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Thermodynamic Properties of A.nilotica var. nilotica and A.seyal var. seyal Gums Solutions

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Abstract— *The thermodynamic properties of A.nilotica gum, A. seyal gum solutions were measured and calculated. The partial specific volume of gum, partial specific volume of the solvent (water) and the volume fractions were measured and calculated. Thermodynamic studies involved the estimation the partial specific volume of gum, partial specific volume of the solvent (water) and solute (gum) and the volume fraction of water (φ_1) and that of gums (φ_2) in gums solutions of different concentrations. For composite samples of A.nilotica var. nilotica and A.seyal var. seyal average were found to be 0.999 cm^3g^{-1} and 0.618 cm^3g^{-1}, 0.998 cm^3g^{-1} and 0.643 cm^3g^{-1} respectively. The results show that the sequences of the specific volumes of the gums under studies are in the order of decreasing molecular weight of these gums. Second virial coefficient (A_2) average for composite samples of A.nilotica var.nilotica were found to be 0.97×10^{-3}, Where as for composite samples of A.seyal var.seyal was found to be 2.09×10^{-3},The results explained that water is good solvent for the tow types of gums .Chemical potential range have been calculated from osmotic measurement for different concentrations and was found to be -1.997×10^{-3} to -8.790×10^{-3} joule g^{-1} on average for composite samples of A.nilotica var.nilotica. For composite samples of A.seyal var.seyal the average it was found to be -1.1576×10^{-4} to -4.1382×10^{-4} joule g^{-1}, The results show that the change in chemical potential of water in A.seyal var.seyal gum solution was greater than the change in chemical potential of water in A.nilotica var.nilotica gum solution. Free energy of mixing range of composite samples of A.nilotica var. nilotica average was found to be (-1.2768×10^{-3} to -3.1773×10^{-3}). For composite samples of A.seyal var.seyal average was found to be (-1.6925×10^{-3} to -5.7145×10^{-3}).The obtained results indicate that A.seyal gum thermodynamically resembles A.nilotica gum and they were interacting with water more than A.nilotica gum.*

Keywords— *Gum ; Acacia nilotica; Acacia seyal; Thermodynamic properties.*

I. INTRODUCTION

1.1 Gum

Acacia gums can be defined as the dry exudates obtained from the stems and branches of botanically aspecific species of a subgenous from family leguminosae [1].

Crud gum arabic, (has different uses) is a complex copolymer of polysaccharide with high molecular mass and complex structure [2-5]. It is a branched molecule [6] with protein content of about 2.0–2.5%. Gum is present in a mixed calcium, magnesium and potassium salts of polysaccharidic acid [7,8]. It is composed of six carbohydrate moieties: galactopyranose, arabinopyranose, arabinofuranose, ramnopyranose, glucuropyranosyluronic acid and 4-o-methylglucuropyronosyl uronic acid [9-12].

According to Bentham's taxonomic classification of the Acacia genus, A. seyal var.seyal belongs to series 4 (Gummiferae) and A.senegal var.senegal to series 5 (Vulgares) [13] subsequently modified somewhat by Vassal [14]: Series 4 Gummiferae Benth.= Subgen. Acacia Vas. also called 'Acacia seyal complex which comprises: - A.abyssinica subsp. calophylla, A. nilotica (syn. A. adansonii and A. arabica), A. drepanolobium, A. farnesiana, A. gerrardii, A. giraffae, A. hebeclada, A. karroo, A. kirkii, A. leucophloea, A. nebrownii, A. nubica, A. reficiens, A. rigidula, A. seyal, A. sieberana (var. villosa, var. woodii), A. seyal (var. fistula, var. seyal), A. tortilis (subsp. heteracantha).

Series 5 Vulgares Benth. = Subgen. Aculeiferum Vas. Also called 'Acacia senegal complex that contains:- A. berlandieri, A. polyacantha subsp. campylacantha, A. catechu, A. erubescens, A. fleckii, A. goetzii subsp. goetzii, A. laeta, A. mellifera, subsp detinens, A. senegal, A. Sundra Acacia nilotica var.nilotica produces a gum which is, highly, soluble in water. However, very few analytical data about the relevant structural features of the polysaccharide from A.nilotica var.nilotica gum have been reported [15-19].

