Physicochemical Properties of Arabic Acid and Arabate Salts

Zulfa, M. Abaker*1, Elfatih, A. Hassan 2, Amin, M. Baraka3 and Mohamed E. Osman4

1 Department of chemistry, College of Applied and Industrial Sciences, Bahri University, Khartoum - Sudan.
2, 4 Department of chemistry, Faculty of science, Sudan University of Science and Technology, P.O. Box (407), Khartoum - Sudan.
3 Department of chemistry, Faculty of science, Cairo University, P.O. Box (11757), Giza – Egypt

*Corresponding author Email: zulfa.abaker@gmail.com

(Received: March 09, 2014; Accepted: June 15, 2014)

Abstract— Arabic acid was prepared from Acacia senegal gum by the removal of metal ions using ion exchange chromatography. Arabate salts of (Na, K, Ca and Mg) were prepared using arabic acid by adding respective cations. Scanning electron microscope (SEM) proved successful production of arabic acid and arabate salts. pH values were 2.6, 6.9, 6.5, 4.9, 4.5 for arabic acid, Na, K, Ca and Mg arabate salts respectively. Intrinsic viscosities of arabic acid, Na, K, Ca and Mg arabate salts in 1M NaCl were determined. The measured viscosities were 8.53, 2.47, 0.11, 0.05 and 1.24 ml g−1 for arabic acid, Na, K, Ca and Mg arabate salts respectively and 10.82, 14.33, 12.9, 10.12 and 9.38 ml g−1 for arabic acid, Na, K, Ca and Mg arabate salts respectively in 0.5M NaCl where they were 18.47, 45.82, 30.72, 11.76 and 10.83 ml g−1 for arabic acid, Na, K, Ca and Mg arabate salts respectively in deionized water. The equivalent conductivities of the arabic acid and arabate salts have been measured in water at 25°C. The results showed a very sharp nonlinear increase with decreasing polyelectrolyte concentration. The overall results of the present work showed that; the bonding of metal ions to arabic acid decreases the viscosity of arabic acid with variation in pH values among arabate salts where the results of equivalent conductivities showed a sharp increase with dilution.

Index Terms — Arabate salts, Electrical conductivity, Intrinsic viscosity, Ion exchange chromatography, Polyelectrolyte.

I. INTRODUCTION

Gum arabic is an exudate collected from the stems and branches of Acacia senegal and other related African species of Acacia. Gum arabic is a natural polymer consists mainly of high molecular weight polysaccharides obtained as a mixed calcium, magnesium and potassium salts, which on hydrolysis yield arabinose, galactose, rhamnose and glucuronic acid [1]. It is the least viscous and most soluble of the hydrocolloids, and is used extensively in the industrial sector because of its emulsification, film forming and encapsulation properties [2].

The viscosity of a liquid is its resistance to shearing, or flow through a capillary tube. Viscosity was considered as one of the most important analytical and commercial parameters, since it is a factor involving the size and the shape of the macro– molecule [3]. It can be presented in many terms such as relative, specific, reduced, inherent and intrinsic viscosity. It is also presented as kinematic or dynamic viscosity. The intrinsic viscosity has great practical value in molecular weight determinations of polymers. This concept is based on the Mark–Houwink relation suggesting that the intrinsic viscosity of a dilute polymer solution is proportional to the average molecular weight of the solute raised to a power in the range of 0.5 to 0.9. Values of the proportionality constant and the exponent are well known for many polymer-solvent combinations. Solutions viscosities are useful in understanding the behavior of some polymers [4]. The physicochemical properties of polyelectrolytes are mainly governed by the interactions between the counterions and the charged groups of the polion. Transport properties, studied by electrical conductivity, are of central importance in accounting for the solution behavior of synthetic and biological polyelectrolytes. However, the lack of experimental data, especially for very dilute solutions, severely hampers the interplay between experiment and theory [5]. Most studies have been carried out on anionic polyelectrolytes, such as polyacrylic and polymethacrylic acids and their sodium and potassium salts etc. However, little or no work has been done on cationic polyelectrolytes, probably because of the limited availability of polyions with different counterions [6]. For simple electrolytes it is customary to plot the equivalent conductivity against the square root of the concentration. At low concentrations a linear plot which conforms to the Onsager theory is generally obtained. When a similar plot is made for a polyelectrolyte a linear plot is not obtained, but instead, the equivalent conductivity generally shows a very sharp nonlinear increase with decreasing polyelectrolyte concentration. This type of behavior has been qualitatively ascribed to an elongation of the polion with dilution and a concomitant increase in the number of free counterions, thus leading to an increase in the number of conducting species in solution [7].
Regarding to the commercial interest and importance of the gum as food additive, physicochemical characterization of it, is of great importance. According to the literature review, few studies have been presented arabic acid and arabate salts as polyelectrolyte in powdered form. The objective of this study is to determine the effect of addition of metal ion to arabic acid on viscosity and the effect of NaCl salt when the gum behave as polyelectrolyte and its electrical conductivity is a matter of current interest.

