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Molecular weight of *Acacia*

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Summary

Studies on *Acacia* were carried out to evaluate its molecular weight and its polydispersity by using a fractional coacervation method. The characterization was done by tonometric and viscosimetric measurements. By the application of Mark-Houwink equation, the viscosity average weight of *Acacia* has been evaluated about 65,400. The theoretical treatment of the experimental data permits to show that the function of distribution of the molecular weights of this polymer follows a log-normal law and the index of polydispersity of the studied sample is little dispersed.

Introduction

Crude gum arabic, an exudate from species of the genus *acacia*, is a complex copolymer of D-galactose, L-rhamnose, L-arabinose and D-glucoronic acid residues of which the evaluation of the molecular weight has been little studied in spite of its industrial importance and particularly its pharmaceutical uses as a protective colloid in emulsion, as a viscosity improver, as a binding agent and fixative in powders, as a coating agent in microencapsulation by complex coacervation.

In emulsion and suspension technology, its ability to stabilize and increase viscosity is directly dependent on molecular weight, the lower the molecular weight, the less effective it is at a given concentration resulting in a less stable preparation. In tabletting its binding characteristics are also dependent on molecular weight, the

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binding power (tackiness) increasing with molecular weight. In addition the molecular weight of gum arabic can have an adverse effect on tablet disintegration, drug dissolution and bioavailability as the molecular weight of acacia increases its rate of hydration and solubility decreases and its viscosity, binding and protective power increases. In microencapsulation by complex coacervation between *acacia* and gelatin the molecular weight characteristics of the colloids directly affect process variables (colloid concentration and ratio, pH of coacervation) as well as product characteristics (yield, composition and quality of coating). For these reasons *Acacia* used in pharmaceutical processes should be evaluated for its molecular weight characteristics in routine quality control.

The first values reported in literature came from Oakley (1936, 1937) who obtained a number-average molecular weight ($\overline{M}_\eta$) of 101,000 and 217,000 samples studied in 0.1 N and 0.5 N sodium chloride. By ultracentrifugal studies, Säverborn (1944) found values in the range of 256,000–326,000 on samples of gum arabic acid and its sodium and calcium salts. After, by use of method of light-scattering, Veis et al. (1954) found a weight-average molecular weight ($\overline{M}_W$) of $1.00 \pm 0.05 \times 10^6$ in 0.02 N hydrochloride acid; later, Mukherjee et al. (1962) gave a $\overline{M}_W$ of 57,000 for arabic gum where as Swenson et al. (1968) found the osmotic-pressure molecular weight of gum arabic to be 250,000 and the light-scattering molecular weight to be 365,000.

Anderson et al. (1967a), using light-scattering methods on the sodium salts of *Acacia Senegal* gum, in molar sodium chloride solutions, gave a $\overline{M}_W$ value of 580,000 and confirmed that the gum had a very broad molecular-weight distribution. Later, Anderson et al. (1969, 1971) published light-scattering $\overline{M}_W$ of gum exudates from 30 *acacia* species from 60,000 to 2,360,000.

Sloniewsky et al. (1971) observed that the average molecular weights obtained by light-scattering for several different preparations of sodium and potassium arabate covered a wide range of values from 570,000 to 2,800,000; they attributed this molecular weight variation to the formation of stable aggregates apparently dependent to the length of time initially needed in order to dissolve the crude gum in water.

More recently, Churms et al. (1970) in molecular-weight distribution studies from acacia podalyriaefolia by gel chromatography, a molecular weight of 31,000 was found for the undegraded gum.

Finally, Adam et al. (1977) and Churms et al. (1977) in studies on structural features of the gum exudates from some *Acacia* species, from which molecular-weight distributions have been measured by gel-permeation chromatography, the various samples of gum of *Acacia podalyriaefolia* have been found to vary considerably in $\overline{M}_W$ with values ranging from 9500 to 32,000, even among samples taken from different branches of the same young tree.

