

Solution Properties of Combretum Glutinosum (Habeil) Gum

M. H. Awad

Correspondence: M. H. Awad, Department of Chemistry, Faculty of Arts and Sciences – Kasr Khair, Al-Mergheb University– Libya. Email: muhash.co1@gmail.com

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Abstract

The solubility of Combretum glutinosum gum in distilled water ranged from 30 to 40% and gel fraction ranges between 60 to 70%. It was found that the gum solubility increased with increase the pH of solution. The reduced viscosity of Gum Habeil in distilled water was increased with decrease the concentration of gum solution, and this is the a behavior of ionic polysaccharide solutions, for that Huggins and Kraemer equations are incapable to derive the intrinsic viscosity value of aqueous gum solution. Some extrapolated equations such as Fous, Schulz–Blaschke, Martin, Heller, and Fedors equations used to estimate the optimum model for measurement intrinsic viscosity of this type of gum. The influence of ion types and ionic strength on the viscosity of gum solutions were also determined. The effect of ionic strength on the intrinsic viscosity of Combretum glutinosum gum was used to determine the salt tolerance value and the chain stiffness parameters of this type of gum. This study exhibited that the values of chain stiffness parameter (B), and salt tolerance (S) of deacetylated gum in the range of 0.0574 to 0.0700, and 0.083 to 0.101 dl × M^{1/2} / g respectively.

Keywords: C. glutinosum, Gum Habeil, intrinsic viscosity, Salt tolerance, Stiffness parameters

1. Introduction

Gums obtained from several genus of Acacia trees are extensively used in food industrial as emulsifiers, a thickeners, and adhesive agents. Combretum glutinosum gum in Sudan known as Gum Habeil, and this tree belongs to the Combretaceae family (Arbonnier, M., 2004, Devineau, J. L., 1999). The leaves of Combretum glutinosum trees have been used traditionally in Sudan for many years in the treatment of malaria, headache, bleeding, and utilized as diuretic (Jefferies, M., et al, 1981). Pousset 1993 publicized that, the hot aqueous extracted solution of Combretum glutinosum leaves has been used to therapy Hepatitis B virus (Jefferies, M., et al, 1978). The present work is an attempt to, determine the solubility of Combretum glutinosum gum in different solvents, measure the intrinsic viscosity and investigate the influence of ion types and ionic strength on the value of intrinsic viscosity of Combretum glutinosum gum. The work also aimed to determine the value of chain stiffness (B), and salt tolerance (S) parameters of deacetylated Combretum glutinosum gum. The author 2013 revealed that; the weight average molecular weight of AGP component of gum equal 8.611×10⁵, 4.456×10⁶, and 1.528 ×10⁶ g / mol., and radius of gyration (R_g) equal 72.16, 30.03 , and 81.3 nm of the freeze dried deacetylated gum, freeze dried soluble part, and freeze dried calcium- free gum respectively. Freeze dried soluble part gum shown a highly branched compact chain backbone (low radius of gyration) with higher weight average molecular weight than the modified gum samples "deacetylated and Calcium-free gums" (Awad, M.H., et al, 2013). The author 2013 revealed that; the thermal analysis of gum samples exhibited endothermic peak ranged from 30 to 45°C combined with heat content value ranged from 0.3 to 1.5 J/ g (Awad, M.H., et al, 2014).

2. Sample Collection and Preparation

Authenticated specimens of Combretum glutinosum gum collected from Blue Nile state – Sudan in seasons 2007 to 2009. The samples were cleaned from debris like sand and bark, then converted to Mechanical powder using an electrical grinder, and sieved using mesh size 250µm.

2.1 Solubility Measurement

1% w/w of gum in electrolyte (water) solution was stirred overnight. The dispersion solution was centrifuged at 3000 rpm for 45 min, then the soluble fraction was decanted and saved in 250 cm³ volumetric flask. Insoluble fraction was dissolved in 20 cm³ distilled water, then the mixture was stirred for 60 min and re-centrifuged at 3000 rpm for 10 min before the supernatant fraction transferred to the soluble part solution using a dropper. The last steps were repeated three times to remove electrolyte salts. Insoluble fraction was stored for 24 hrs. in oven

at 105 °C and then weighed, while the assembled soluble part solution was completed to 250 cm³ by adding distilled water, then 20 cm³ of soluble part solution was dried for 24 hrs. in oven at 105 °C and weighed (Jefferies, M., et al., 1981; Jefferies, M., et al., 1978).