The chemical constituent, the molecular structure and the molecular weight affect the behavior of molecules in solutions. Gum arabic finds a wide application in food and beverages as a natural emulsifier particularly for citrus water and low viscosity [20- 22]. In food industry, gum arabic is primarily used in confectionery, bakery, dairy, beverage, microencapsulating agent and to a lesser extent in textiles, ceramics, lithography, cosmetics and pharmaceutical industry[23].

1.2 Thermodynamics study

To understand the behavior of gum molecule in solutions it is necessary to measure and calculate some thermodynamic parameters and functions. Thermodynamics has an immense predictive power and the thermodynamic laws can be used to predict the direction in which a process would proceed. Thermodynamic parameters and functions include the partial specific volume, the volume fraction, the osmotic pressure, the chemical potential of solute and solvent, the second virial coefficient, and the free energy of mixing.

One of the most function characteristics in the behavior of each component in a solution is the chemical potential of the component. It is equal the change in internal energy of a solution in addition to an infinitely small number of moles of ith component, referred to that amount of substance at constant volume, entropy, and quantity of each of the other components. Moreover, the chemical potential could be calculated from the partial specific volume and osmotic pressure [24,25 and 26].

Osmosis 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, is due to the inequality of chemical potential of pure solvent and solution estimated quantitatively by osmotic pressure, which has the dimension of pressure (atm, Nm^{-2}). The osmotic pressure, the density of solvent and the density of solid gum measurements lead to calculate the second virial coefficients (A_2).The free energy of mixing (ΔG^m) could be calculated from the chemical potential and the weight fractions of solute and solvent, its value is an indication of the interacting of the solute with solvent[25].

The aim of this work is to investigate the thermodynamic properties of *A. nilotica* and *A. seyal* gum solutions and to determine some important thermodynamic parameters and functions. This includes the partial specific volume, the volume fraction, the osmotic pressure, the chemical potential of solute and solvent, the second virial coefficient and the free energy of mixing. The other aim is to compare and contrast the thermodynamic properties of *A. nilotica and, A. seyal* gum solutions.

II. EXPERIMENTAL

2.1 Materials

Tow samples of each type of *Acacia* gum (*A.nilotica and A. seyal*) were collected, and one sample of each type had been made by coning and quartering [27]. The gum samples used in this study were cleaned by hand to ensure they were relatively free from sand, dust and bark impurities. Then were grounded using pestle and mortar, backed in labeled self sealing polyethylene bags.

2.2 Thermodynamic measurements and calculations

The thermodynamic of polymer solutions can be applicable to gum solutions since gum molecules are classified as biopolymer molecules, the gum arabic solutions were characterized by different thermodynamic parameters.

2.2.1 Partial specific volume of solvent

The tangent method was used [24] by dissolving a constant weight of gum sample in different weights of water. The densities of solutions were determined by a pyknometer at 294K, and then the total volumes of the solutions were calculated. The volumes of solutions were plotted against weight of solutions. The partial specific volume of water is equal to the $\partial V / \partial g$ which can be calculated from graph [24, 25].

2.2.2 Partial specific volume of the gum

Tangent method was used in which different weights of gum were dissolved in a constant weight of water. The densities of solutions were determined by a pyknometer at 294K and then the total volumes of the solutions were calculated. A graph of the volume of solutions versus the weights of gum was plotted. The partial specific volume of gum sample is equal to the $\partial V / \partial g$ which can be calculated from the graph [24].

2.2.4 Osmotic pressure of gum solutions

Osmotic pressures of gum solutions were measured using osmomatR050 colloidal osmometer at 294K by preparing different concentrations of gum solutions.

III. RESULTS AND DISCUSSION

The partial specific volume of the solvent and solute were calculated by using the tangent method [24]. From the slopes values (Fig. 1-4), the partial specific volumes of solvent (water) and solute (gum) were obtained. The partial specific volume of water and *A.nilotica* gum for a *A.nilotica* gum solutions were obtained from the slopes value (Fig.1 and 2), which were found to be 0.999 cm^3 g^{-1} and 0.618 cm^3 g^{-1} respectively. For *A.seyal* gum solutions the partial specific volume of water and *A.seyal* gum (Fig. 3 and 4) were found to be 0.998 cm^3 g^{-1} and 0.643 cm^3 g^{-1} respectively. The results show that the sequences of the partial specific volume of the gums under studies are in the order of decreasing molecular weight of these gums i.e. *A.nilotica and A. seyal*. The partial specific volume of *A.nilotica* is very close to that of the *A. seyal*, although there is noticeably difference between their molecular masses; This, may be, due to the compactness of *A.seyal* molecules which is greater than the *A.nilotica molecules*.The results of the partial specific volume of gums also show that A.*nilotica* molecule expands in water more than *A. seyal* molecule.