It is well to know that at the beginning, the authors used unspecified species of *Acacia* but after, it was recognized by Anderson et al. (1966a) and Joubert (1954) that the composition and physical properties of *Acacia* varied from species to species and, furthermore, within a particular species (Adam et al., 1977; Churms et al., 1977; Anderson et al., 1963; Anderson et al., 1966b). Because of this state of the

laconic description of *Acacia NF* in view of its molecular weight, parameter found very important on its physical properties, a molecular weight characterization has been made on commercial *Acacia NF* sample used in pharmaceutical and complex microencapsulation process.

Experimental

Fractional precipitation

A 90 g sample of anhydrous acacia [1] was dispersed in 600 ml of bidistilled water [2] and kept at rest for 24 h at room temperature to ensure full hydration. A sufficient quantity of *n*-propyl alcohol [3] was added to the *Acacia* sol to obtain titer of 35% v/v and to induce coacervation of the highest molecular fraction. The whole solution was centrifuged [4] for 30 min at 2000 rpm. The supernatant was decanted and the coacervate was dried in an oven [5] to constant weight to obtain fraction I. The remaining solution was submitted again to an other coacervation process by addition of *n*-propyl alcohol so that the alcohol concentration was 40% v/v. This procedure was repeated using increasing alcohol concentration in order to obtain smaller molecular fractions.

Viscosimetric measurements

A suspended-level Ubbelohde, dilution viscosimeter having solvent flow-times greater than 119.2 s at 25°C and negligible kinetic energy correction is used to evaluate the flow time of 1% w/v polymer in aqueous 1 M NaCl solution. The measurements of solution viscosity are usually made by comparing the efflux time t required for a specified volume of polymer solution to flow through the capillary tube with the corresponding efflux time t_0 for the solvent. These data permit the evaluation of the molecular weight of a polymer by using the Mark (1938)-Houwink (1940) equation as follows:

$$\left[\left(\frac{t - t_0}{t_0}\right) \cdot \frac{1}{C}\right]_{C \to 0} \cong \left[\frac{\eta - \eta_0}{\eta_0 C}\right]_{C \to 0} = [\eta] = KM^{\alpha} \tag{1}$$

where $[\eta]$ is the intrinsic viscosity; M, the molecular weight of a polymer; K and α, constants for a polymer–solvent–temperature system but independent of the concentration and the molecular weight.

[1] BDH Chemicals, lot 86697, Toronto, Canada.
[2] 4-litre Zellnerwater Bidistiller.
[3] Anachemia Chemicals, No A.C. 7828, lot 660630, Toronto, Canada.
[4] Sorval Super Speed RC2-B.
[5] Power-O-Matic 60, Blue M Electric, Blue Island, IL, U.S.A.

Tonometric measurements

A vapor phase osmometer [6] was used to determine the number average molecular weight ($\overline{M}_\eta$) of three fractions of *Acacia* gum, required to establish the Mark-Houwink's equation parameters. An aliquot was dissolved in bidistilled water and neutralized with 0.1 N NaOH [7] to pH 6 [8]. The evaluation of the $\overline{M}_\eta$ of the sample is based on the temperature difference measured by the variation of resistance ΔR [9] of a thermistor, observed between the solution and its solvent at the same vapor pressure in comparison with a known molecular weight product such as sodium salicylate [10] in the same solvent used. This standard sample was employed to calibrate the instrument and evaluate the instrument constant, K_{inst}, in calculating the slope of the straight line relation between the change in ΔR value for different concentrations. Finally, the polymer sample was measured in the same manner to find the ΔR value for different concentrations and to calculate the molecular weight as follows:

$$\overline{M}_\eta = \frac{K_{inst}}{\lim_{C \to 0} \frac{(\Delta R)}{C}} \qquad (2)$$

Results and Discussion

Molecular weight

In order to estimate the average molecular weight of *Acacia* by using the Mark Houwink relation, the whole gum and its seven fractions have been evaluated by viscosimetric and tonometric methods.