2.2 Determination of Gel Volume

50 cm³ of 2 % w /v of gum in electrolyte solution was stirred overnight. The dispersion solution was centrifuged at 3000 rpm for 45 min, then the supernatant was decanted. 50 cm³ of electrolyte solution was added to the insoluble fraction, then the solution was stirred for 60 min and re-centrifuged at 3000 rpm for 10 min and the supernatant was decanted. The last step was repeated three times before the final centrifugation. Lastly 50 cm³ of electrolyte solution was added to the gel fraction and the mixture was stirred for 10 min, and allowed to stand for 20 hrs., then the gel volume was measured. The above experiment was carried using 0 to 0.3 ionic strength solutions of magnesium chloride, and calcium chloride, and sodium chloride (Brito, A. C. F., et al., 2004).

2.3 Preparation of Deacetylated, and Soluble Part Gum Solutions

Standard methods were used to prepare soluble part, and deacetylated gum solutions (Le Cerf, D., et al., 1990, Lapasin, R., & Pricl, S., 1995).

2.4 Intrinsic Viscosity Measurement

0.875 g /dl of deacetylated gum, and soluble part solutions in different ionic strengths were prepared. Ubbelohde viscometer (75 / N94 or 75/ N 104) immersed in a viscometer bath (C.T-500 Series II, USA) was used to determine the flow time of the gum solutions flowing through the Ubbelohde capillary tube. The relative viscosity was measured by comparing the flow time of 3cm³ of gum solution to the flow time of solvent passage through the Ubbelohde capillary tube, then the relative viscosity was converted to inherent, specific, and reduced viscosity (Le Cerf, D., et al., 1990).

2.5 Salt Tolerance and Chain Stiffness Parameter

The value of salt tolerance (S) was obtained from the following equation (Smidsrod, O., et al., 1971):

$$[\eta] = [\eta]_{\infty} + S \times 1/\sqrt{\mu} \quad (1)$$

where $[\eta]_{\infty}$ is the intrinsic viscosity at infinite ionic strength (μ). The relative stiffness parameter (B) was determined from the below equation:

$$S = B \times ([\eta]_{\mu=0.1})^{\nu} \quad (2)$$

where the ν constant used for this study equal 1.3 (Lapasin, R., et al., 1995).

3. Results and Discussion

3.1 Solubility and Gel Volume

Table 1 shows the solubility of Gum Habeil increased with the solvent basicity directly, the high solubility of gum solution in sodium carbonate due to calcium ion depletion. The weight of gel was calculated by discounting the weight of insoluble materials (sand and bark) from the total weight of the insoluble fraction.

Table 1. Solubility of Gum Habeil in several solvents

Solvents	Solubility w/w%
H ₂ O	29.25
0.25M NaBH ₄	79.70
0.05M NaOH	97.55
0.05M Na ₂ CO ₃	95.80
1M NaCl	37.35
0.05M EDTA	42.43
1M HCl	37.80
0.05M CaCl ₂	34.90
0.1M H ₂ SO ₄	33.11
2M CO(NH ₂) ₂	26.25
0.1M NaCl + 2M	24.30

Fig.1 shows that solubility of Gum Habeil was effected by ionic strength of the dispersing medium.

When the ionic strength of sodium chloride increased from 0.001 to 0.9 at pH equal 7 progressively the gum solubility was increased from 30.5 to 37.5 % w/w and this could be attributed to the greater activity and binding capacity of the chloride ions to the positively charged protein and polysaccharides groups, thereby enhancing its solubility. Fig.1 also showed that at high ionic strength up to 0.9 the solubility of Gum Habeil was decreased steeply with the ionic strength increases, the relationship between the solubility of Gum Habeil and alkali salts ionic strength obeyed Cohn equation (Cohn, E. J.,1925).