The volume fractions of water (φ_1) and that of gums (φ_2) in gums solutions of different concentrations (Table 1) were calculated using equations (1) and (2) [22]. The results show that *A.seyal* has the larger volume fraction followed by *A.nilotica*. The sequences of the volumes fraction were related to the sequences of the weight average molecular weight and the partial specific volumes of the exudates samples of the gums.

$$\varphi_1 = V_1 / V_1 V_2 \quad (1)$$

$$\varphi_2 = V_2 / V_1 V_2 \quad (2)$$

Where:

V_1= partial specific volume of the solvent (water)

V_2 = partial specific volume of the solute (gum)

Table 2-3 shows the osmotic pressures of different concentrations of *A.nilotica* and *A.seyal*. The results obtained show that at the same concentration of *A.seyal* has high value of osmotic pressure than the *A.nilotica*. This mean that they interact with water more than *A.nilotica* and this was due to the structural variations. According to equation (3) [24], it was possible to determine the change in chemical potential of water as a solvent in different gums solutions (Table 2- 3). The results show that the change in chemical potential of water in A.seyal var.seyal gum solution was greater than the change in chemical potential of water in A.nilotica var.nilotica gum solution, and the results also show that A.seyal var.seyal values are closed to values of A.nilotica var.nilotica.

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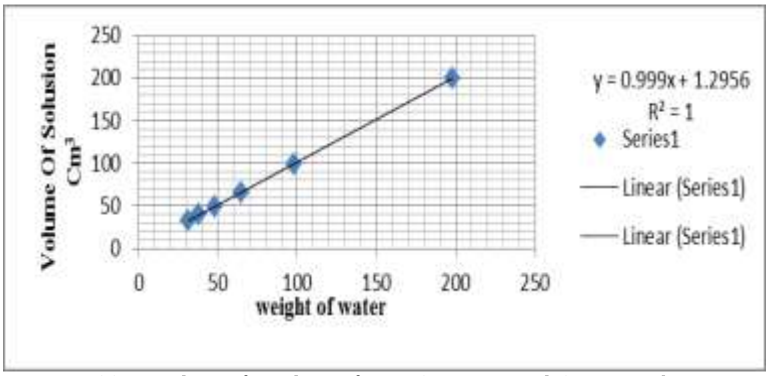

Fig (1): Partial Specific Volume of water (Comps. Sample) *Acacia nilotica*

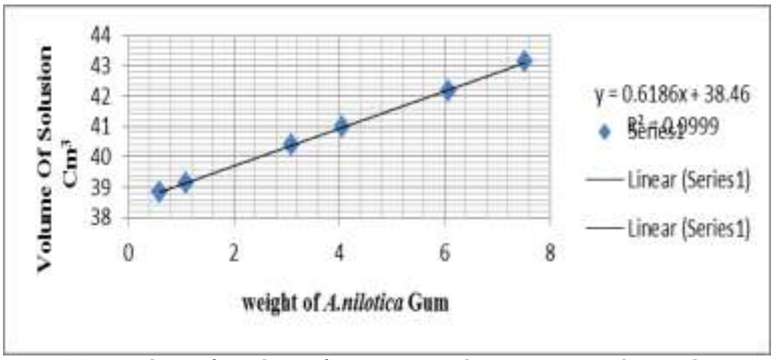

Fig (2): Partial Specific Volume of Gum *Acacia nilotica* in *Acacia nilotica* solution