Table 1 reports the viscosimetric data illustrated as reduced times taken as equivalent to reduced viscosity which must be extrapolated to infinite dilution to obtain the intrinsic viscosity by means of the Huggins' (1942) equation:

$$\frac{t - t_0}{t_0 C} \cong \frac{\eta - \eta_0}{\eta_0 C} = [\eta] + k^1 [\eta]^2 C \qquad (3)$$

where k^1 is a constant for a series of polymers of different molecular-weight in a given solvent. The experimental results expressed in Table 1 are calculated for an average five-point time joined with a standard deviation near to 0.2 s for most of them.

The purely subjective straight-line graph technique is substituted for the more probable straight-line calculation by the use of the least-squares method to evaluate

[6] Hitachi/Perkin Elmer Molecular Weight Apparatus, Model 115.
[7] Anachemia Reagent A.C.S., AC-8370, Toronto, Canada.
[8] pH meter E 512 Metrohm Herisau.
[9] Instruction Manual Catalog. No 115-400, June 1969, N-6058 E-6.
[10] Anachemia Chemicals, AC 8492, Toronto, Canada.

TABLE 1

VISCOSITY DATA FOR *ACACIA* AND ITS FRACTIONS IN MOLAR SODIUM CHLORIDE SOLUTION AT 25°C

Conc. ×10³ (g/ml)	Fraction I $\frac{t-t_0}{t_0 C}$ (ml/g)	Fraction II $\frac{t-t_0}{t_0 C}$ (ml/g)	Fraction III $\frac{t-t_0}{t_0 C}$ (ml/g)	Fraction IV $\frac{t-t_0}{t_0 C}$ ml/g	Fraction V $\frac{t-t_0}{t_0 C}$ ml/g	Fraction VI $\frac{t-t_0}{t_0 C}$ (ml/g)	Fraction VII $\frac{t-t_0}{t_0 C}$ (ml/g)	Whole gum $\frac{t-t_0}{t_0 C}$ (ml/g)
10.00	22.21	18.76	18.15	15.81	12.47	12.03	10.39	17.72
8.70	21.69	18.41	17.87	15.40	12.36	11.15	10.03	17.42
7.69	21.59	18.32	17.71	15.25	12.17	10.91	9.88	17.36
6.90	21.29	18.12	17.32	15.25	11.99	10.73	9.58	17.17
6.25	21.30	17.91	17.07	15.17	12.00	10.84	9.40	16.78

By linear regression calculation (Huggins' Equation):

	Fraction I	Fraction II	Fraction III	Fraction IV	Fraction V	Fraction VI	Fraction VII	Whole gum
$\lim_{c \to 0}$	19.67	16.62	15.38	14.10	11.08	8.59	7.81	15.54
r^2	0.93	0.97	0.95	0.87	0.95	0.82	0.98	0.90
k^1	0.63	0.77	1.20	0.81	1.14	4.82	4.24	0.916

the slope and the ordinate of the straight-line. The calculated parameters, $[\eta]$ and k^1 joined with the correlation coefficient r^2 are listed in Table 1.

The obtained $[\eta]$ values seem right at first sight as far as the correlation coefficient is highly significant; however, the Huggins' k^1 values generally found between 0.3 in a good solvent and 0.5 in a bad solvent can be higher than 0.5 up to 1 and sometimes 2 reflecting thus the ramification of macromolecular chains (Manson et al., 1958; Orofino et al., 1963) or the formation of aggregates (Kalpagam et al., 1963; Peterson et al., 1963). The highest values of k^1 for fractions VI and VII are questionable because the relative viscosity for each concentration might be higher than 1.1 for a better accuracy in obtaining $C \rightarrow 0$.