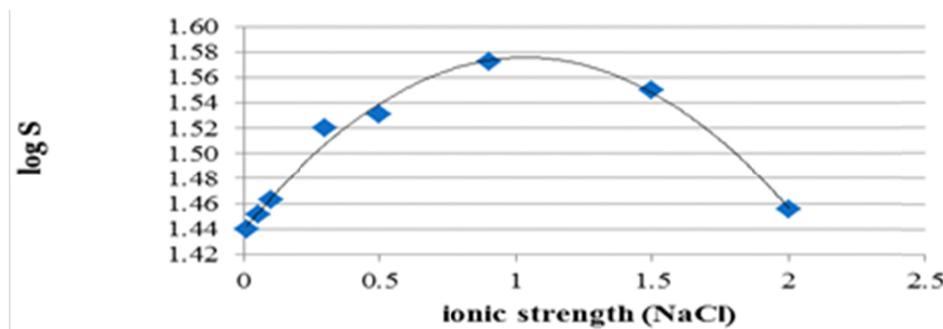


Figure 1. Ionic strength of sodium chloride versus log (solubility) of the Gum Habeil

Fig.2 illustrated the influencing of concentration of sodium carbonate, and pH on solubility of Gum Habeil. As the graph indicated, Gum Habeil solubility was pH –dependent (the researcher attributed this for H-bonding broken in alkali medium and sugar hydrolysis), and a higher solubility increases observed at pH above 10 (Solubility >95%), also the solubility was steeply increased with removing of calcium ions that means H-bonding and Calcium ions responsible for the hydrogel form. The behavior of Gum Habeil differs from Gum Gatti and similar to Khaya grandifoliolia (Aslam, M., et al., 1978, Greenwood, C. T., & Matheson, N. K., 1956).

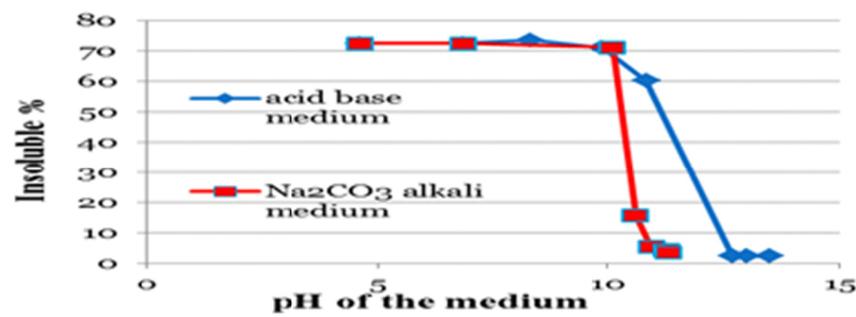


Figure 2. Effect of pH on the solubility of Gum Habeil solution

Fig.3 showed that at the same ionic strength, the divalent ions (Mg^{+2} and Ca^{+2}) have a greater effect than monovalent ions (Na^{+}) on decreasing the gel volume of Gum Habeil. Also Fig.3 shows the same Valente ions (Mg^{+2} and Ca^{+2}) at the same ionic strength, the small and light ions (Mg^{+2}) have a greater effect than the big and heavy ions (Ca^{+2}) on decreasing the gel volume of Gum Habeil. For all cations, at ionic strength more than 0.2 the gel volume is in depending on the charge of cations.

