

# Mark-Houwink Parameters for Aqueous-Soluble Polymers and Biopolymers at Various Temperatures

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Received April 16, 2014; Revised May 28, 2014; Accepted May 28, 2014

**Abstract** The intrinsic viscosity measurements used to calculate the Mark-Houwink (M-H) parameters are generally performed for different molecular weights at a constant temperature, with the standard value of this temperature being 25°C, or else 37°C in the case of mammalian proteins, or else under theta conditions for polymers and biopolymers. In the polymer industry, polysaccharides and proteins must circulate through pipes during transport processes where pumps have a very high-energy expenditure and where temperatures must be greatly increased, and at this point calculation of the Mark-Houwink parameters becomes important. The M-H parameters are calculated at standardized temperatures and in many cases, these are not useful because of the errors they carry, and it then becomes very difficult to calculate the molecular weight. It is therefore necessary to know the change in molecular weight as evidence of a change in the product obtained, as this may create a need to halt the production process, transport, or extrusion. The basic criterion is that the molecular weight does not change with temperature, or at least within one discrete range of temperatures, but that there is hydrodynamic change (intrinsic viscosity). The method is simple and requires iterative mathematical processing and measurement of intrinsic viscosity at different temperatures.

**Keywords:** *intrinsic viscosity, macromolecules, Mark-Houwink parameters, temperature*

**Cite This Article:** Martin Alberto Masuelli, "Mark-Houwink Parameters for Aqueous-Soluble Polymers and Biopolymers at Various Temperatures." *Journal of Polymer and Biopolymer Physics Chemistry*, vol. 2, no. 2 (2014): 37-43. doi: 10.12691/jpbpc-2-2-2.

## 1. Introduction

Quality control in the polymers or biopolymers industry is essential in order to achieve an acceptable product for the consumer. Problems can arise when the temperature of the raw material (biopolymer in the production process) must be increased so that it can be pumped through pipes to reach its destination. In many cases, this process cannot be stopped since this would involve economic losses and time delays. Thus, there is a need for a simple procedure to address the need to molecular weight determinate of the polymer or biopolymer using a single sample, without having to wait too long for an optimal molecular weight result, and with this procedure requiring only one densimeter and viscometer as well as perhaps a simple equation point such as the Solomon-Ciuta.

The main difficulty in the calculation of molecular weight using the Mark-Houwink 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.

Given the difficulty involved in calculating the Mark-Houwink parameters at different temperatures, the intrinsic viscosity (of the same type of macromolecule)

can be measured at various molecular weights. These data can be used to construct the log-log graph between  $[\eta]$  and  $M$ , and the slope can be used to find the value of " $a$ " and the intercept, giving us " $k$ " for each temperature [1-5]. 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 Mark-Houwink 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 " $a$ ". 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.

Utracki and Simha [6] measured the intrinsic viscosities of polystyrene between the  $\theta$  and the critical temperatures in cyclohexane for molecular weights varying between 6000 and 6,000,000 g/mol, where the exponent  $a$  in the Mark-Houwink relation decreases with increasing molecular weight for temperatures sufficiently below  $\theta$  in accordance with the theoretical predictions. Dohmen et al. [7] worked with low molar mass polyethylene glycol, at 200 to 1000 g/mol, in a homologous series of primary

alcohols, acetone, and toluene, as determined from viscosity measurements in a range of  $T$  from 298.2 to 323.2 K, and concluded that the influence of the temperature was not significant. Sadeghi et al. [8], measured the density and viscosity of polyvinylpyrrolidone in aqueous solutions at temperatures 298.15, 308.15, 318.15, and 328.15 K, where intrinsic viscosity decreased with increased temperature. Guner [9] and Catiker & Guner [10] studied dextran samples (of different molecular weights) evaluated in ethylene glycol solutions with viscosity measurements from 25–45°C. The Mark-Houwink constant,  $k$ , also decreases with increasing temperature in the same temperature range, while the “ $a$ ” value evaluated for the system also decreased to a lower value of 0.534 with increasing temperature, which may be interpreted as the solvent approaching a theta solvent type by the temperature increase. Using previously reported viscometric constants data, Kasaai [11] found a functionality of  $a$  and  $k$  with temperature for chitosan in any solvent–temperature system. The Tsai [12,13] group also carried out similar studies with chitosan. For pectins, Masuelli [14] worked with an iterative method and found that the Mark–Houwink parameters had functionality with temperature. The numerical value of  $a$  indicated that pectin acquires a rod-like shape in an aqueous solution, while the values of  $a$  and  $k$  were shown to decrease with temperature in a water solution.