Tonometric measurements of gum fractions III, IV and V and sodium salicylate as standard sample, useful for determining the constant, K_{inst} of the apparatus are reported in Table 2. These values are a three-reading average taken after a 10-min equilibrium. The evaluation of $\Delta R/C$ at infinite dilution is calculated by linear regression and found highly significant. These data are applied in Eqn. 2 and used in the calculation of the Standinger constants for *Acacia* in the Mark-Houwink equation. By significant linear regression of $\log [\eta]$ versus $\log M$ for the three known fractions, the relation deduced, for the present system, can be expressed in the form of $[\eta] = 2022 \ \overline{M}_n^{0.184}$ and used in the $\overline{M}_v$ evaluation of each fraction and the whole gum listed in Table 3. The whole gum is found to have $\overline{M}_v$ of 65,400.

This $\overline{M}_v$ value is compatible with others molecular weights $\overline{M}_w$ found for some *Acacia* (Anderson et al., 1971), but nevertheless the parameters K et α for the Mark-Houwink equation are very different of those normally expected. For random coiled polymers, the exposant α varies from 0.5 in a bad solvent to a maximum of about 1; generally α lies between 0.6 and 0.8 and K between 0.5 and 5×10^{-4}. Both K et α are functions of the solvent as well as the polymer type. Anderson et al. (1967b) found $K = 1.3 \times 10^{-2}$ and $\alpha = 0.54$ for data obtained for *Acacia senegal*

TABLE 2

NUMBER AVERAGE MOLECULAR WEIGHT DETERMINATION OF THREE FRACTIONS OF *ACACIA* BY TONOMETRIC MEASUREMENTS

Fraction III		Fraction IV		Fraction V		Na Salicylate	
conc. (g/kg)	$\dfrac{\Delta R^*}{C}$	conc. (g/kg)	$\dfrac{\Delta R^*}{C}$	conc. (g/kg)	$\dfrac{\Delta R^*}{C}$	conc. $\times(10^3)$ (mole/kg)	ΔR^*
17.541	0.1539	12.666	0.1429	12.941	0.3632	14.887	50.15
34.070	0.2489	25.143	0.1818	25.767	0.36364	24.689	88.20
50.668	0.3462	37.402	0.2273	38.536	0.36875	37.187	134.50
84.151	0.5241	62.173	0.2895	64.094	0.37554	43.169	155.65
						55.979	203.96
By linear regression calculation							
$\lim_{C \rightarrow 0}$ 0.0594		$\lim_{C \rightarrow 0}$ 0.1083		$\lim_{C \rightarrow 0}$ 0.3587			
$\overline{M}_n$	63,070		34,420		10,390		
r^2	0.999		0.993		0.955		

*Main-oven temperature: 60.0°C; sub-oven temperature: 55.0°C

TABLE 3

SUMMARY OF RESULTS OBTAINED BY FRACTIONAL COACERVATION OF *ACACIA*

	Alcohol solution % v/v	Weight fraction % w/w	$W(M_1)$ $\times 10^2$	$\overline{M}_n$ (ml/g)	$[\eta]$	$\overline{M}_v$
Fraction I	35	19.09	9.54	–	19.67	235 300
Fraction II	40	22.03	30.11	–	16.62	94 200
Fraction III	45	28.27	55.25	63 070	15.38	61 810
Fraction IV	50	10.69	74.74	34 420	14.10	38 540
Fraction V	55	7.34	83.75	10 390	11.08	10 400
Fraction VI	60	–	–	–	8.59	2 610
Fraction VII	62	–	–	–	7.81	1 550
Whole Gum					15.54	65 380

and its fractions as sodium salts in 1 M sodium chloride but these values were not of general applicability within the *Acacia* genus. Sloniensky at al. (1971) described the relationship between the molecular weight of the arabate in 20 mM potassium chloride and their intrinsic viscosities by the relationship $[\eta] = 0.103 \, M^{0.42} \, ml \cdot g^{-1}$ and explained the value of the exposant of this equation as consistent with a highly branched, macromolecular model.

Finally, Sevenson et al. (1968) found values of α for gum arabic lower than ours, the determination of the viscosity and molecular weight of the fractions had been done in 0.35 M NaCl at pH 10 to which 0.25% of the sodium salt of ethylene diaminitetraacetic acid had been added as a sequestrant.