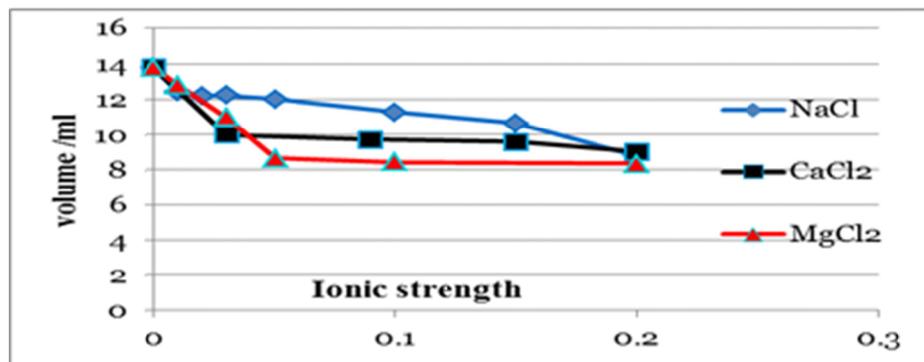


Figure 3. The effect of salt ionic strength on gel volume (cm^3) of Gum Habeil

3.2 Estimation of Intrinsic Viscosity

Fig.4 Showed that without salt addition, the reduced viscosity of Combretum glutinosum gum was increased steadily with dilution (from 0.5 to 0.2% w/v), and a clear increase was observed for gum concentrations less than 0.235 g/dl. The ionic polysaccharides solutions have the same behavior, Pricl and Lapasin 1995 reported that, the neutral polysaccharide such as Acacia Senegal and locust bean gums observed linear relationships between experimentally reduced viscosity data and concentration of gum solution, while the ionic polysaccharides such as xanthan gum given a noticeable increases reduced viscosity value with decreases the concentration of gum solutions, and this attributed to the charge-charge electrostatic repulsion between ionic groups on polymer backbone and extended coil dimensions (Lapasin, R., & Pricl, S., 1995), for this reason the experimentally data of reduced and inherent viscosity did not obey the Huggins and Kraemer equations.

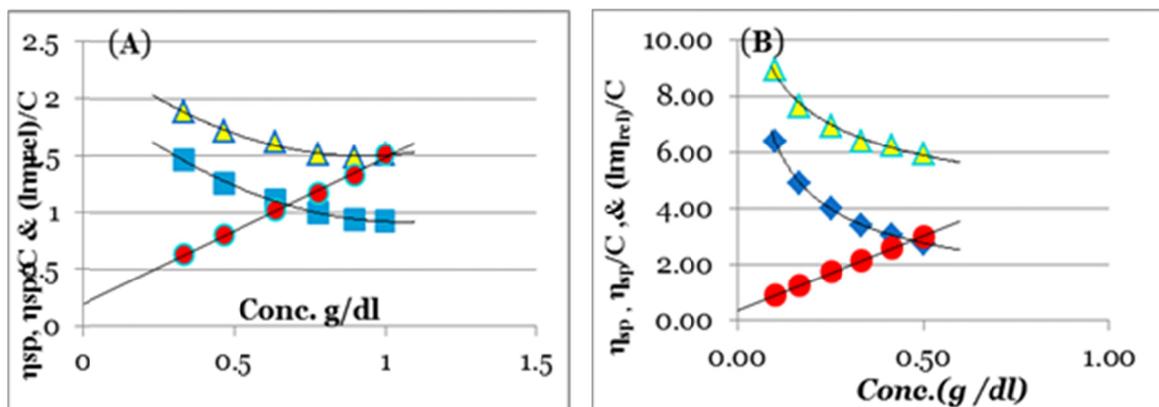


Figure 4. η_{sp} ● , η_{sp}/C ▲, and $(\ln \eta_{rel})/C$ ◆ versus concentration plots for (A) water soluble part, (B) deacetylated gum in de- ionized water at $25 \pm 1^\circ C$

The aim of this part of work is to apply some intrinsic extrapolated equations such as, Fouss, Schulz-Blaschke, Martin, Heller, and Fedors equations to linearize the viscometric data obtained in this study (Fedors, R. F., 1979). According to the data analysis; Fedors equation given the best linearize viscometric data with the lower standard deviation errors, this appeared that Fedors equation the best equation to calculating the value of intrinsic viscosity of Gum Habeil in aqueous solution. Table 2 shows the value of intrinsic viscosity of freeze dried soluble part gum calculated by the different extrapolated equations is lower than the value of freeze dried deacetylated gum, and this emphasized that the freeze dried soluble part gum have the compacted structure with smaller size than freeze dried deacetylated gum.

Table 2. Shows the intrinsic viscosity of freeze dried, soluble part and deacetylated gum in water by different extrapolated equations

Equation	Fouss	Schulz.-Blaschkl	Martin	Heller	Fedors
Soluble part:					
A	0.338	-0.210	-0.169	0.413	-1.89
$[\eta]$ dl / g	2.899	2.099	2.050	2.058	2.074
R^2	0.931	0.848	0.887	0.967	0.999
DA:					
A	-0.246	0.158	-0.129	-0.355	-0.113
$[\eta]$ dl / g	3.115	2.418	2.370	2.439	2.439
R^2	0.956	0.885	0.907	0.981	0.998

Soluble part = water soluble fraction; DA= Deacetylated gum fraction; A =extrapolated equation constant