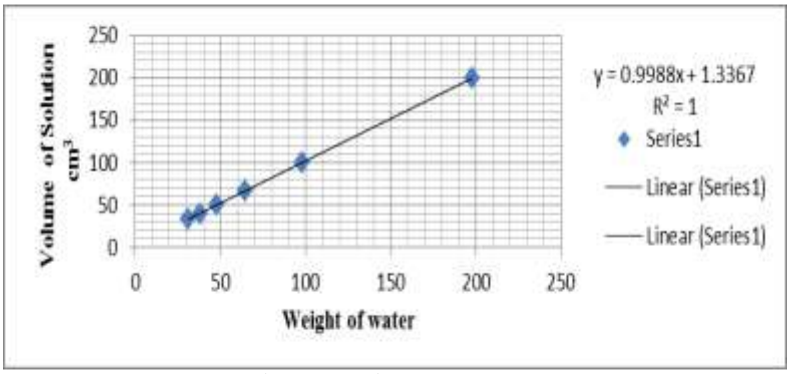

Fig (3): Partial Specific Volume of water (Comps. Sample) *Acacia Seyal*

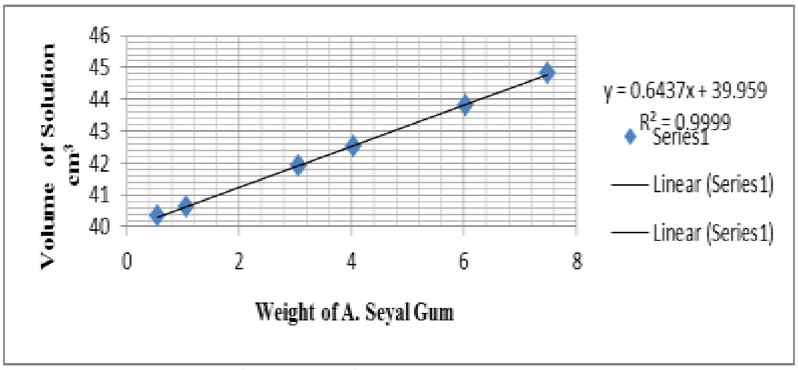

Fig (4): Partial Specific Volume of Gum *Acacia Seyal* in *Acacia Seyal* solution

Table (1): Partial specific volume of water (V_1), of gum (V_2), volume fraction of water (φ_1), of gum (φ_2) and second virial coefficient (A_2) for composite samples of *A. nilotica var.nilotica* and *A.seyal var.seyal* gums aqueous solution

Gum sample	V1(cm3 g-1)	V2 (cm3 g-1)	φ1	φ 2	A2	Mn
A.nilotica	0.999	0.618	0.6178	0.3823	0.97×10-3	$1.89x10^5$
A.seyal	0.998	0.643	0.6081	0.3918	2.09×10-3	$1.67x10^5$

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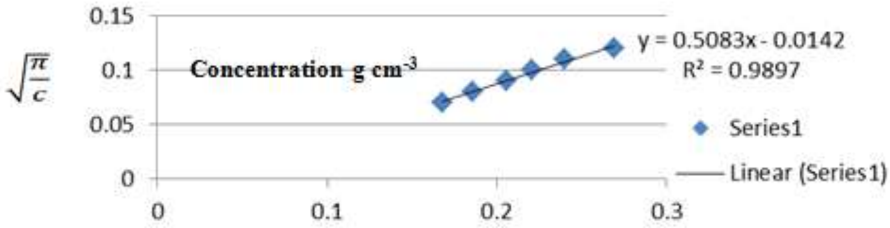

Figure (5) Osmotic pressure Concentration profile of *Acacia nilotica*

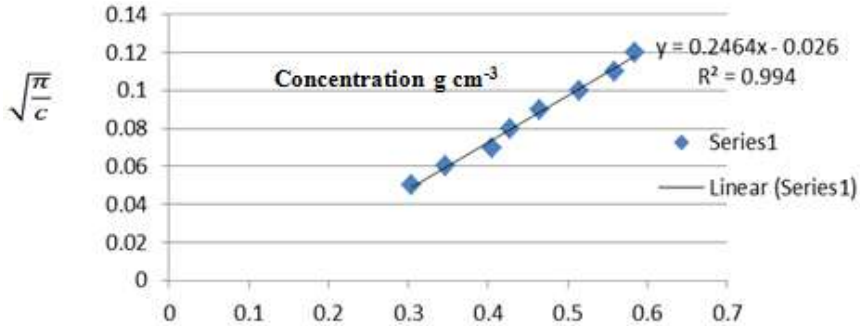

Figure (6) Osmotic pressure Concentration profile of *Acacia Seyal*

Table (2) Chemical potential $\Delta\mu_1$ and weight fractions of water in *Acacia nilotica var. nilotica* gum solutions (Composite sample)