This exceptionally low value of α has never been found with branched poly-styrene (Thurmond et al., 1952), with branched dextran (Senti et al., 1955), with sodium lignosulfate (Tachi et al., 1960), with cross-linked glucomannan (Linnel et al., 1966), with copolymers as poly(butyl-itaconate-cO-dibutyl itaconate) (Bekturov et al., 1970), and some other polymers reported in handbook (Brandrup, 1975).

Molecular weight distribution

The fractionation of *Acacia* has been done to establish subsequently the curve of distribution of constituent species and to get an idea of the state of polymolecularity of this gum. All the fractions were characterized by their $\overline{M}_v$ in using the Mark-Houwink equation in the same solvent–temperature conditions. The evaluation of this extraction is summarized in Table 3.

In order to find the function of distribution of molecular weight, Mark and Raff's method (1944), consisting in the evaluation of cumulated weights of the different fractions in relation with their own molecular weight was used; the cumulative curve is illustrated in Fig. 1 where the cumulative function has been calculated according to Schulz and Dinglinger method (1939).

This method is founded on the following hypothesis: each fraction is composed of half of the molecules having a molecular weight above average and of molecules having a molecular weight under average. Such a process supposes implicitly that the diverse fractions are monodisperse samples.
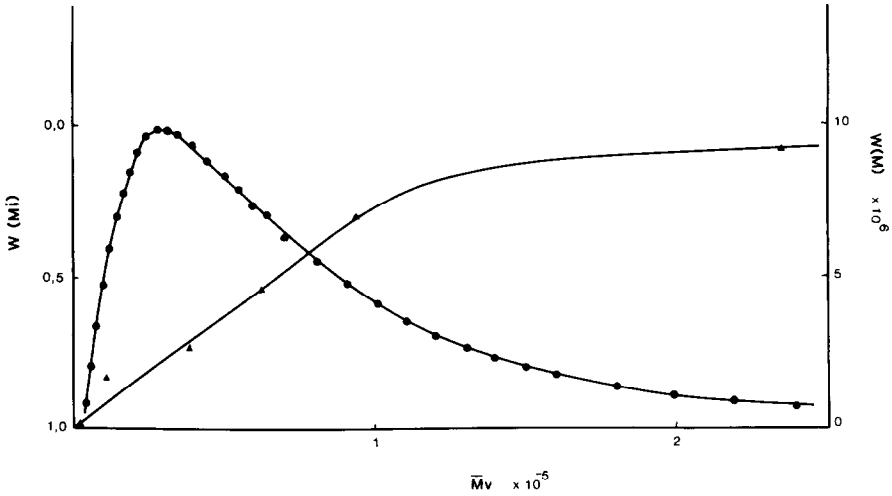
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Fig. 1. Integral molecular weight distribution and calculated distribution curves of fractional precipitation of *Acacia*.

In order to describe the polymolecularity of a polymer, many distribution laws (Schulz, 1939; Tung, 1956; Lansing et al., 1935; Wesslau, 1956) can be used. On a log-probit scale sheet, illustrated in Fig. 2, were graphically represented the cumula-
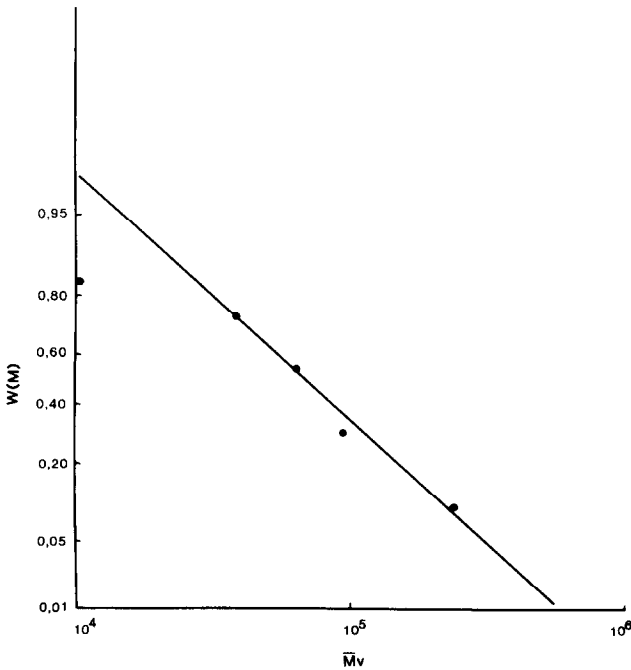