3.3 Influence of Alkali Salts on $[\eta]$ of Deacetylated Gum Solution

The hydrolysis of hydrophilic and hydrophobic functional groups performs a significant role on the polymer backbone conformation stability. The physicochemical study of the relation between solvent influence, and the hydrolysis properties of hydrophilic, and hydrophobic groups should provide insights into the role of solvent – solute interactions associated with fundamental biopolymers phenomena (Wang, J. J., et al., 2000). The relation between relative viscosity of electrolytes solutions and solvent – solute interactions could be described by Jones and Dole equation below (Jones, G., & Dole, M., 1925):

$$\eta_s / \eta_o = \eta_{rel} = 1 + A \sqrt{C} + BC \quad (3)$$

where η_s is viscosity of gum solution, η_o represent viscosities of solvent, A and B are constants, and C is the molar concentration of gum solution. A -Falkenhagen coefficient following the value of electrostatic forces related to ion–ion interactions, and B -coefficient exhibit the influence of solvent – solute interactions on the value of solution viscosity. Viscosity of neutral polysaccharides solution could be represented by the following equation:

$$\eta_{mix} / \eta_o = \eta_{rel} = 1 + BC \quad (4)$$

where η_{mix} represented viscosity of gum dissolved in mixture of two solvents with a fixed molar concentration, η_o is viscosities of mixture solvent.

Table 3. The values of A- Falkenhagen coefficient and B- coefficients of deacetylated gum in deionized water and different salts at 25 °C

Salts	H ₂ O			KCl			NaCl			CaCl ₂	
mM	0.00	2.5	25	100	500	2.5	25	100	1000	2.5	25
A/dl.g ^{1/2}	1.67	-0.60	-0.30	-0.21	-0.19	-0.46	-0.43	-0.41	-0.23	-0.89	-0.39
B/dl.g ⁻¹	3.62	4.67	2.23	1.86	1.63	4.57	2.67	2.33	1.90	3.94	2.26
R^2	0.99	0.99	0.992	0.97	0.99	0.99	0.995	0.997	0.994	0.990	0.98

Table 3 showed that the B- coefficients value was decreased with the alkali salts concentration increased, in contrast A- Falkenhagen coefficient value was increased with the alkali salts concentration decreased. Also Table3 exhibited that the B- coefficients values of Gum Habeil in alkali salts concentration are positive and higher than A- coefficients, and this emphasizes that the increases of alkali salts concentration lead to decrease the B- coefficients values, increases the interaction between gum and alkali salt solvent, and this decreases the gum viscosity.

3.4 Influence of Alkali Salts on Viscosity of Deacetylated Gum

Fig. 5 to 7 showed that with alkali salts addition, the repulsion forces between the opposite functional group in chain segments was eliminated. Results exhibited that internet, and reduced viscosity versus gum concentration are given linear relationship in high concentration of alkali salt, and experimentally viscosity data obey Huggins and Kraemer equations with the lower standard deviation errors. Thus, this observation may be due to shielding the charge on the side chain of the polymer.