Conc.gcm^{-3}	V_1cm^{3}g^{-1}	πmmHg	$\Delta\mu_1$mmHg cm^{3}g^{-1}	$\Delta\mu_1$erg g^{-1}	ω_1	ω_2	ω_1/ω_2
0.07	0.999	1.5	-1.4985	-1997.95005	0.93	0.07	13.2857
0.08	0.999	2.1	-2.0979	-2797.13007	0.92	0.08	11.50
0.09	0.999	2.9	-2.8971	-3982.7004	0.91	0.09	10.1111
0.1	0.999	3.7	-3.6963	-4928.2767	0.90	0.1	9
0.11	0.999	4.8	-4.7952	-6393.4401	0.89	0.11	8.0909
0.12	0.999	6.6	-6.5943	-8790.9802	0.88	0.12	7.3333

* Where ω_1 and ω_2 weight fractions of water and gum

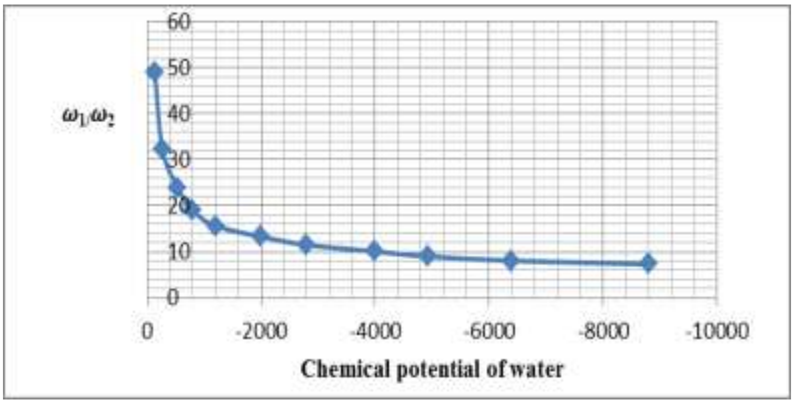

Figure (7) variation of ω_1/ω_2 with the chemical potential of water

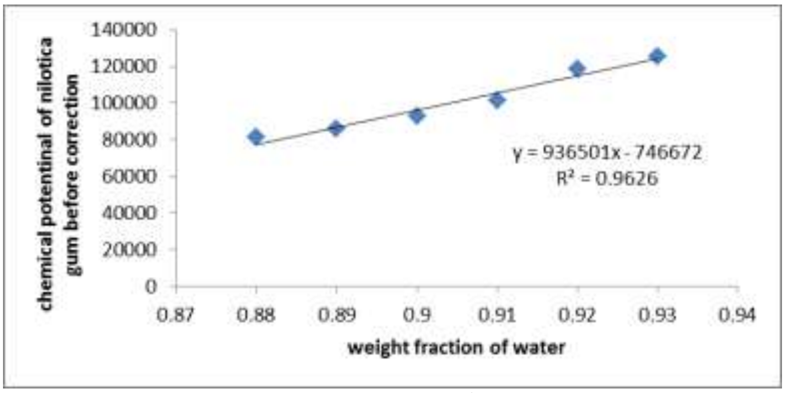

Fig (8) segment A to correct the chemical potential of *Acacia nilotica var. nilotica* ($\Delta\mu_2$)

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Table (3) Chemical potential $\Delta\mu_1$ and weight fractions of water in *Acacia seyal var. seyal* gum solutions

Conc.gcm^{-3}	V_1cm^{3}g^{-1}	πmmHg	$\Delta\mu_1$mmHgcm^{3}g^{-1}	$\Delta\mu_1$erg g^{-1}	ω_1	ω_2	ω_1/ω_2
0.07	0.998	8.7	-8.6826	-11576.511	0.93	0.07	13.2857
0.08	0.998	11.1	-11.0778	-14770.031	0.92	0.08	11.50
0.09	0.998	14.8	-14.7704	-19693.374	0.91	0.09	10.1111
0.1	0.998	20.1	-20.0598	-26745.731	0.90	0.1	9
0.11	0.998	26.1	-26.0478	-34729.532	0.89	0.11	8.0909
0.12	0.998	31.1	-31.037	-41382.699	0.88	0.12	7.3333

