



Physicochemical, Spectroscopic and Rheological Characterization of *Anacardium occidentale* gum Exudates

Nnabuk Okon Eddy^{1,2*}, Inemesit Udofia¹, Edward Okey³,
Anduang O. Odiongenyi² and Patrick Udofia⁴

¹Department of Chemistry, Ahmadu Bello University, Zaria, Kaduna State, Nigeria.

²Department of Chemistry, Akwa Ibom State University, Ikot Akpaeden, Mkpatt Enin, Akwa Ibom State, Nigeria.

³Department of Biological Sciences, Akwa Ibom State University, Ikot Akpaeden, Mkpatt Enin, Akwa Ibom State, Nigeria.

⁴Department of Science Technology, Akwa Ibom State Polytechnic, Ikot Osurua, Ikot Ekpene, Akwa Ibom State, Nigeria.

Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

Anacardium occidentale gum exudate was analyzed for physicochemical, spectroscopic and rheological characteristics. Physicochemical analysis revealed that the gum is mildly acidic, ionic, extremely rich in carbohydrate and calcium. GCMS spectrum revealed the presence of some carboxylic acids, ketone and alkanes. The FTIR spectrum of the gum closely resembled those of other polysaccharides. Scanning electron micrograph revealed the presence of pores containing particles with irregular shapes. The average value of intrinsic viscosity of the gum was 3.28 dL/g.

*Corresponding author: E-mail: nabukeddy@yahoo.com;

which compared favourably with those obtained for some plant gums. From the Huggins, Kraemer and Power law models, it was deduced that there is absence of molecular association and that the conformation of the gum is more rod like. Viscosity of the studied gum was found to be greatly influenced by the presence of urea, K⁺, Ca²⁺ and Al²⁺. *Anacardium occidentale* gum exhibited a non-Newtonian property with characteristics dilatant and shears thickening properties.

Keywords: *Anacardium occidentale* L. gum; characterization; GCMS; SEM; FTIR and rheology.

1. INTRODUCTION

Gums are useful in the paper, mineral processing, pharmaceutical, food and other industries [1]. However, selectivity in the utilization of gums has been an issue of concern. Gums from Acacia species are used for pharmaceutical, confectionary, food, textile and beverage production [2]. Gums as additives play important roles in pharmaceutical preparations such as tablet, lotions, suspensions, syrups and ointments [3]. Carob bean gum is used as thickener, stabilizer, emulsifier, gelling agent. The gum is compatible with xanthan gum and forms gel, which can influence the gelling properties of carrageenan and agar. Also, Gum arabic is an efficient emulsifier and a long-term stabilizer in food and cosmetic products containing oil–water interfaces [4].

Most gums meet their industrial potentials best on their physicochemical and rheological characteristics [5]. For example, food gums must not be toxic, its viscosity should be within the expected range [6], gums use as pharmaceutical excipients should have good compatibility factor (which is a function of its rheological properties) and must not be toxic [7] and the nitrogen or protein content of a gum is an index for assessing its emulsifying properties [8]. In our research group, we have studied physicochemical and rheological properties of some gums and found that most of them have great potentials for numerous industries [2]. Gum is cheap and abundant in the various regions in Nigeria. Therefore, our present study is aimed at investigating the physicochemical and rheological properties of *Anacardium occidentale* L. (AO) gum exudate using instrumental and conventional techniques.

AO gum is gotten from AO (cashew) tree, which is a medium-sized tree, spreading, evergreen and much branched. The tree grows to a height of about 12 m but rarely exceeds 6 m on lateritic coastal sandy areas. The leaves of the plants are simple, alternate, glabrous, and obovate-rounded at the ends. The bark contains acrid sap of thick

brown resin, which becomes brownish on exposure to air. This gum has been found to be useful as indelible ink in marking and printing linens and cottons. The resin is also used as a varnish and as a preservative for fishnets. The stem of the plant can also yields an amber-coloured gum, which is partly soluble in water, and has the capability of swelling into a jelly-like mass. This gum is a good adhesive for wood work and has strong anti-insecticidal properties.

In view of the broad spectrum of industrial applications of some plant gums and the need to search for more gums, whose properties could match the requirement for such applications, the present study is aimed at investigating the physicochemical, spectroscopic and rheological properties of AO gum exudates.

2. MATERIALS AND METHODS

2.1 Collection and Purification of Samples

Crude AO gum exudate was obtained in dry season from cashew tree obtained in Ikot Ekpene (geographical coordinates: 5° 10' 0" North, 7° 43' 0" East) in Akwa Ibom State, Nigeria. Injury was sustained on the stem of the tree and the gum samples that exudated from the injured stem were collected. In order to purify the gum, the gum sample was dried in an oven at 40°C for 2 hours. The dried gum was grounded with a blender, dehydrated in chloroform water (ratio: 70: 30 for water: chloroform) for five days and then strained through a 75 µm sieve to obtain particulate free slurry which was allowed to sediment. Thereafter, the gum was precipitated from the slurry using absolute ethanol, filtered and defatted, using diethyl ether. The precipitate was re-dried at 40°C for 48 hours. The dried flakes were pulverized using a blender and stored in an air tight container.

2.2 Physicochemical Analysis

In order to characterize the gums, it was subjected to the following physicochemical analysis.

2.2.1 Percentage yield of the purified gums

In order to estimate the percentage yield of the gum, the purified sample was weighed and the yield was calculated as a percentage of crude gum.

2.2.2 Percentage moisture sorption

In order to determine the water sorption capacity of the gum, 2.0 g of the gum was weighed into a dried evaporating dish. The final weight of the dishes was noted and placed over water in a desiccator. After 5 days, the dish was transferred to another desiccator for another 5 days. The percentage sorption was calculated by difference in weight.

2.2.3 Determination of solubility

The solubility of the gum (in water and other solvents) was determined by adding 1.0 g of the gum to 50 ml of the solvent and left overnight. 25 ml of the clear supernatants were taken in small pre-weighted evaporating dishes and heated to dryness over a digital thermostatic water bath. The weights of the residue with reference to the volume of the solutions were determined using a digital top loading balance (Model.XP-3000) and expressed as the percentage solubility of the gums in the solvents [6].

2.2.4 Concentration of metal ions

Concentrations of Fe, Mg, Cu, Cd, Ni, Pb, Zn, Mn, Ca and Cu ions in the gums were determined using Perkin Elmer atomic absorption spectrophotometer. Calibration curve for each of the metal ions was prepared and the concentration of the respective metal ion was estimated by extrapolation method [9].