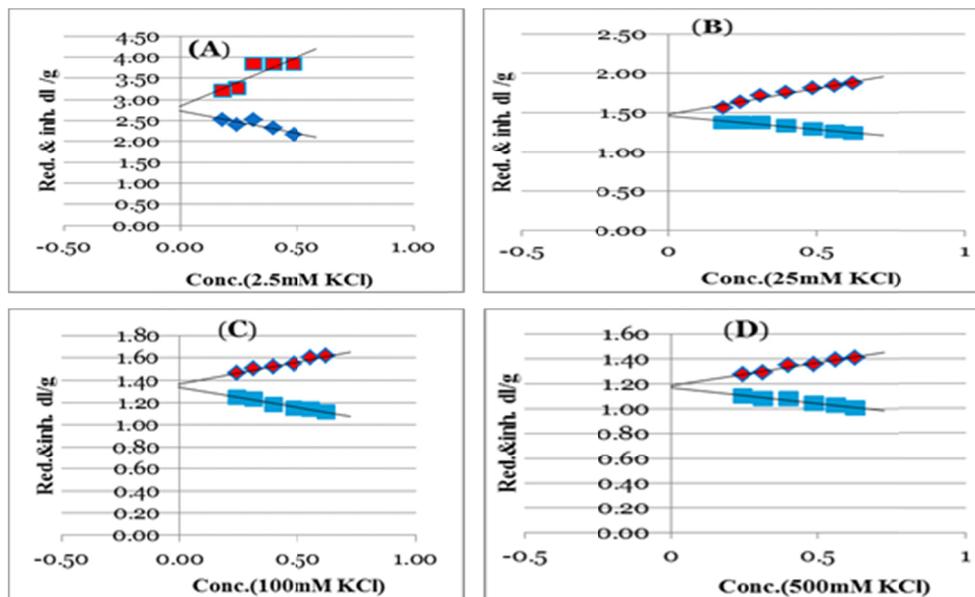


Figure 5. A, B, C and D, represented $\diamond \eta_{sp}/C$, and $\blacksquare \eta_{inh}$ viscosity vs. gum concentration in different solvent concentrations, A 2.5, B 25, C 100, and D 500 mM of KCl

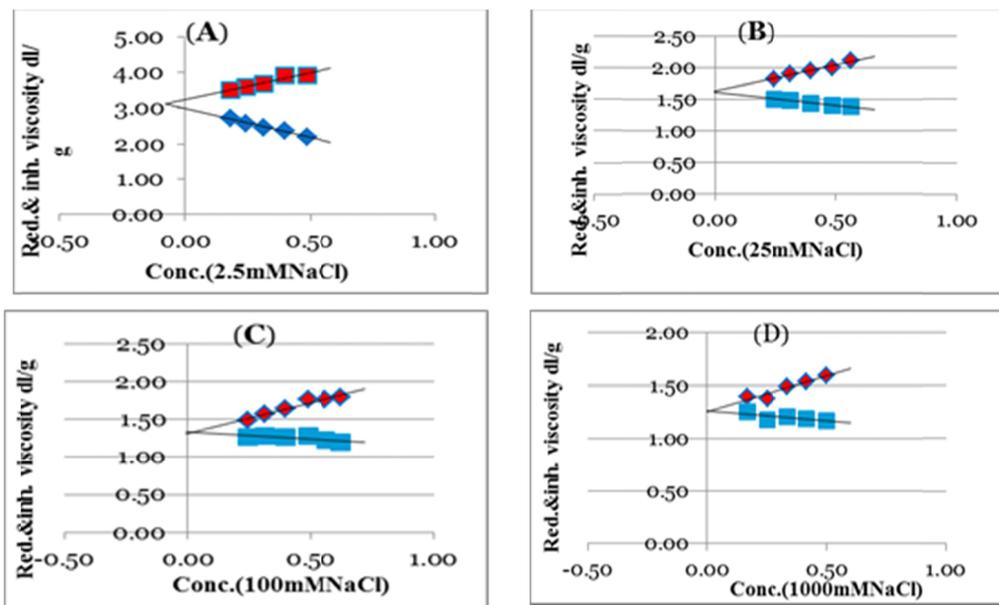


Figure 6. A, B, C and D, represented $\diamond \eta_{sp}/C$, and $\blacksquare \eta_{inh}$ viscosity vs. gum concentration in different solvent concentrations, A 2.5, B 25, C 100, and D 500mM of NaCl

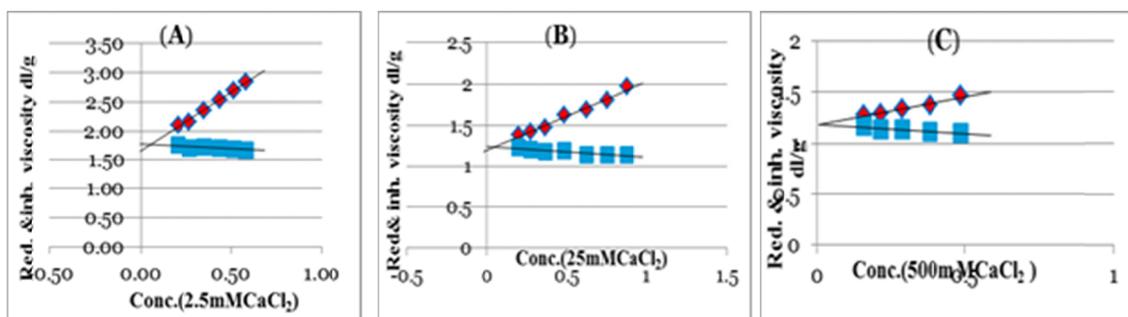


Figure 7. A, B, and C, represented $\diamond \eta_{sp}/C$, and $\blacksquare \eta_{inh}$ viscosity vs. gum concentration in different solvent