II. MATERIALS AND METHODS

Materials
The gum arabic (Acacia senegal) used in this study was collected from Blue Nile state (Eddamazin) during 2009. Other materials were:
- Amberlite resin IR 120 H+ from Sigma Aldrich Company, Egypt, Cairo.
- Sodium, potassium, calcium and magnesium chloride, HCl from laboratories of Cairo University.
- Whatman cellulose nitrate membrane filter paper 0.8µm from Sigma Aldrich Company, Egypt, Cairo.

Equipments
The equipments used in this study were:
- Freeze Dryer Modulo: Edwards (England).
- Microprocessor PH meter combined PH or ORP electrode, USA.
- Scanning electron microscope (SEM), model JXA - 840A Electron Probe Microanalyzer (JEOL, Japan).
- Ubbelohde viscometer (SCHOTT instruments, type 530 03 Germany)
- Conductivity cell of the PL-700 series bench top multi-parameters type.

Methods
Preparation of arabic acid and arabate salts
Arabic acid was prepared using column chromatography method, a glass column backed with an amberlite resin IR 120 H+ (a strong cation exchange resin). Gum solution 20% was prepared (on dry weight basis). After the sample was completely dissolved, the solution was left until it became free from bubbles and insoluble matter before using. The solution was passed slowly through the column in order to replace its cations by the hydrogen bonded to the resin; the collected eluent was arabic acid [8]. The pH of the arabic acid solution was measured using a pre calibrated pH meter (ORP electrode, USA). The column was regenerated again by washing with 10% solution of hydrochloric acid followed by deionized water until it became free from chloride ion. Solution of arabate salts were prepared by dissolving 1.2g of potassium, calcium, magnesium and sodium chloride in water which equal to the specific amount of these cations present in Acacia senegal gum under study. The salts solutions were passed through the column until it was saturated by cations, followed by deionized water until it is free of chloride ion. 20% arabic acid solution was passed slowly through the column in its salt form, the collected eluent was arabate salt. The solutions prepared by the above procedure were dried using Freeze Dryer Modulo: Edwards (England). A fluffy, white, fine powder was obtained [9 and 10].

Scanning Electron Microscopy (SEM)
The fine powder of the sample were prepared by making a thin film of desirable size and mounted on copper stubs with double – side's adhesive tape and coated with gold using Sputter Coater S150A Edwards – England. The specimens were examined under JXA – 840A Electron Probe Microanalyzer – JEOL – JAPAN [11, 12, and 13].

Viscosity measurements
12 ml of arabic acid and arabate salts solutions (1% w/v in 1 M and 0.5 M NaCl) were transferred into an Ubbelohde viscometer (SCHOTT instruments, type 530 03 Germany) and left for 30 minutes to reach the thermostat temperature, adjusted at 25° C. Each gum solution was diluted several times and the flow time was measured for each concentration in triplicates. Finally the flow time for the pure solvent (1 M and 0.5 M NaCl) were measured. Determinations were made both with and without the presences of NaCl. Intrinsic viscosity was obtained by plotting reduce viscosity vs. concentration. [14].

III. RESULTS AND DISCUSSION

Scanning Electron Microscopy (SEM)
Figures (1 – 6) show morphological examination of Acacia senegal gum, arabic acid and arabate salts which carried out using (SEM). The specimens were examined under JXA – 840A Electron Probe Microanalyzer – JEOL – JAPAN. It was observed that the surface of arabic acid and arabate salts are clearly different from each other and they were all together different from the parent Acacia senegal gum, which has a rocky surface. The surface evidence supports successful cross – linking of the cations into the surface of...
arabic acid. SEM also determines the weight percentage of the cations present in the samples. Figure (7) show quantitative data of weight percentage of Na, K, Ca and Mg in arabic acid which give additional support, good evidence and successful evaluation to the results.

**Figure (1).** Typical SEM images of *A. senegal* gum

**Figure (2).** Typical SEM images of arabic acid.

**Figure (3).** Typical SEM images of sodium arabate.

**Figure (4).** Typical SEM images of potassium arabate.

**Figure (5).** Typical SEM images of calcium arabate

**Figure (6).** Typical SEM images of magnesium arabate.
Viscosity of arabic acid and arabate salts

Gum arabic, from which the arabic acid, under investigation, was derived is an example of a colloid with a negative charge. This charge is due to the carboxyl groups in the molecule. It would be expected, therefore, that a charge would exist on molecules of arabic acid and its salts as it does on gum arabic [15]. The pH of *Acacia Senegal* gum, arabic acid, Na, K, Ca and Mg arabate salts show insignificant variation in the pH for parent gum, calcium and magnesium arabases (4.6, 4.9, 4.5) respectively. Na and K arabates are in a similar pH range (6.9, 6.5). Arabic acid show a significantly different pH of 2.6. Figure (8) show intrinsic viscosity of *Acacia senegal* gum, arabic acid and arabate salts in1M NaCl. The *Acacia senegal* gum, arabic acid, Na, K, Ca and Mg arabate salts show 12.00, 8.53, 2.47, 0.11, 0.05 and -1.24 ml g⁻¹ respectively, the results show that arabate salts have smaller viscosity than that of arabic acid and the parent gum. It was observed that the viscosity of arabic acid solution is decreased with the addition of metal ions and it was further decrease with increasing concentration of NaCl. Self-suppression of the charge by the colloidal particles of the solution may also give explanation for the decrease in viscosity. The results are in good agreement with these reported by Schleif [15].

