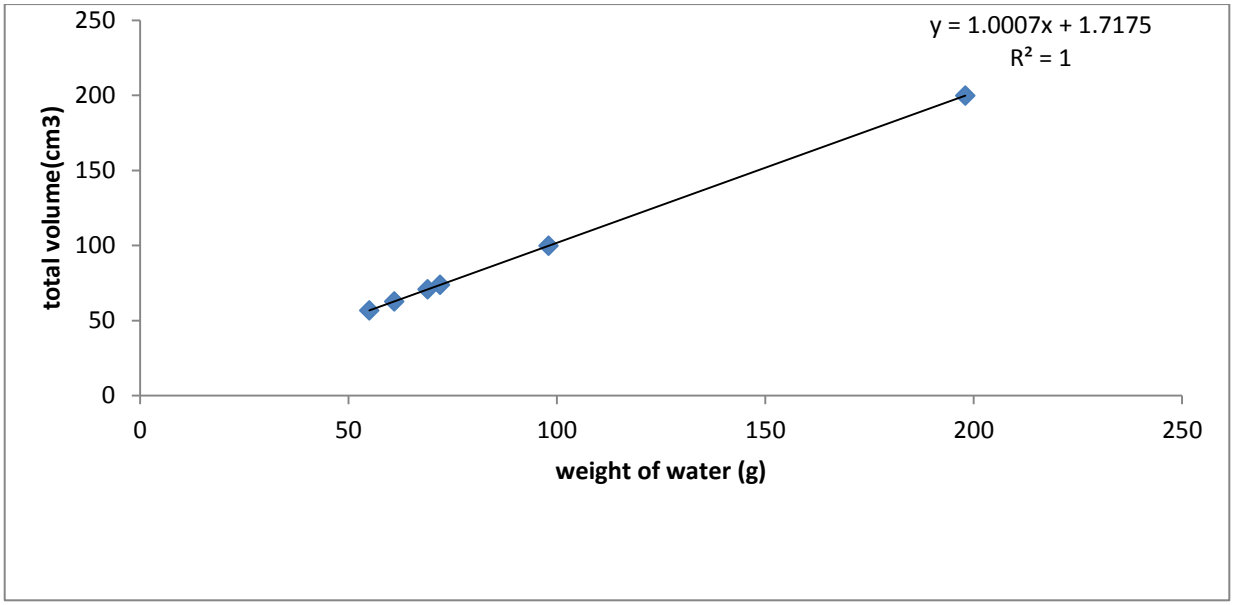

Figure 3.1 Partial Specific Volume of Water in *AzadirachtaIndica*Gum solution.