concentrations, A 2.5, B 25, and C 500mM of CaCl₂

3.5 Salt Tolerance and Chain Stiffness Parameters

Fig.8 shows that the salt tolerance of deacetylated gum ranged from 0.083 to 0.101 dl × M^{1/2} / g with mean value of intrinsic viscosity at infinite ionic strength equal 1.0425 dl / g. For electrolyte solution of polymer, the salt tolerance parameter is significantly depending on the nature of counter ions (cation) and polymer molecular mass, the salt tolerance (S) of some polysaccharides can be developed only when the comparison was expressed at a specific molecular mass. According to this fact, Smidsrod and Haug suggested a new parameter (B) is independent on the polysaccharide molecular mass, but the parameter (B) depends only on chain stiffness, for this reason the comparison with polyelectrolyte's of different chemical structures is possible, also the (B) parameter can be calculated without molecular weight determination (Smidsrod, O., & Haug, A., 1971, Anthonsen, M.W., et al., 1993). The chain stiffness parameter (B) of deacetylated gum was ranged from 0.0574 to 0.0700, which was similar to the some polysaccharides, such a carboxyl methyl cellulose, carrageen an and chitosan (Lapasin, R., & Priel, S., 1995).

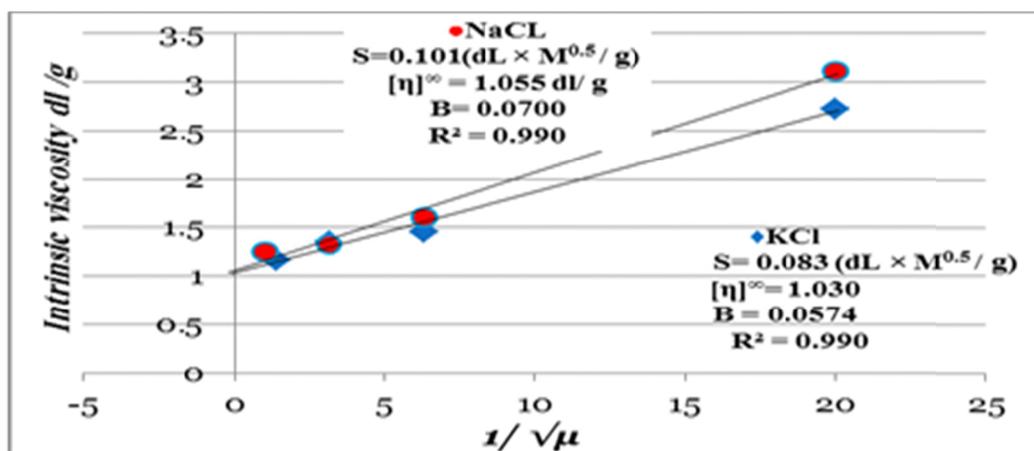


Figure 8. $[\eta]$ versus inverse square root of ionic strength plot for deacetylated gum solutions with ● sodium chloride, and ♦ potassium chloride addition

4. Conclusion

Combretum glutinosum gum was fractionated to a water soluble part 30 to 40 % w/w, and gel fraction 70 to 60% w/w. Although the percentage of calcium ion in gum samples equal 1.3 %w/w. This study revealed that the gel fraction have a higher ratio of calcium ion 62.23% of the total amount of calcium in gum samples, and this is the reason of gel formation, when solvents precipitate calcium ions this increases the gum solubility. In the absence of alkali salts, the viscosity experimental data of freeze dried soluble part and freeze dried deacetylated gum solutions over a wide concentration range was plotted in terms of Fous, Schulz – Blaschke, Martin, Heller, and Fedors equations. All the equations linearized the viscosity experimental data and straight lines were attained, but Fedors equation showed the best fitting of viscosity data with low value of standard deviation error. By Fedors equation, intrinsic viscosity of freeze dried soluble part, and freeze dried deacetylated gum in distilled water equal 2.0741 and 2.439 dl /g respectively. Results show that the salt tolerance parameter (S) of Habeil gum was found to be in the range of 0.083 to 0.101 dl × M^{1/2} / g , and stiffness parameter (B) of gum was ranged from 0.0574 to 0.0700.

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