2.2.5 Determination of nitrogen and protein contents of the gum

The nitrogen content of the gum was determined using the Kjeldahl method and the protein content was estimated by multiplying the nitrogen content by a conversion factor of 6.25 [9].

2.2.6 pH of the gum

The pH of the gum was determined by shaking 1% w/v of the gum dispersion in distilled and deionized water (pH = 6.98) for 5 minutes and the pH was determined using a pre-calibrated Oaklon pH meter (Model 1100).

2.2.7 Refractive index

In the determination of refractive index of the gum, Eloptron refractometer was used.

2.2.8 Moisture content

In the determination of the moisture content of the sample, the oven drying method was used as described in AOAC [9].

2.2.9 Ash content

The ash content of the sample was determined using the method recommended by AOAC (1986).

2.2.10 Crude lipid content

The lipid content was determined using the method recommended by AOAC [9].

2.2.11 Crude fibre

The method described by AOAC [9] was adopted for the determination of the fibre content of the sample.

2.2.12 Determination of total carbohydrate content

The total carbohydrate content of was determined by the method of difference. The sum of the percentage moisture, ash, crude lipid, crude protein, and crude fibre contents of the gum was subtracted from 100, in order to estimate the total carbohydrate content of the gum [9]:

$$\% \text{ Total carbohydrate} = 100 - (\text{Moisture} + \text{Ash} + \text{Fat} + \text{Protein} + \text{Fibre}) \%$$

2.2.13 Measurement of turbidity, conductivity and salinity

The turbidity of the gum solution was measured using turbidity meter while conductivity and salinity were measured using Mettler Toledo conductivity meter.

2.2.14 Determination of wavelength of maximum absorption (λ_{max})

Wavelength of maximum absorption of the gum solution was determined by scanning for the absorption of the gum solution through various wavelengths, using a spectrophotometer. The

wavelength that gave maximum absorption was recorded as the λ_{\max} for the sample [9].

2.3 Gas Chromatography Mass Spectrophotometer (GCMS)

GCMS analysis was carried out on a GC clarus 500 Perkin Elmer system which has a AOC-20i Autosampler and a Gas Chromatograph interfaced to a Mass Spectrometer (GC-MS). The instrument employed the following conditions: a column Elite-1 fused silica capillary column (30 × 0.25 mm ID × 1 μ mdf, composed of 100% Dimethyl poly dioxane), operating in electron impact mode at 70 eV. The carrier gas (99.9% helium) was injected at a constant flow rate of 1 ml/min and an injection volume of 0.5 μ L was employed (split ratio of 10:1) while the injector and the ion-source temperatures were 250°C and 280°C respectively. The oven temperature was programmed from 110°C (isothermal for 2 min), with an increase of 10°C/min, to 200°C, then 5°C/min to 280°C, ending with a 9 min isothermal at 280°C. Mass spectra were taken at 70 eV; a scan interval of 0.5 seconds and fragments from 40 to 450 Da were also used. The total GC running time was 36 minutes.

2.3.1 Interpretation of GC-MS spectrum

Interpretation of the GCMS mass spectrum of the gum was done using the database of the National Institute Standard and Technology (NIST) library, which has more than 62,000 patterns. The spectrum of the unknown component was compared with the spectrum of the known components (stored in the NIST library). The name, molecular weight and structure of the components of the test materials were also ascertained through the data base in the library. Concentrations of the identified compounds were determined using average values obtained from area and height normalizations.

2.4 Viscosity Measurements

The intrinsic viscosity of the gum sample was determined in distilled water using a Cannon Ubbelohde capillary viscometer (Cannon Instruments, model I-71), immersed in a precision water bath maintained at 25°C. The apparent viscosity of the mucilage was measured using a digital Brookfield DV I prime viscometer while shear rate was measured using Schott Iberica, S.A 18549 rotational viscometer.

2.5 Scanning Electron Microscopy

The morphology of the gum was studied using an EVOS 13LS-Zeiss model of scanning electron microscope. The dried sample was mounted on a metal stub and sputtered with gold in order to make the sample conductive, and the images were taken at an accelerating voltage of 10 kV using different magnifications.

2.6 FTIR Analysis

FTIR analysis of gum was carried out using Shimadzu FTIR-8400S Fourier transform infrared spectrophotometer. The gum sample was prepared in KBr and the analysis was carried out by within a wave number range of 400 to 4000 cm^{-1} .

3. RESULTS AND DISCUSSION

3.1 Physicochemical Properties

Table 1 presents physicochemical properties of AO gum exudate. From the results obtained, AO gum was found to be milky yellow in colour (Figure not shown) and had a stinky odour. The gum is mildly acidic (pH = 4.88), with a sour taste as expected. The gum is soluble in water but insoluble in ethanol, acetone and chloroform. The solubility of the gum in water increases with increase in temperature while its conductivity (219 $\mu\text{s}/\text{cm}$) was comparable to the range of values expected for ionic compounds, suggesting that the gum is ionic. Total dissolved solute content of the gum was measured as 160 mg/L while its salinity was as low as 0.4 ‰, indicating that the conductivity or ionic character of the gum is less influenced by concentrations of chloride ions in the gum. The maximum wavelength of adsorption by the gum was measured as 310 nm. Consequently, spectroscopic study on the gum can be done at this wavelength.

The nitrogen and protein contents of AO gum were 0.71 and 4.46% respectively. Nitrogen and amino acid contents of gums are useful parameters for distinguishing gums of different species. For example, Karamalla et al. [9] stated that the range of value expected for the nitrogen content of purified gum arabic is 0.26–0.39%, which is lower than the value obtained in this study. In Acacia sengal gum, concentration of nitrogen is reported to be in the range, 0.21 to 0.35% [10-13]. Jafar et al. [14] stated that the mean nitrogen content of Ferula gumosa gum is 0.69%, Mhinzi [15] gave the range of values for the nitrogen content of some Albizia gums to be