**Figure (7)**. weight percentage of cations in arabic acid.
Figure (9) show intrinsic viscosity of *Acacia senegal* gum, arabic acid and arabate salts in 0.5M NaCl. It exhibited, 15.27, 10.82, 14.33, 12.9, 10.12 and 9.38 ml g⁻¹ for *Acacia senegal* gum, arabic acid, Na, K, Ca and Mg arabate salts respectively. It was observed that as concentration of NaCl solution decreases the viscosity of the arabate salts increases and this may be due to the polar groups in gum which are sufficiently neutralized with counter ions (salts ion) so the repelling effect increases in diluted NaCl solutions hence, reducing the electrostatic repulsion, making the network more compact and formed [16].

Figure (10) show intrinsic viscosity of *Acacia senegal* gum, arabic acid and arabate salts in deionized water. The samples yield 22.34, 18.47, 45.82, 30.72, 11.76 and 10.83 ml g⁻¹ for *Acacia senegal* gum, arabic acid, Na, K, Ca and Mg arabate salts respectively. The results show an increase in the viscosity of Na and K arabate salts as well as Ca and Mg arabates. The rapid increase in the viscosity of arabate salts has been attributed by Schleif [15] to the charge on the molecule (electroviscous effect) which affects the viscosity to a large extent. It was also observed that electrolyte added to the colloidal solutions will suppress the charge, resulting in a curve which is linear.
Figure (10): viscosity of *Acacia senegal*, arabic acid, Na, K, Ca and Mg arabate salts in deionized water

Figure (11) show intrinsic viscosity of Na, K, Ca and Mg arabate salts at pH 5.5 (food preparation setting) and low concentration (3%). The measurements show, 118.37, 116.73, 21.27, 18.91 ml g⁻¹ for Na, K, Ca and Mg arabate salts respectively. By comparison, Na and K arabate salts have the highest viscosity, while the arabic acid has the lowest [17]. It was observed that a considerable difference exists in the viscosity curves of sodium arabate and arabic acid without the presence of NaCl salt and pH adjusted to 5.5. One possible explanation is that the higher viscosity of the sodium arabate was due to a higher charge on the molecule. Colloids with carboxylic acid groups lose their negative charge quite readily at a low pH, but in the region of neutrality ionization is practically complete, thus the charge would be high. The potassium arabate curve is the same in magnitude and appearance as the sodium arabate curve. In the case of the divalent salts the curve were much lower than the monovalent arabate salts and also do not exhibited rapid increase in viscosity, as shown by the monovalent salts at low concentrations. Apparently, instead of an intermolecular attraction linking the carboxyl groups of two molecules, an intramolecular attraction occurred effectively linking the carboxyl groups on one molecule, thus making the molecule more compact, resulting in less hydration and lowered viscosity. The curve for the magnesium arabate salt is the same in magnitude and appearance as the curve for the calcium salt.

3.3. Electrical conductivity of arabic acid and salts arabate.

Electrical conductivity for arabic acid, Na, K, Ca and Mg arabate salts at 25°C are determined using a conductivity cell of the PL-700 series bench top multi-parameters type. Figure (12) show the results of electrical conductivity as a function of the square root of the equivalent concentration for arabic acid, Na, K, Ca and Mg arabate salts. The results are the same as other polyelectrolytes results which were determined by Nelson [7]. The electrical conductivities show a sharp increase with dilution and thus cannot be extrapolated to infinite dilution. However, the curve for each arabate salt shows a distinct minimum before the sharp increase. K arabate show a maximum at very high dilution while magnesium salt gives minimum conductivity among arabate salts.
IV. CONCLUSION
The addition of metal ions to arabic acid decreases the viscosity of arabic acid and NaCl decrease it further where the results of equivalent conductivities showed a sharp increase with dilution and thus can not be extrapolated to infinite dilution.

ACKNOWLEDGEMENTS
The authors would like to thank Cairo University, National Research Centre (Cairo Egypt) for providing facilities and support.

REFERENCES

Figure (12). Electrical conductivity of arabic acid, Na, K, Ca and Mg arabate in deionized water

\[ \sqrt{C} \]

\[ \begin{array}{c}
\text{arabic acid} \\
\text{Na arabate} \\
\text{K arabate} \\
\text{Ca arabate} \\
\text{Mg arabate}
\end{array} \]