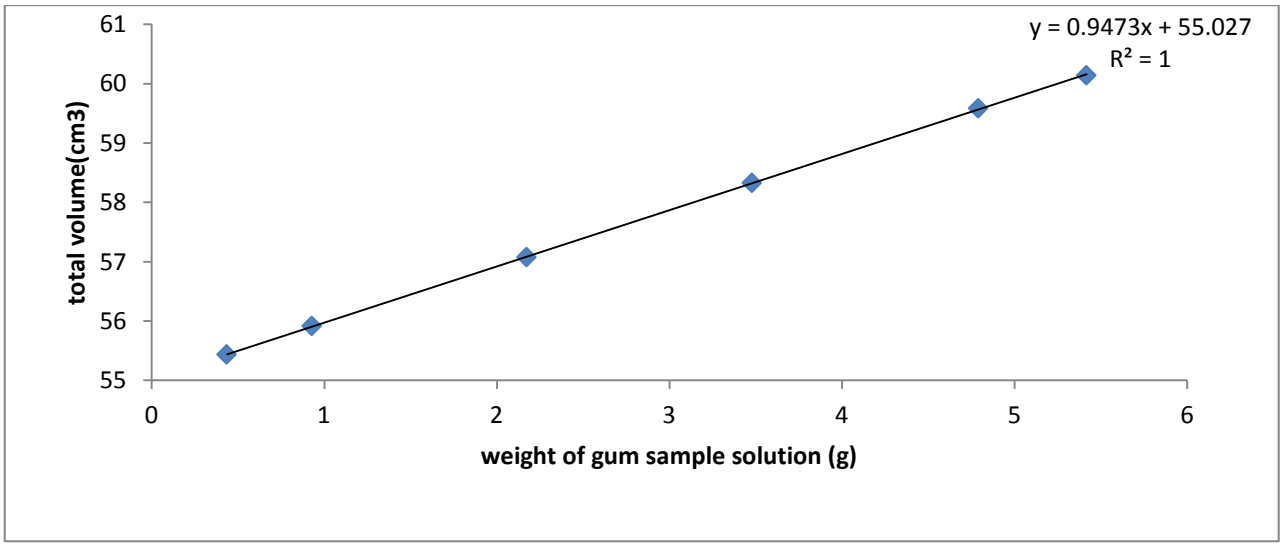

Figure 3.2 Partial Specific Volume of *Azadirachta indica* Gum in *AzadirachtaIndica*Gum Solution.

The Values in Table (3.4) indicate that the partial specific volume of water is so closely to that of *A.seyal* and *A.Senegal* (Malik, 2008) rather than that of*A.polycantha* (Malik, 2008) and *Acacia*

gum (Makka, 2011). The partial specific volume of gum in *Azadirachta indica* gum solution in Table (3.5) is higher than others.

The volume fraction of water Φ_1 and that of gum Φ_2 in gum solution of different concentrations were calculated using equations (1.4.4.1) and (1.4.4.2), results shown in Table (3.6).

Table (3.7) shows osmotic pressure of different concentration of aqueous *Azadirachta indica* gum solution.

Table (3.4) Partial Specific Volumes of Water in Different Gum Solutions in (cm^3g^{-1})

Gum sample	**Partial specific volume of water in gum**
*A.seyal*Malik(2008)	1.0016
*A.Senegal*Malik(2008)	1.0018
A.polycantha Malik(2008)	1.0021
Acacia gum Makka(2011)	1.0040
Neem gum(2016)	1.0000

Table (3.5) Partial Specific Volumes of Gum in different Gum Solutions in (cm^3g^{-1})

Gum Sample	**Partial Specific Volume of Gum**

A.seyal Malik(2008)	0.6426
A. Senegal Malik(2008)	0.6425
Apolycantha Malik(2008)	0.6421
Acacia gum Makka(2011)	0.6420
Neem gum(2016)	0.947

Table (3.6)Volume Fraction of Water (Φ_1) and *Azadirachta indica* Gum (Φ_2)in *Azadirachta indica* Gum Solution.

Gum Sample	Water Volume Fraction Φ_1	Gum Fraction Φ_2
Azadirachta indica gum	0.5136	0.4863

Table (3.7) Osmotic Pressure of *Azadirachta indica* Gum of Different Concentrations