Table 1. Physicochemical parameters of AO gum

Parameter		Parameter(ppm)	
Colour	milky-yellow	Mn	1.427
Odour	offensive	Fe	1.211
Taste	sour	Zn	1.199
pH (29.2°C)	4.88	Pb	0.126
Percentage yield (% w/v)	86.60	Mg	0.425
Swelling capacity	12	Cd	Not detectable
Solubility in cold water	8.4	Ca	19.050
Solubility in hot water	8.9	Cu	0.068
Acetone	0.0	Ni	0.110
Chloroform	0.0		
Ethanol	0.0		
TDS (mg/l)	160.2		
Conductivity ($\mu\text{s}/\text{cm}$)	218.5		
Salinity (0/00)	0.4		
Turbidity (FAU)	1098		
λ_{max} (nm)	310		
Melting point ($^{\circ}\text{C}$)	204-216		
Nitrogen (%)	0.49		
Protein (%)	3.06		
Ash content (%)	0.47		
Fat and Oil (%)	1.00		
Moisture content (%)	12.0		
Carbohydrate (%)	83.47		
Fibre content (%)	0.0		

0.46 – 1.09%. From the above, it can be seen that the nitrogen contents (hence protein contents) of the studied gum is relatively higher than those reported for some plant gums. The important of nitrogen (hence protein) in gum cannot be overemphasized. According to Pablyana et al. [16], the presence of protein in polysaccharide can induce inflammatory response to tissue and the response may have a vital role to play in its pharmacological applications.

A close examination of the proximate composition of AO gum reveals that the gum is rich in carbohydrate (81.82%). This data agrees with values obtained for some carbohydrate polymers. For example *Raphia hookeri* gum (77.42 – 85.40%: [17]) and those in eleven species of some *Acacia* gums ($\approx 90\%$: [18]). Although fibre is absent in AO gum exudate (0.00%), the ash content of the gum (hence its inorganic composition) was found to be 0.47% indicating that the gum has higher organic than inorganic content. In order to ascertain the inorganic contents of the gum, determination of metallic ions was carried out and the results obtained are also presented in Table 1.

The cationic compositions of AO gum are also presented in Table 1. The results show that AO gum exhibited a decreasing trend in metal ion composition as follows, Ca (19.050 ppm) > Mn (1.407 ppm) > Fe (1.211 ppm) > Zn (1.191 ppm) > Mg (0.425 ppm) > Pb (0.126 ppm) > Ni (0.110 ppm) > Cu (0.068 ppm) > Cd (-0.001 ppm). The order reveals excessive concentration of calcium ion; trace concentrations of trace elements (i.e elements needed in minute quantities) and very low concentration of Pb, Ni, Cd and Cu (which are heavy metals that are toxic, at concentration above permissible limit). Therefore, the measured concentrations of cations in AO gum do not pose toxicity threat [19]. Hence, AO gum may be suitable as food additive or pharmaceutical excipients, if properly purified.

The water sorption capacity of the gum (Figure, not shown) was found to increase with time but between 4 and 5 days, the sorption capacity started decreasing indicating that the gums reaches its maximum adsorption capacity after 5 days of contact. Sorption capacity of a gum may be used as an index for estimating the duration, under which the gum can be in a stable condition.

3.2 Spectroscopic Studies

Table 2 presents information deduced from the GCMS spectrum of AO gum (spectrum not shown). The results obtained indicated the presence of 1.13% of 2-(3-hydroxy-2-nitrocyclohexyl)-1-phenylethanone (retention time = 5.483 minutes) in the first fraction (i.e line 1). Between lines 2 and 5, some alkanes including decane (3.70%), undecane (4.93%), n-dodecane (3.58%), and hexadecane (1.46%) were identified. These alkanes were identified at retention time values of 5.717, 7.775, 9.883 and 11.917 minutes respectively. In lines 6 to 11, various streams of carboxylic acids were identified. These included 12.54% palmitic acid, 11.53% n-hexadecanoic acid, 14.13% 9,12-octadecadienoic acid, 30.86% 9-octadecenoic acid, 5.12% octadecanoic acid and 11.03% hexadecenoic acid.

The FTIR spectrum of AO gum is presented in Fig. 1. The FTIR spectrum is seen to exhibit features that are typical for polysaccharides. The presence of strong and broad absorption bands at 3546, 3333 and 3220 cm^{-1} indicated the presence of OH stretch vibrations [20]. The =CH stretch and a sharp CH stretch at 3133 and 2911 cm^{-1} respectively, were also observed in the spectrum of AO gum. Other prominent peaks were C-O stretch at 1631 cm^{-1} , OH bending at 1402 and 1277 cm^{-1} respectively, C-O stretches at 1141 and 1067 cm^{-1} respectively and C-H bending vibrations due to alkynes were also found at 698 and 614 cm^{-1} respectively.

Scanning electron microscopy (SEM) is utilized to record the images of a surface of a material at a desired position. It is capable of producing topographic/morphological picture with better resolution and depth of focus compare to an ordinary optical microscope. In application to polymers, scanning electron micrograph aids in the visualization of phase morphology, surface and cross-sectional topography, surface molecular order and elucidation of failure mechanism [21]. SEM image for AO gum at different magnifications are presented in Fig. 2. At a magnification of 1.00 KX, AO gum is seen to have a smooth structure with irregular spaced pores and network. At higher magnifications (3.00 and 5.00 KX), it was seen that each pores contains particles with irregular shapes and dimensions.

3.3 Rheological Study

3.3.1 Effect of concentration and pH on the viscosity of AO gum

The absolute viscosity of AO gum was found to vary with concentration and pH (Figure not shown) such that the viscosity increases with increase in concentration. This may be attributed to increase in intermolecular attraction arising from increasing molecular mass. It was also found that the gum exhibited an initial pH value of 4.62 which is within the range of 2.48 to 6.52 expected for gum solutions [22]. Increase in pH of AO gum was accompanied by corresponding increase in absolute viscosity of the gum, a trend that has been observed for most plant gums.