* Where ω_1 and ω_2 weight fractions of water gum

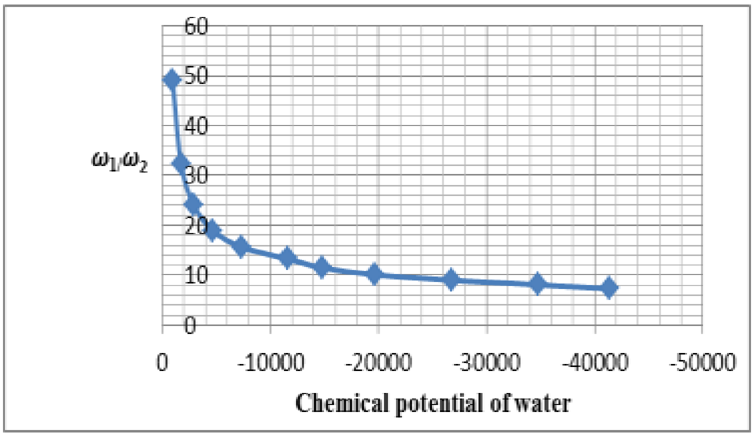

Figure (9) variation of ω_1/ω_2 with the chemical potential of water

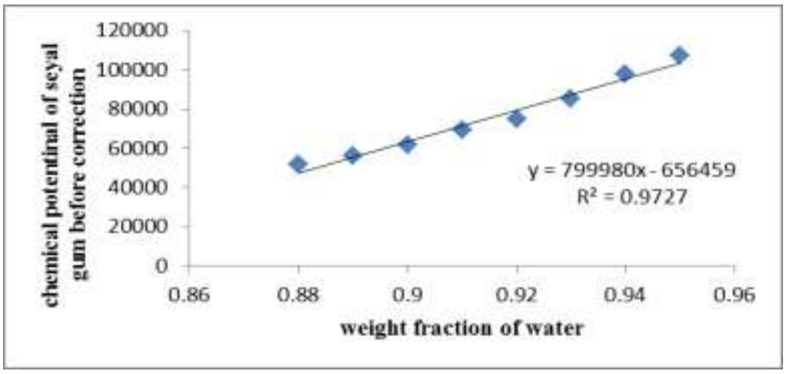

Figure (10) Segment A to correct the chemical potential of *Acacia seyal var. seyal* ($\Delta\mu_2$)

Table (4) Calculating the Free energy of mixing of *Acacia nilotica var.nilotica* gum

$\Delta\mu_1$erg $^{-1}$	ω_1	$\Delta\mu_1 \times \omega_1$	$\Delta\mu_2$erg g^{-1}	ω_2	$\Delta\mu_2 \times \omega_2$	$\Delta G^m = \Delta\mu_1 \times \omega_1 + \Delta\mu_2 \times \omega_2$
-1997.95005	0.93	-1858.093547	-155864.97	0.07	-10910.5479	-12768.64145
-2797.13007	0.92	-2573.359664	-160664.85	0.08	-12853.188	-15426.54766
-3982.7004	0.91	-3624.257364	-167464.68	0.09	-15071.8212	-18696.07856
-4928.2767	0.90	-4435.44903	-175797.81	0.1	-17579.781	-22015.23003
-6393.4401	0.89	-5690.161689	-193064.04	0.11	-21237.0444	-26927.20609
-8790.9802	0.88	-7736.062579	-200313.87	0.12	-24037.6644	-31773.72698

Table (5) Calculating the Free energy of mixing of *Acacia seyal var.seyal* gum solutions

$\Delta\mu_1$erg g^{-1}	ω_1	$\Delta\mu_1 \times \omega_1$	$\Delta\mu_2$erg g^{-1}	ω_2	$\Delta\mu_2 \times \omega_2$	$\Delta G^m = \Delta\mu_1 \times \omega_1 + \Delta\mu_2 \times \omega_2$
-11576.511	0.93	-10766.15523	-126943.26	0.07	-8886.0282	-19625.18343
-14770.031	0.92	-13588.42852	-134943.26	0.08	-10795.4608	-24383.88932
-19693.374	0.91	-17920.97034	-140343.13	0.09	-12630.8817	-30551.85204
-26745.371	0.90	-24071.1579	-150842.55	0.1	-15084.255	-39155.4129
-34729.532	0.89	-30909.28348	-163742.55	0.11	-18011.6805	-48920.96398
-41382.699	0.88	-36416.77512	-172742.32	0.12	-20729.0784	-57145.58352

$$\mu_1 - \mu_1^0 = \Delta\mu_1 = -V_1 \Pi \quad (3)$$

Where:
$\Delta\mu_1$ change in chemical potential of water
V_1 partial specific volume of water
Π osmotic pressure of the solution