Fig. 2. Fractionation of *Acacia* represented on a log-probit scale sheet.

tive weight fractions of *Acacia* as function of their respective $\overline{M}_v$. The obtained linear graph is subject to the interpretation that the polymers are following the normal log distribution law. The parameters of this linear relation have been evaluated and the linear straightness has been tested by the Fisher method and found to be highly significant in discarding the fraction V for a threshold of probability 0.05. This linear regression could justify the selection, for *Acacia* as function of theoretical molecular weight distribution, the normal-log distribution function expressed as follows:

$$W(M) = \frac{1}{\beta\sqrt{\pi}} \frac{1}{M} \cdot \exp\left(-\frac{1}{\beta^2} \cdot \ln^2 \frac{M}{M_0} \right) \tag{4}$$

This distribution function [W(M)] has two parameters: M_0 and β, representing, respectively, the median value and the breath of the distribution. These values are easily evaluated by graphical interpolation at I (M) = 0.5 for M_0 and i (M) = 0.8413 for β or by calculation from the theoretical straight line equation represented as follows:

$$\text{Probit}\left[M(W)\right] = 17.2358 - 2.5341 \log \overline{M}_v \tag{5}$$

The values of M_0 and β were found to be 67,340 and 1.2779 and were used in the calculation of the curve of differential distribution illustrated in Fig. 1; in addition, they could be used to evaluate the average molecular weight in accordance with the theoretical distribution, where;

$$\overline{M}_\eta = M_0 e^{-\beta^2/4} = 44,760 = 45,000 \tag{6}$$

$$\overline{M}_w = M_0 e^{\beta^2/4} = 101,300 = 100,000 \tag{7}$$

$$\overline{M}_z = M_0 e^{3\beta^2/4} = 229,360 = 230,000 \tag{8}$$

The different average molecular weights bring information on the polydispersity of *Acacia* gum. In fact, these values, identical for an isomolecular compound, are progressively more different when the heterogeneity of the polymer increases but they are always in the following order:

$$\overline{M}_\eta \leqslant \left(\overline{M}_{Vexp}\right)_{\alpha < 1} \leqslant \overline{M}_w \leqslant \overline{M}_z \tag{9}$$

Other authors have characterized the polymolecularity of a polymer not by the distribution curve but only by an index of polymolecularity, I, defined as it follows:

$$I = \beta^2/2 = \frac{\overline{M}_w}{\overline{M}_n} = 2.26 \tag{10}$$

In order to estimate the polydispersity of *Acacia*, by means of normal-log distribution function, the viscosity-average molecular weight of the different fractions of *Acacia* were used; however, there is a relation between $\overline{M}_v$ and the parameters of this chosen distribution function, expressed as following:

$$\overline{M}_v = M_0 e^{\alpha \beta^2 / 4} \qquad (11)$$

where α is the exponent of the Mark-Houwink equation. Generally, $\overline{M}_0$ is significantly lower than $\overline{M}_w$ when the distribution is wide (Chiang, 1959). The value of $\overline{M}_v$, calculated from Eqn. 11 has given a molecular weight of about $72,590 \pm 5\%$ near. This value is so significantly similar to that obtained experimentally on the whole gum and found to be $65,380 \pm 3270$.

This demonstrates that the polydispersity of *Acacia* follows well a log-normal distribution law and also the index of polydispersity calculated from this hypothesis supports a light polydispersity in comparison of that of 1.46 already found (Swenson et al., 1968) but in contradiction with that announced earlier (Anderson et al., 1967).

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