Table 2. Analytical parameters deduced from GCMS spectrum of AO gum

Line no	IUPAC name	Molecular formula	Molar mass (g/mol)	Retention time (minute)	Concentration (%)
1	2-(3-hydroxy-2-nitrocyclohexyl)-1-phenylethanone	$\text{C}_{14}\text{H}_{17}\text{NO}_4$	263	5.483	1.13
2	Decane	$\text{C}_{10}\text{H}_{22}$	142	5.717	3.70
3	Undecane	$\text{C}_{11}\text{H}_{24}$	156	7.775	4.93
4	n-dodecane	$\text{C}_{12}\text{H}_{26}$	170	9.883	3.58
5	Hexadecane	$\text{C}_{16}\text{H}_{34}$	226	11.917	1.46
6	Palmitic acid	$\text{C}_{17}\text{H}_{34}\text{O}_2$	270	22.508	12.54
7	n-hexadecanoic acid	$\text{C}_{16}\text{H}_{32}\text{O}_2$	256	23.417	11.53
8	9,12-octadecadienoic acid	$\text{C}_{19}\text{H}_{34}\text{O}_2$	294	26.450	14.13
9	9-octadecenoic acid	$\text{C}_{19}\text{H}_{36}\text{O}_2$	296	26.650	30.86
10	Octadecanoic acid	$\text{C}_{19}\text{H}_{38}\text{O}_2$	298	27.258	5.12
11	Hexadecenoic acid	$\text{C}_{16}\text{H}_{30}\text{O}_2$	254	27.558	11.03

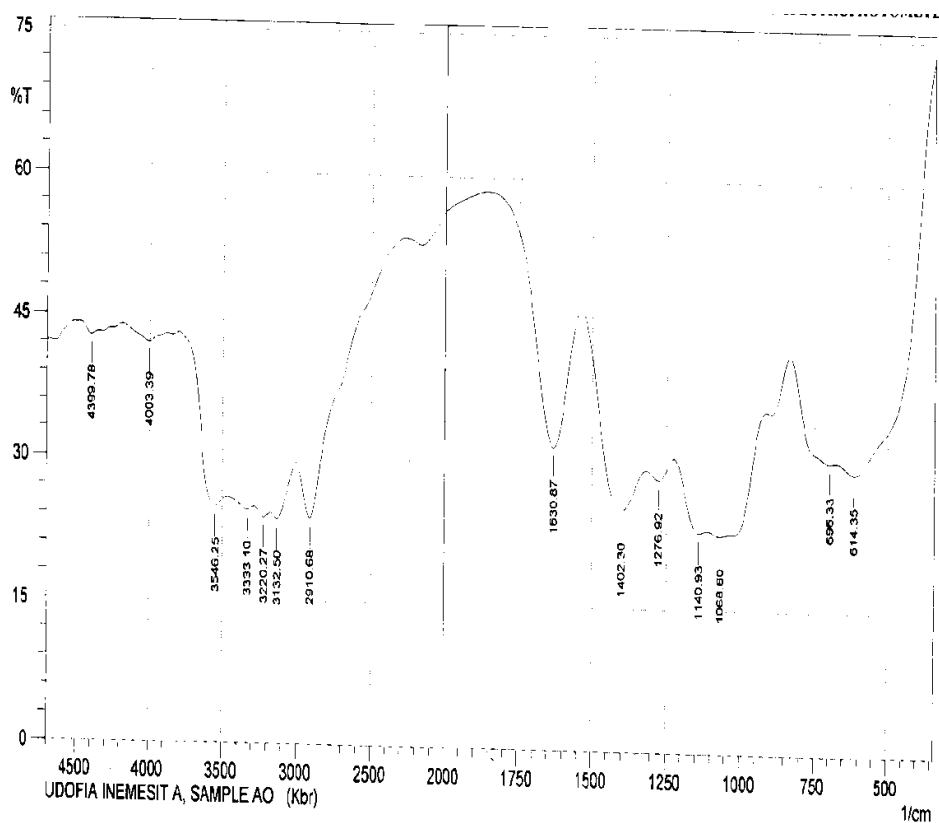


Fig. 1. FTIR spectrum of AO gum

3.3.2 Intrinsic viscosity

The intrinsic viscosity of a polymer solution can be defined in terms of the following limit,

$$[\eta] = \lim_{C \rightarrow 0} \frac{\eta_{sp}}{C} = \lim_{C \rightarrow 0} \frac{\eta_r - 1}{C} \quad (1)$$

Intrinsic viscosity is a measure of hydrodynamic volume occupied by a polymer solution. Classically, it can be determined by measuring the viscosity of various concentrations of a polymer solution, followed by extrapolation of a plot of η_{sp}/C to zero concentration. It has been found that in the range of moderate concentrations, the dependence is linear and shows obedient to the Huggins equation expressed in equation 2 [24]:

$$\frac{\eta_{sp}}{C} = [\eta] + k_H [\eta]^2 C \quad (2)$$

where k_H is the (dimensionless) Huggins constant and C is the concentration of the polymer. From equation 2, the intrinsic viscosity can be obtained as the intercept in the linear least square fit. Alternatively, the intrinsic viscosity can be obtained by a linear

extrapolation of the inherent viscosity, $\eta_{inh} = (\ln \eta_{rel})/C$ according to the Kraemer equation [24]

$$\frac{\ln \eta_{rel}}{C} = [\eta] + k_K [\eta]^2 C \quad (3)$$

Fig. 3 shows Huggins and Kraemer plots for AO gum. The figure displayed a high degree of fitness of the data for both models ($R^2 = 0.9047$ and 0.9096). Also, the intrinsic viscosity was evaluated as 3.6965 and 2.863 dL/g from the Huggins and Kraemer plots respectively. These values gave an average of 3.2798 dL/g, which corresponded to the range of values reported for some plant gums [23]. Based on several experimental observations, the k_H has some physical meaning. In a theta solvent, value of k_H is expected to be low and theoretically, the value should be within the range of 0.3 to 0.8 in a theta solvent [24]. Calculated value of k_H for AO gum (0.3) is relatively low and is within the range of values expected for most gums in a theta solvent and indicate the absence of polymer-polymer aggregation [25]. Ideally, the sum of k_H and k_K should be equal to 0.5 ± 0.1 . Larger or smaller values are attributed to molecular association. In this study, the absence of molecular association

was upheld since the sum (0.6) falls within the expected.

