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Effect of Temperature on Mark-Houwink-Kuhn-Sakurada (MHKS) Parameters of Chañar Brea Gum Solutions

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Abstract Chañar brea gum (CBG) is a water soluble exudate from the *Cercidium praecox* tree. The CBG was incorporated into the Argentine Food Code in 2013, due to its ancestral background and its current food uses. CBG could also be used as additive and/or excipient in pharmacological formulations. In this work Mark-Houwink-Kuhn-Sakurada (MHKS) parameters of CBG solutions and temperature effect on hydrodynamic parameters are reported. The analyzed values for this constants indicated a spherical conformation, and it can be concluded that CBG macromolecule has a very good solubility in water.

Keywords: *Chañar Brea Gum, Mark-Houwink-Kuhn-Sakurada Parameters, Temperature Effect.*

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1. Short Communication

In biopolymers industry the intrinsic viscosity and molecular weight calculation are essential for quality control. The intrinsic viscosity is determined by the Huggins equation through measurements of flow times in capillary viscometers and the density of biopolymeric solutions in the Newtonian zone. From this measurement, the molecular weight, hydrodynamic radius, form factor, etc., are determined [1].

In Huggins' method, intrinsic viscosity [η] is defined as the ratio of the increase in relative viscosity (η_i) to concentration (c in g cm^{-3}) when the latter tends to zero:

$$\frac{\eta_i}{c} = [\eta] + K_H [\eta]^2 \, c \qquad (1)$$

IUPAC recommends the term "increment of relative viscosity (η_i)," instead of "specific viscosity," because it has no attributions of specific quantity, meaning: $\eta_i = \eta_r - 1$, where $\eta_r = \eta/\eta_0$, with η (solution viscosity) and η_0 is dissolvent viscosity. The term of the Huggins equation "$\eta_i/c = \eta_{red}$".

The (MHKS) equation is,

$$[\eta] = KM^a \qquad (2)$$

where k and a are MHKS constants, these constants depend on the type of polymer, solvent, and temperature of viscosity determinations. The exponent "a" is a function of polymer geometry.

The main difficulty in the calculation of molecular weight using MHKS parameters is that the polymer or biopolymer requires at least five different molecular weight determinations, and given that these must be calculated at different temperatures, this determination requires an extended period [2].

The MHKS parameters at different temperatures, the intrinsic viscosity (of the same type of macromolecule) can be measured at various molecular weights, but is very difficult. These data can be used to construct the log-log graph between [η] and M, and the slope can be used to find the value of "a" and the intercept, giving us "k" for each temperature [3,4,5,6,7]. In many cases, there can be various molecular weights, while in many other cases there is a single molecular weight, and these macromolecules must be studied against macromolecular consistence patterns similar to the one intended to be characterized. This situation becomes much more difficult when there is a need to determine the MHKS parameters at other temperatures. The classic approach in this type of study is to measure a "standard" temperature and then use this to calculate parameters "k" and "a" using iterative method [2]. However, these parameters are not valid when the temperature changes and cannot be used, since they represent very different molecular weights and diverge substantially from the real molecular weight. The central hypothesis is that M does not change with increasing temperature, but its macromolecular hydrodynamics modifies.

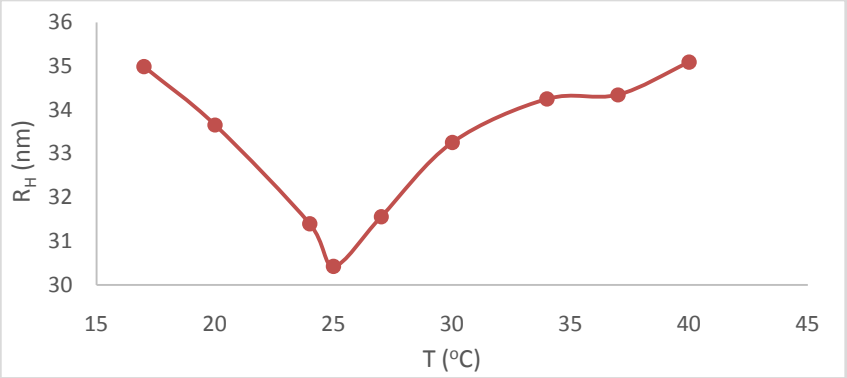

Figure 1. Hydrodynamic radius vs T for CBG

It can be seen in Figure 1 that the hydrodynamic radius (R_H) increases with increasing temperature from 25°C. This is due to the opening of biopolymer (CBG) chains and the incorporation of water molecules in its structure that causes the expansion of the molecule. It should be noted that this situation does not change the molecular weight of CBG. From the data in Figure 1 this conclusion is reached, data is seen in Table 1.

Regarding the other hydrodynamic properties, it can be observed that parameters "k" and "*a*" increase with temperature increasing, as shown in Table 1. These parameters "k" and "*a*" are calculated by the iterative calculation method, see reference [2]. The data of k accounts for the biopolymer-solvent interaction in a suitable modality; that the shape of the macromolecule in solution is spherical (value of "*a*") and that it has a slight decompression due to the increase in temperature. The reported molecular weight in [1] is 1890000 g/mol and is used as reference for this publication.

In a similar context the value of *P* is 1.0524 and that of $\nu_{a/b}$ is 2.5031 [1,8], that of β is $2.01\text{x}10^{6}$ and that of φ_0 is $2.42\text{x}10^{23}$ mol^{-1}.

The hydrodynamic radius (R_H), is given by the Einstein relation,

$$R_H = \left(\frac{M[\eta]}{\nu_{a/b} N_{Av}} \right)^{1/3} \tag{3}$$

where N_{av} is Avogadro number, and $v_{a/b}$ is form factor.

$$\nu_{a/b} = \frac{[\eta]}{V_s} \tag{4}$$

where V_s is specific volume (cm^3/g).

Thus, it is a common practice to express the frictional coefficient of solution (*f*) and dissolvent (f_0), as,

Table 1. Hydrodynamic Data of CBG Solutions

T (°C)	[η] (cm^3/g)	*k* (cm^3/g)	a	M (g/mol)	ER%	R_H (nm)
17	80.20	0.1233	0.4481	1897090.86	0.37	34.98
20	71.58	0.1271	0.4382	1892987.51	0.16	33.66
24	58.11	0.1308	0.4218	1892390.43	0.13	30.45
25	52.91	0.1347	0.4133	1891142.83	0.06	30.42
27	59.02	0.1418	0.4173	1891621.97	0.08	31.55
30	68.98	0.1415	0.4282	1893925.09	0.20	33.25
34	75.26	0.1425	0.4337	1896512.08	0.34	34.25
37	75.91	0.1429	0.4341	1896632.32	0.35	34.35
40	81.03	0.1455	0.4374	1894566.85	0.24	35.09

$$P = \frac{f}{f_0} \tag{5}$$

where *P* is Perrin number.

The Scheraga-Mandelkern parameter, given by,

$$\beta = \frac{\eta_0}{f} \left(\frac{M[\eta]}{100} \right)^{0.3333} \tag{6}$$

where η_0 is solution viscosity in poise.

Other classical size-independent combination is the Flory parameter, as,

$$\varphi_0 = \frac{M[\eta]}{14.7 R_H{}^3} \tag{7}$$

These parameters value lead sphericity of the CBG macromolecule in its interaction with water. Analyzing them it can be concluded that CBG has a very good solubility in water [8,9].

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