Conc.(gcm^{-3}) %	$\sqrt{\frac{\pi}{C}}$

5	0.295
6	0.35
7	0.39
8	0.44
9	0.49
01	0.54
11	0.59

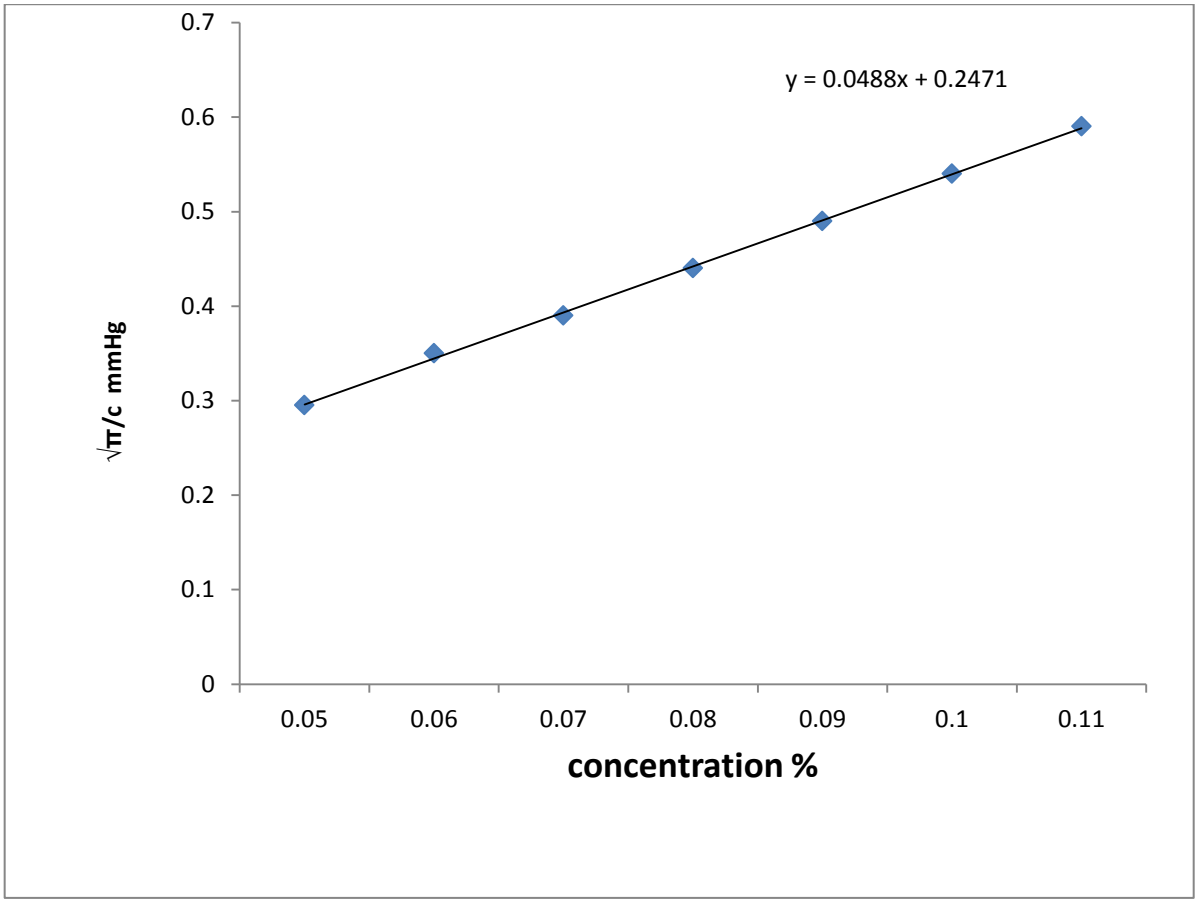

Figure 3.3 The Number Average Molecular Weight of Neem Sample

The second virial coefficient (A_2) was obtained from the slope of the graph of osmotic pressure equation (1.4.8.15) and Figure 3.3; also the number average molecular weight was obtained from the intercept of the same graph.

The second virial coefficient of *Azadirachta indicca* gum was found to be0.949×10^{-5}; which was higher compared to of A,oerfota (0.44×10^{-5}, Makka 2010) This result explained that water is good solvent for *Azadirachta indica* gum.

According to equation (1.4.6.11), it was possible to determine the chemical potential of water as a solvent in *Azadirachta indica* gum solution. Table (3.8)

Table (3.8) Chemical Potential ($\Delta\mu_1$) and Weight Fractions of Water in *Azadirachta indica* Gum Solution

Conc. gcm^{-3}	**$\bar{V}1$ $cm^3\ g^{-1}$**	**π (mmHg)**	**$\Delta\mu_1$mmH $g.cm^3g^{-3}$**	**$\Delta\mu_1$ J $g^{-1}\times10^{-3}$**	**ω_1**	**ω_2**	**ω_1/ω_2**
0.05	1.00	0.435	–0.435	-0.0 5799	0.95	0.05	19
0.06	1.00	0.735	–0.735	-0.0 9799	0.94	0.06	15.6667
0.07	1.00	1.065	–1.065	-0. 1419	0.93	0.07	13.2857
0.08	1.00	1.549	–1.549	- 0.2065	0.92	0.08	11.5
0.09	1.00	2.161	–2.161	-0. 2881	0.91	0.09	10.1111
0.1	1.00	2.916	–2.916	-0. 3888	0.90	0.1	9
0.11	1.00	3.829	–3.829	- 0.5105	0.89	0.11	8.0909

Where ω_1 and ω_2 are weight fraction of water and gum

The chemical potential of *Azadirachta indica* gum is calculated by plotting ω_1/ω_2 versus $\Delta\mu_1$, Figure(3.4) using result in Table (3.10) .The areas under the curve, that are bounded by ordinates corresponding to $\Delta\mu_2^{/}$ which less than the true areas values obtained of $\Delta\mu_2$, to correct these areas a graph of dependence $\Delta\mu_2^{/}$ versus ω_1 was plotted to obtain segment A,Table (3.11)and Figure (3.5), Then obtained the true values of $\Delta\mu_2$, Table (3.12). Free

energy of *Azadirachta indica* gum calculated by using equation (1.4.9.5).