3.3.3 Molecular conformation and coil overlap parameter

Molecular conformation and levels of interaction of the gums were studied using the power law equation, which can be written as follows [26]:

$$\eta_{sp} = aC^b \quad (4)$$

From the natural logarithm of equation 4, equation 5 was obtained. Thus a plot of $\ln(\eta_{sp})$ versus C is expected to be linear with slope and intercept equal to 'b' and $\ln(a)$ respectively.

$$\ln \eta_{sp} = \ln a + b \ln C \quad (5)$$

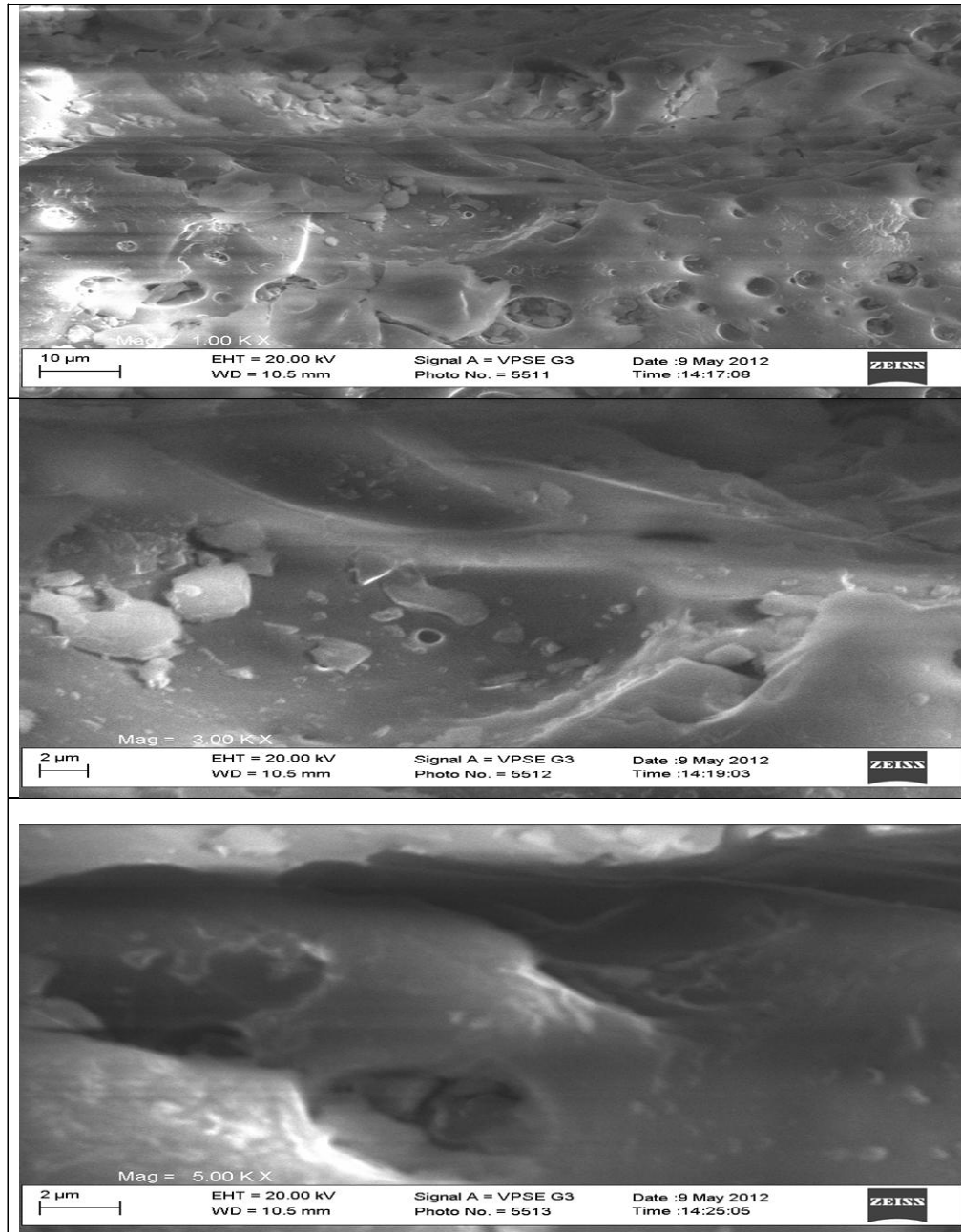


Fig. 2. Scanning electron micrograph of AO gum at various magnifications

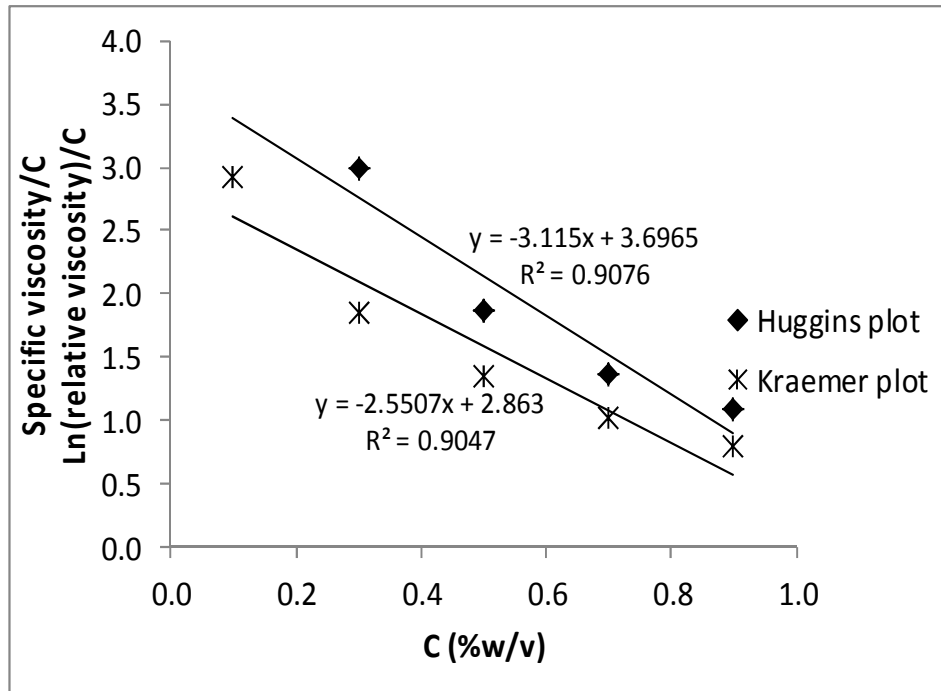


Fig. 3. Huggins and Kraemer plots for AO gum

Using equation 5, the Power law plot was developed for AO gum (Plot, not shown) and the measured degree of linearity was good ($R^2 = 0.9356$). Values of 'b' and 'a' deduced from the intercept and slope of the plot were 0.052 and 0.9707 respectively. According to Lapasin and Prici [27], 'b' value greater than unity is associated with random coil conformation while 'b' value less than unity is associated with rod like conformation. Therefore, molecular conformation of AO gum is more rod/coil like than random like. In dilute solutions, the polymer coils are separated from each other and are free to move independently but with increasing concentrations, the coil will start to overlap and interpenetrate one another and may give rise to a change in conformation [28]. Morris et al. [29] also stated that the transition from dilute solution to concentrated solutions is usually accompanied by pronounced change in concentration dependence of solution viscosity and the corresponding concentration is called critical or coil overlap concentration (C^*). In this study, a plot showing the dependence of the specific viscosity (at zero shear rate) of AO gum on the coil overlap parameter, $C[\eta]$ revealed the existent of concentrated and dilute regimes (Figure, not shown). The slope values for the first and second regimes were 0.07 and 0.20 respectively. This

indicates that at $C < C^*$, $\eta_{sp0} \propto C^{0.07}$ and at $C > C^*$, $\eta_{sp0} \propto C^{0.20}$. The corresponding coil overlap parameter and critical concentration for the gum were calculated as, $C^*[\eta] \sim 2.81$ and 1.13 g/dL respectively.