The second virial coefficient (A_2) was obtained from the slope of the graph by plotting $(\Pi/c)^{1/2}$ versus concentration (c) equation (4) [24,28,29] of different *A.* gum samples (Fig.7-

9).The second virial coefficients were found to be $0.97x10^{-3}$, $2.09x10^{-3}$ for the *A.nilotica* and *A. seyal* respectively (Table 1). The results explained that water is good solvent for the tow types of gums ($A_2 > 0$), also the result indicate that *A. nilotica* gum has closer and higher values of second virial coefficient than *A. seyal*, indicating that was interacting with water more than the *A. seyal* gum.

$$(\Pi /c)^{1/2} = (RT/Mn)^{1/2} + (RT/Mn)^{1/2} A_2Mn/2\ c \quad (4)$$

Where:
R is the gas constant
T is the temperature in Kelvin

The number average molecular weights (Mn) of *A.nilotica* and *A.seyal* were calculated from the intercept of graphs of Fig. 5 and 6 using equation (4), they were found to be $1.89x10^5$ and $1.67x10^5$ respectively. osmotic pressure methods improve the accuracy of all results obtained in this study by the osmotic pressure technique.

The changes in chemical potential of the three gum samples were calculated by plotting weight fractions of water divided by weight fractions of gum (ω_1/ω_2) versus the change in chemical potential of water ($\Delta\mu_1$) (Fig.7 and 9). The areas under the curve, bound by ordinates corresponding to $\Delta\mu_2/$ which was less than the true areas values were obtained by $\Delta\mu_2$ (true change chemical potential of gum), to correct these

areas [24], a graph of $\Delta\mu_2/$ versus weight fraction of water (ω_1) was plotted to obtain segment A from the intercepts of (Fig. 8 and 10) and then to obtain the true values of gums ($\Delta\mu_2$) by using equation (5). (Table 2 and 3) shows that the change in chemical potential of *A.nilotica* and *A.seyal*, the results show that *A.seyal* gum has great changes in chemical potential. This means it interacts with water more than *A.nilotica* which interacts with water more than *A. seyal*.

$$\Delta\mu_2 = \Delta\mu_2/ + A \quad (5)$$

The change in free energy of the mixing of the three gum samples were calculated by using equation (6) [24]. The obtained results were reported in (Table 4 and 5). The results show that *A.seyal* has closed values, those were higher than the values obtained for *A.nilotica* values. This means that *A.seyal* interacts with water more strongly than *A.nilotica*.

$$\Delta G^m = \omega_1\Delta\mu_1 + \omega_2\Delta\mu_2 \quad (6)$$

The tow *Acacia* gums samples under studies have large values of osmotic pressure, great changes in chemical potential and free energy of mixing of the entire system and positive values of second virtial coefficient. This indicates that water is a good solvent for the tow types of A. gums samples. The order of the interaction with water is greater in *A.seyal*, then in *A.nilotica.*

IV. CONCLUSION AND RECOMMENDATION

Comparative studies were carried out to measure and calculate the thermodynamic properties such as the partial specific volume, the volume fraction, the osmotic pressure, the chemical potential, the second virial coefficient, the free energy of mixing of the tow gum solutions. The results show that water is a good solvent for the tow types of gums although *A.seyal* interacts with water more strongly than *A.nil*otica. Thermodynamically, it was found that water has good affinity for the tow types of gum samples. The results also show that *A.nilotica* molecules are compact compared with *A. seyal*, and A. *seyal* molecule expands in water more than *A.nilotica* molecule. Blending studies of those gum solutions depending on the thermodynamic properties.

The two gums under studies have large values of osmotic pressure, great changes in chemical potential and free energy of mixing of the entire system and positive values of second virial coefficient this indicates that water is a good solvent for both types of gums. The order of the interaction of gum with water is that *A.seyal var.seyal* > *A.nilotica var.nilotica*.

Different thermodynamic parameters have been calculated were used to compare and contrast the two types of gums A.nilotica var.nilotica and A.seyal var.seyal which fall within the range of the gummeferae species.

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