Table (3.9) Data for Plotting the Chemical Potential of Water Versus ω_1 / ω_2

ω_1 / ω_2	$\Delta\mu_1$(erg g^{-1})
19	579.9855
15.6667	979.9754
13.2857	1419.9644
11.5	2065.2816
10.1111	2881.2611
9	3887.9025
8.0909	5105.2053

Table (3.10) Data for Plotting Chemical Potential before Correction versus Weight Fraction of Water of *Azadirachta indica* Gum Solution

$\Delta\mu_2^{/}$(erg g^{-1})	ω_1
11019.7245	0.95
15352.9804	0.94
18865.2210	0.93
23750.7384	0.92
29132.8191	0.91

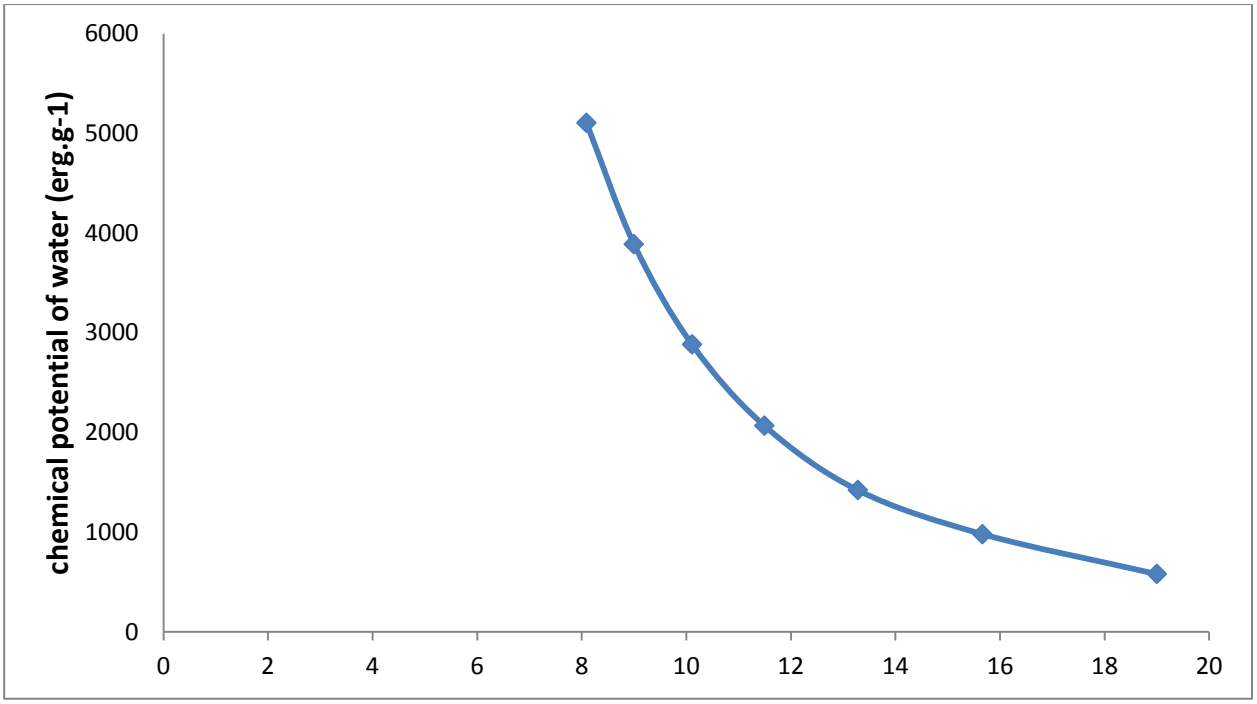

Figure 3.4 Variation of (ω_1/ω_2) with $\Delta\mu_1$

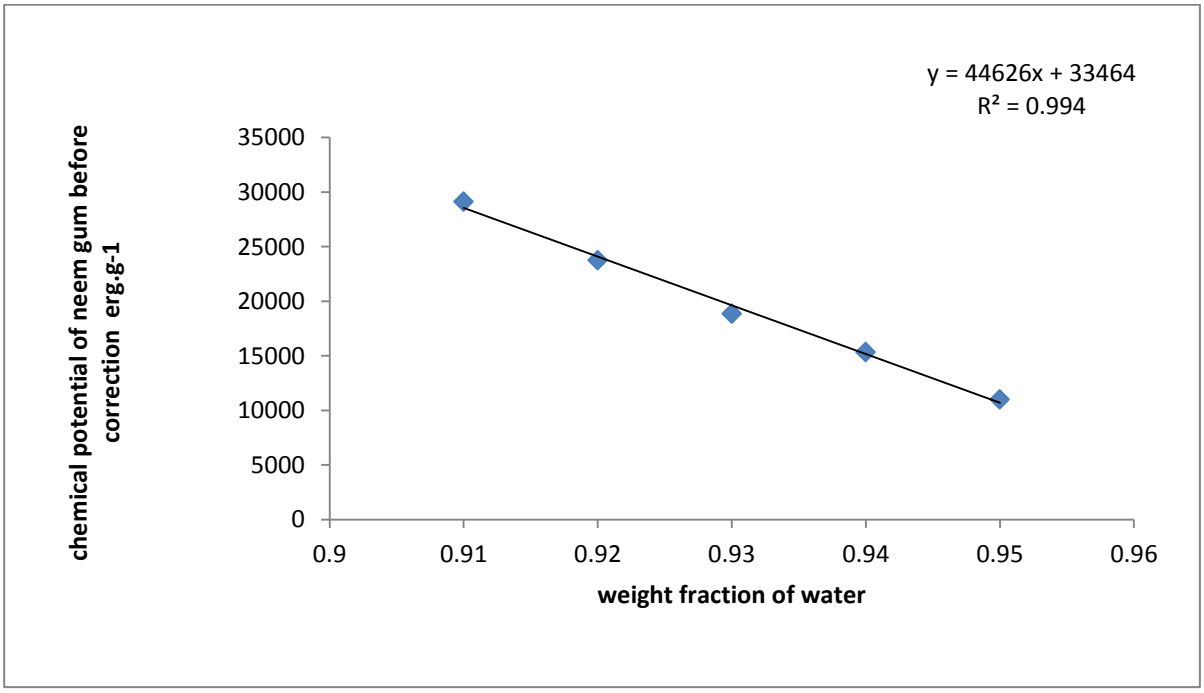

Figure 3.5 Segment A to Correct the Chemical Potential of *AzadirachtaIndica*Gum ($\Delta\mu_2$)in AzadirachtaGum Solutions.

Table (3.11) Chemical Potential ofNeemGum ($\Delta\mu_2$) inNeemGum Solution after Correction

ω_1 / ω_2	$\Delta\mu_2^{/}$(erg g^{-1})	A	$\Delta\mu_2$(erg g^{-1})
19	–11019.7	–33464	–44483.7
15.667	–15352.9	–33464	–48816.9
13.2875	–18865.2	–33464	–52329.2
11.5	–23750.7	–33464	–57214.7
10.111	–29132.8	–33464	–62596.8

Table (3.12)Calculating the Free energy of Mixing of *AzadirachtaIndica*Gum Solution