3.3.4 Thermodynamic parameter of viscous flow

The specific viscosity of AO gum was also found to decrease with increase in temperature, which indicated that temperature tends to destroy molecular association. In order to verify the possibility of degradation or conformational changes during heating, the viscosities of the gum were also measured during cooling and no differences in viscosity were observed indicating the absence of degradation or conformational transition.

The activation energy of flow of AO gum was calculated using the Arrhenius-Frenkel-Eyring equation (equation 6) [30,31]:

$$\eta = A \exp\left(\frac{-E_f}{RT}\right) \quad (6)$$

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 6, equation 7 was obtained,

$$\ln \eta = \ln A - \frac{E_F}{RT} \quad (7)$$

Equation 7 reveals that a plot of $\ln \eta$ versus $1/T$ should be linear with slope and intercept equal to E_F and $\ln A$ respectively. Fig. 4 shows the Arrhenius-Frenkel-Eyring plots for AO gum. The plot revealed a good degree of linearity ($R^2 = 0.8833$) while calculated value of E_F was 15.85 kJ/mol, which is within the range of values reported for Albezia lebbeck gum by de Paula et al. [32] and for those of gum Arabic (15 kJ/mol; [33]), *A. occidentale* gum (16.2 kJ/mol; [34]) and that of *A. macrocarpa* gum (16.8 kJ/mol; [35]). It has been found that low activation energy of flow indicates few inter- and intra-interactions between polysaccharide chains in the concentration range investigated. Also, the higher the value of E_F , the less sensitive is the polymer to temperature change [36,37]. From the results of the present study, it can be deduced that there is existence of few inter and intra molecular interactions in the studied gum.

Thermodynamic parameters of viscous flow were calculated using the Frenkel-Eyring equation which can be written as follows [38],

$$\ln \left(\frac{\eta}{T} \right) = \left(\ln A - \frac{\Delta S_V}{R} \right) + \frac{\Delta H_V}{RT} \quad (8)$$

where A is the pre-exponential factor, R is the universal gas constant, T is the absolute temperature, ΔS_V and ΔH_V are the entropy change and enthalpy change of viscous flow respectively. From equation 8, a plot of $\ln(\eta/T)$ versus $1/T$ is expected to be linear with slope and intercept equal to $\Delta H_V/R$ and $(\ln A - \Delta S_V/R)$ respectively. Fig. 4 reveals that the flow behavior of AO gum fitted the Frenkel-Eyring model ($R^2 = 0.9043$). Calculated values of ΔH_V and ΔS_V were 13.27 and -56.02 kJ/mol respectively. From the results obtained, it can be stated that the attainment of the transition state for viscous flow is accompanied by bond breaking. The entropy change of activation from the initial to the transition states at a given composition is significant during an activated viscous flow process; therefore this process is entropy-controlled. According to Ahmad et al. [39] negative values of ΔS_V is associated with uncoiling and orientation of the polymer molecules and the system becomes more ordered in the course of flow. On the other hand, calculated values of ΔH_V are related to the amount of energy needed by the gum molecules to jump from one equilibrium position to another (i.e the potential energy barrier).

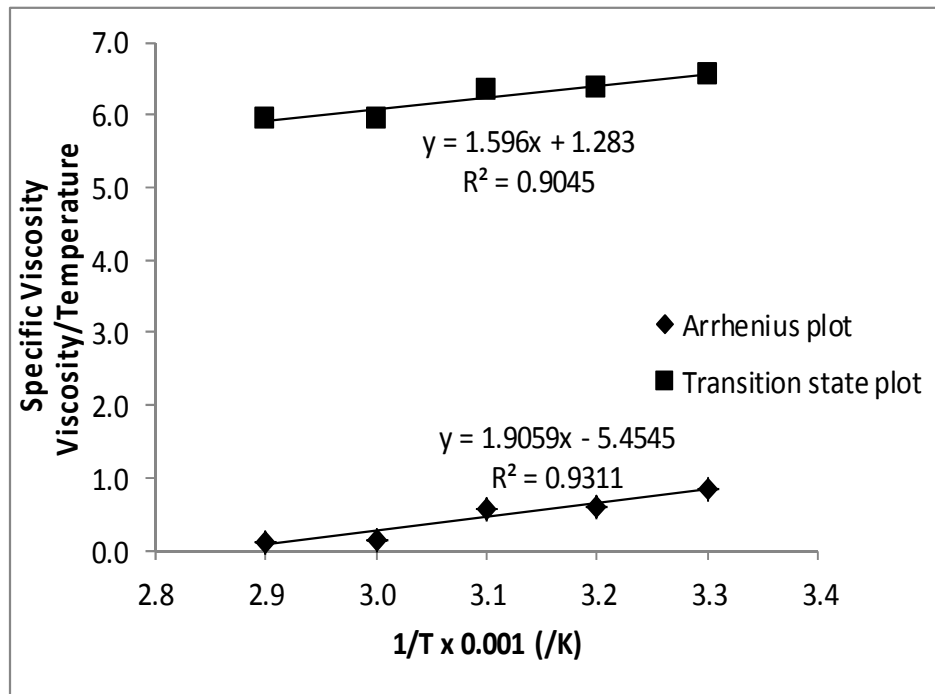


Fig. 4. Arrhenius and transition state plots for viscous flow of AO gum

3.3.5 Effect of electrolyte

AO gum is acid polysaccharides containing various metal ions (including Mn, Fe, Zn, Mg, Ca, Cu, Ni, Na and K ions) as neutralized cations. It has been found that due to their cationic content, exudate gums behaves as polyelectrolyte [32]. Therefore, the solution viscosity of the gums can be affected by the addition of other electrolytes. Fig. 5 shows the variation of absolute viscosity of AO gum with concentration in the presence of 0.1 M of KCl, CaCl₂, AlCl₃ and urea respectively. The figure revealed that the viscosity of the studied gum increased when 0.1 M of urea, K⁺, Ca²⁺ and Al³⁺ were respectively added. This increase, correlated with the magnitude of charges on the ions (i.e. K⁺>Ca²⁺>Al³⁺). According to de Paula et al. [32], increase in viscosity through addition of electrolyte can be attributed to alteration in the strength of intermolecular interactions between the gum molecules and the added electrolyte. This alteration is due to screening of charges and contraction of the macromolecule in the presence of counter ion. It was also found that the presence of K⁺ increases the viscosity of AO gum because it has a better steric capability of gelling the gum compared to Ca²⁺. This capability is less or absent in Al³⁺ hence K⁺ exhibited the greatest potential to increase the viscosity of AO gum, followed by Ca²⁺ and lastly by Al³⁺. It has also been found that in a dilute solution, the turbidity of dilute polyelectrolyte increases with increase in the charge of the ions due to the effect of charged ions on the turbidity of the gum solution [39]. The terms kosmotrope and chaotrope are used to describe ions that are capable of reinforcing or breaking the hydrogen-bonded network of the water molecules. Kosmotropes are usually small (in terms of crystallographic radii), strongly hydrated ions while chaotropes are relatively large and poorly hydrated. K⁺, Ca²⁺ and Al³⁺ are all chaotropes but their relative strength correspond to their ionic radii, which is also related to the charge/ionic ratio. Thus Al³⁺ is more chaotropic than Ca²⁺, which in turn is more chaotropic than K⁺. Therefore K⁺ has the highest tendency to bind the water molecule in the gum into their hydration sheath leaving behind less free water molecule to hydrolyse/solubilize the polymer chain. Under this condition strong polymer-polymer interactions are more favourable than polymer-solvent interactions hence the viscosity of the polymer will increase and vice versa [25]. Generally, ion with higher charge will have a stronger affinity to be binded to the molecular

chain of the gum. The ratio of charge to ionic radius for K⁺, Ca²⁺ and Al³⁺ are 0.66, 1.75 and 4.41 respectively hence the expected order for the interaction of the studied gums with metal ions is Al³⁺> Ca²⁺>K⁺, which is in agreement with the findings of this study. Urea significantly increases the viscosity of the gum solution due to its tendency to form a porous framework. Urea has the ability to trap many organic compounds. In its so-called clathrates, which held organic "guest" molecules in channels formed by interpenetrating helices composed of hydrogen-bonded urea molecules. Therefore the increase in viscosity of AO gum due to the addition of urea may be attributed to the formation of hydrogen bond between urea and the gum.

Ionic strength affects the thickness of the electrical double layer around the charged interfaces and can modify the conformation of the polymer attached to the surface (i.e. spatial extension) [7]. Effect of ionic strength on the viscosity of AO gum was studied by measuring the apparent viscosity of 1 % (w/v) of the gum (containing various concentrations of K⁺, Ca²⁺, Al³⁺ and urea). Plots were developed (plots, not shown) for the variation of apparent viscosity of 1% AO gum with concentrations of electrolytes (K⁺, Ca²⁺, Al³⁺ and urea). The plots revealed that the apparent viscosities of the gum decrease with increase in the logarithm of the salt concentration, a trend that can be explained in terms of shielding and cross linking effects. The cross linking effect seems to prevail for Al³⁺ but in Ca²⁺ contribution of screening effect led to chain contraction. In K⁺, the shielding effect dominated the chain contracting effect. Also, shielding and cross linking effect is associated with the ratio of charge to ionic charge of the metal. In Al³⁺, the ratio is highest therefore cross linking effect dominates but K⁺(which has the least ratio)exhibited strong shielding effect. An increase in the ionic strength of a polymer solution will lead to a decrease in viscosity because as more ions are added to the system, the viscosity starts to give less response, changing minimally [40]. In this case, the electrical double layer is compressed at high ionic strengths, particles and flocs may assume closer localities with each other and the surface polymer may also assume a coiled conformation rather than a stretch conformation [6]. The apparent viscosity of 1 % solution of AO gum was also found to increase with increase in the logarithm of urea concentration indicating the interferences of hydrogen bond between the gum and the urea. Urea is a weak electrolyte and at

similar concentration, its ionic strength is lower than those of Al^{3+} , Ca^{2+} and K^+ . According to Sanin [40], electrolyte with low ionic strength is expected to create a higher viscosity since this type of a system creates a higher resistance during flow. At low ionic strengths, the floc structure of a polymer may become more compact. In addition, significant amount of polymer will be extending out into the solution since their charged are not screened out.

3.3.6 Steady shear properties

Generally, polymers can be classified as Newtonian and non Newtonian and the classification can be established based on the variation of shear rate with shear stress, speed of rotation versus viscosity or viscosity versus shear rate. Newtonian fluids are fluids which exhibit a linear relationship when shear stress is plotted against shear rate [41]. Deviations from Newtonian systems have been attributed to several factors and it varies from one polymer to another polymer systems.

Fig. 6a shows plots for the variation of shear stress with shear rate for AO gum exudate. The shape of the plots suggests that AO gums exhibited a dilatant flow behavior and is characterized with shear thickening effect. According to Ameh et al. [42], Newtonian and non-Newtonian behavior of gums can also be investigated by plotting speed of rotation versus

corresponding viscosity. If such plots are linear, then a non Newtonian behavior is upheld. Fig. 6b shows plots of viscosity against speed of rotation for AO gum. From the plots, non-Newtonian behavior of the studied gum was established by a high degree of linearity ($R^2 = 0.9876$). The yield stress (i.e the amount of force needed to be applied to the gum before it can flow) of AO gum was estimated through the intercept of Fig. 14b. Also, the angle formed between the plots and y-axis is related to the power law index N , thus, Power law index, $N = \tan(\text{the angle between the plot line and y-axis})$. If the angle is less than 45° , the fluid is pseudoplastic, if greater than 45° then it is dilatant. Values of yield stress, N (5.77) and θ (85°) obtained in this study ($\theta > 45^\circ$) confirmed that AO gum is a dilatant and is characterized with shear thickening. Triantafillopoulos [43] also characterized a non Newtonian behavior through patterns of plots obtained for the variation of the rotation speed versus the applied torque. Fig. 6c shows the variation of rotation speed with torque for AO gum. The pattern of variation also confirmed that AO gum is a dilatant characterized with shear thickening [44]. Dilatancy is characterized by an isothermal and reversible viscosity increase as a function of shear rate. Shear-thickening property can be subdivided into volumetric and rheological dilatancy. However, AO gum exhibited volumetric dilatancy. Volumetric dilatancy (or shear blocking) is characteristic of highly concentrated dispersions (i.e., above 60% by weight) where