$\Delta\mu_1$(erg g^{-1})	ω_1	$\Delta\mu_1 \times \omega_1$	$\Delta\mu_2$(erg g^{-1})	ω_1	$\Delta\mu_2 \times \omega_2$	$\Delta G^m = \omega_1 \times \Delta\mu_1 + \omega_1 \times \Delta\mu_2$ (erg g^{-1})
–11019.7	0.95	–10469	–44483.7	0.05	–2224.185	–12693
–15352.9	0.94	–14432	–48816.9	0.06	–2929.014	–17361
–18865.2	0.93	–17545	–52329.2	0.07	–3663.044	–21208
–23750.7	0.92	–21851	–57214.7	0.08	–4577.176	–26428
–29132.8	0.91	–26511	–62596.8	0.09	–5633.712	–32145

Table (3.13) Free energy of Mixing of *AzadirachtaIndica*Gum Solution in Different Units

Conc. gcm^{-3}	**ΔG^m(erg g^{-1})**	**ΔG^m(j g^{-1})**
0.05	–12693	-1.2693×10^{-3}
0.06	–17361	-1.7361×10^{-3}
0.07	–21208	-2.1208×10^{-3}
0.08	–26428	-2.6428×10^{-3}
0.09	–32145	-3.2145×10^{-3}

The change in the chemical potential of *AzadirachtaIndica*, *A.oerfota, A. Seyal, A. Senegal and A. Polyacantha* gums at different concentrations was shown in table (3.15). The great change in the chemical potential was in *Polyacantha* gums and then A. Senegal gum then A. Seyal gum then A.oerfota gum and

finally *AzadirachtaIndica*gum which have small vaues.This indicated that A. Polyacantha inter act with water more than the other four types.