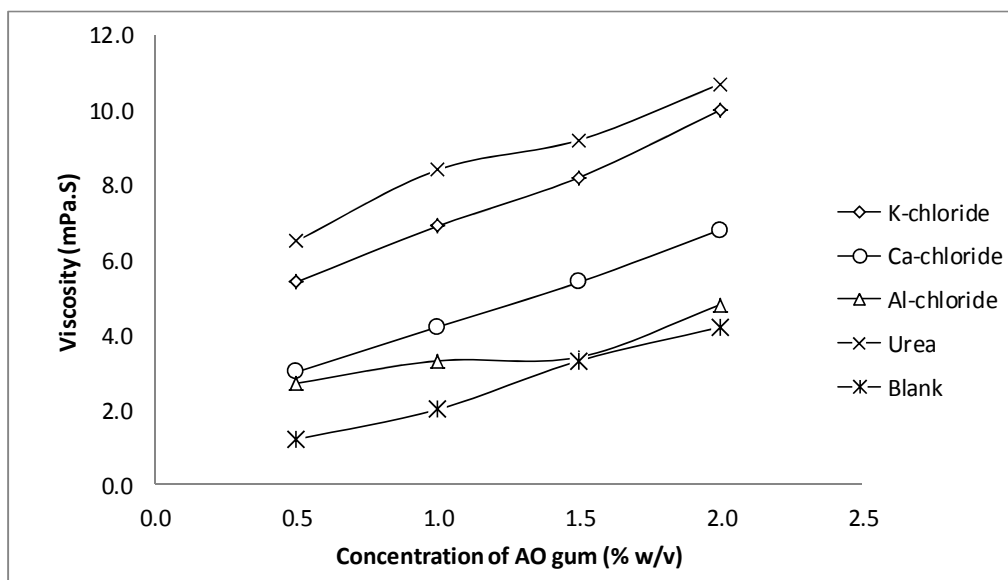


Fig. 5. Variation of viscosity of AO gum with concentration in the presence of 0.1 M of various electrolytes (KCl, $CaCl_2$, $AlCl_3$ and urea)

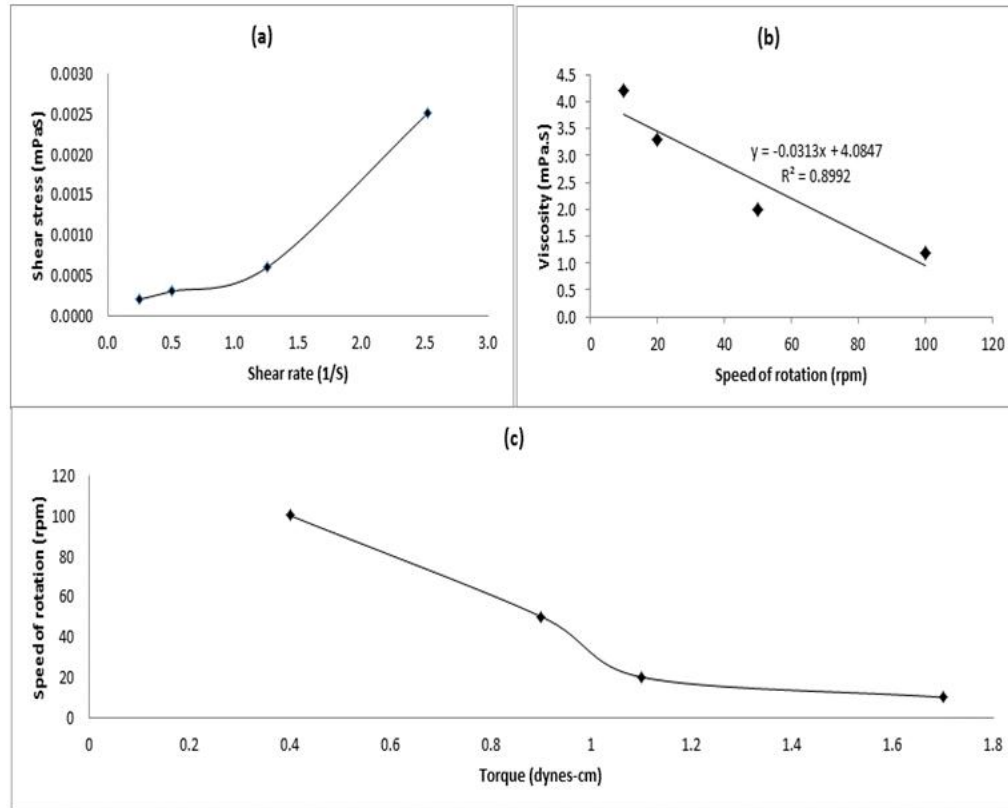


Fig. 6. Variation of (a) shear stress with shear rate (b) viscosity with speed of rotation and (c) speed of rotation with torque

the particles are closely packed together. At low shear rate, the particles fit into the voids of adjacent layers and flow is possible. On the other hand, at high shear rates, the particles begin to slide over adjacent layers since they can no longer fall into the voids. Under these circumstances resistance to flow increases and may cause the fluid to behave in a solid-like manner. Characteristics of shear-blocking fluid are volumetric expansion (dilation) and a noticeable surface drying next to the high shear region.

4. CONCLUSION

AO gum is ionic and mildly acidic gum. The GCMS spectrum of the gum revealed the presence of useful chemical intermediates while carbohydrate and calcium dominated its proximate composition. The gum offers good nutritional prospect for the food and pharmaceutical industries, if properly purified. The rheology of the gum is affected by concentration, temperature, pH and the presence of electrolytes. Its chemical constituents,

rheological properties and non-Newtonian behavior makes the gum a potential intermediates for some industries. Thermodynamic study on the gum revealed that the attainment of transition state of flow by the gum is accompanied by bond breaking while the calculated value of the activation energy indicated the existence of few inter and intra molecular interactions in the studied gum.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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