The free energy of mixing of *AzadirachtaIndica*, A.oerfota, A. Seyal, A. Senegal and A. Polyacantha gums at different 0concentrations was shown in table (3.16). These results show that A. *Polyacantha* gum has a great change in free energy of mixing values, followed by A. *Senegal* gum, A. *Seyal* gum, *A.oerfota* gum and finally *AzadirachtaIndica*gum .athis indicates that the the order of interaction of the gums decreases from A. *Polyacantha* gum to A. *Senegal* gum, A. *Seyal*gum to *A.oerfota*gum and then *AzadirachtaIndica*gum.

Table (3.14) Chemical Potential of *AzdirachtaIndica, A.oerfota, A. Seyal, A. Senegal and Polyacantha*Gums Solutions

Conc % (gcm^{-3})	$\Delta\mu_2(j\ g^{-1})\times10^{-2}$				
	This study(2017)	**A, oerfota (Makka 2010)**	**A.seyal (Malik 2008)**	**A. Senegal (Malik 2008)**	**Polyacantha (Malik2008)**
3%	ND	ND	ND	–14.10909091	–23.59673469
4%	ND	ND	ND	–13.96363637	–23.35346939
5%	–0.444837	ND	–7.1236875	–13.81818182	–23.11000408
6%	–0.488169	ND	–7.0981750	–13.67272728	–22.86693877
7%	–0.523292	–0.887637	–7.0226625	–13.52727273	–22.62367347
8%	–0.572147	–0.95991	–6.9471500	–13.38181819	–22.38040516
9%	–0.625968	–0.998799	–6.8716397	ND	ND
10%	ND	–1.13366	–6.7961250	ND	ND

Table (3.15) Free energy of Mixing of *AzdirachtaIndica, A.oerfota, A. Seyal, A. Senegal and Polyacantha*Gums with Water in (j g^{-1})

Conc % (gcm^{-3})	ΔG^m(j g^{-1}) × $\mathbf{10^{-2}}$				
	This stud (2017)	A, oerfota (Makka 2010)	A.seyal (Malik 2008)	A.senegal (Malik 2008)	Apolyacantha(Malik2008)
3%	ND	ND	ND	–0.5075	–0.8090
4%	ND	ND	ND	–0.6957	–1.0983
5%	–0.12693	ND	–0.475	–0.9091	–1.4220
6%	–0.17361	ND	–0.588	–1.1518	–1.7392
7%	–0.21208	–0.20016608	–0.714	–1.3617	–2.0940
8%	–0.26428	–0.2547507	–0.833	–1.6615	–2.4780
9%	–0.32145	–0.30367833	–1.010	ND	ND
10%	ND	0.3687722	–1.150	ND	ND

The values of free energy of mixing, change in chemical potential, secondvirial coefficient and the partial specific volumes indicate the good interaction of *AzadirachtaIndica*gum under study with water as a solvent.

3.3Conclusion

The physiochemical properties of the sample were tested:

- Moisture Content 13.07%.
- Ash Content 3.13%.
- Protein Content 32%.
- PH 6.5.
- Optical rotation +65.5%.
- Average molecular weight 4.08×10^{6} g /mole.

The Thermodynamic properties f *AzadirachtaIndica*(Neem) gum was estimated:

- Partial Specific Volume $0.947cm^{3}g^{-1}$.
- Volume Fraction $0.4863\ cm^{3}g^{-1}$.
- Chemical Potential in range between $(-0.444837$ to $-0.625968)\times10^{-2}jg^{-1}$.
- Free energy of mixing between $(-0.12693$ to $-0.32145)\times10^{-2}jg^{-1}$.
- The second virial coefficient $0.94x10^{-5}$.

3.4Suggestion for further work

- Determination of enthalpy.
- Studding of the toxicity of the samplefor Food application.
- Fractionation of the gum.

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