In the present work, an iterative method is proposed in order to determine the Mark-Houwink parameters for xanthan gum, pectin, gelatin, and polyvinylalcohol-co-vinylacetate at different temperatures. The density and viscosity measurements were performed for polymer solutions using the Huggins method.

### 1.1. Intrinsic Viscosity

In macromolecular chemistry in dilute solutions, the relative viscosity  $\eta_r$  is often measured. The relative viscosity is the ratio of the viscosity of the solution to that of the solvent:

$$\eta_r = \frac{\rho t}{\rho_0 t_0} \quad (1)$$

The specific viscosity  $\eta_{sp}$  is obtained from the relative viscosity by

$$\eta_{sp} = \eta_r - 1 \quad (2)$$

### 1.2. Methods for Determination of Intrinsic Viscosity

The intrinsic viscosity, denoted by  $[\eta]$ , is defined as

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} = \lim_{c \rightarrow 0} \frac{1}{c} \ln \eta_r \quad (3)$$

or as

$$[\eta] = \lim_{\eta_{sp} \rightarrow 0} \frac{\eta_{sp}}{c} \quad (4)$$

where  $c$  is the concentration of the polymer in g/mL of the solution. The quantity  $\eta_{sp}/c$  is called the reduced viscosity. The unit of intrinsic viscosity is (mL/g) or (cm<sup>3</sup>/g) depending upon the concentration unit of the solution. The

intrinsic viscosity is also called the limiting viscosity number. The plot of  $\eta_{sp}/c$  versus  $c$  or  $1/c \ln \eta_r$  versus  $c$  often gives a straight line, the intercept of which is  $[\eta]$ .

### 1.3. Intrinsic Viscosity Methods

Huggins (1942) [15] showed that the slope is

$$\frac{d\eta_{sp}/c}{dc} = k_H [\eta]^2 \quad (5)$$

With rearrangement and integration the resulting equation becomes

$$\frac{d\eta_{sp}/c}{dc} = k_H [\eta]^2 \quad (6)$$

where  $k_H$  is a dimensionless constant called the Huggins constant. The value of  $k_H$  is related to the structures of polymers or biopolymers.

For molecules of high intrinsic viscosity, a correction must be made for the effect of the rate of shear strain. With relatively low intrinsic viscosity, the rate of shear strain does not have any appreciable effect.

Mark (1938) [17] and Houwink (1940) [18] independently correlated the intrinsic viscosity with molecular weight:

$$[\eta] = k M^a \quad (7)$$

where  $k$  and  $a$  both are constants. The Mark-Houwink equation is applicable to many polymers and is extensively used to determine molecular weight. The constants  $k$  and  $a$  both vary with polymers and solvents [19].

Equation (7) describes the relationship between intrinsic viscosity and molecular weight. Since molecular weight is related to the size of the polymer chain, for proteins [20] the following equation is generally used:

$$[\eta] = k \left( \frac{M}{M_0} \right)^a \quad (8)$$

where  $M_0$  is the molecular weight of the amino acid repeating unit. The calculation of Mark-Houwink (M-H) parameters is carried out by the graphic representation of the following equation:

$$\ln [\eta] = \ln k + a \ln M_w \quad (9)$$

where  $k$  and  $a$  are M-H constants, and with these constants depending upon the type of polymer, the solvent, and the temperature of viscometric determinations. The exponent  $a$  is a function of polymer geometry and varies from 0.5 to 2.0. These constants can be determined experimentally by measuring the intrinsic viscosity of several polymer samples for which the molecular weight has been determined by an independent method (e.g., osmotic pressure or light scattering). Using the polymer standards, a plot of  $\ln [\eta]$  versus  $\ln M_w$  usually gives a straight line. The slope of this line is the value of  $a$  and its intercept is equal to  $\ln k$ . The M-H exponent bears the signature of a polymer chain's three-dimensional configuration in the solvent environment:  $a$  values from 0.0–0.5 reflect a rigid sphere in an ideal solvent; those from 0.5–0.8 a random coil in a good solvent; and from 0.8–2.0 a rigid or rod like configuration (stiff chain). The fact that the intrinsic

viscosity of a given polymer sample differs depending upon the solvent used provides an insight into the general shape of polymer molecules in solution. A long-chain polymer molecule in solution takes on a somewhat kinked or curled shape, intermediate between a tightly curled mass (coil) and a rigid linear configuration. Any molecule may display all possible degrees of curling, but there will be an average configuration, which will depend on the solvent. In a good solvent, which shows a zero or negative heat of mixing with the polymer, the molecule is loosely extended, and the intrinsic viscosity is high. The Mark-Houwink “ $a$ ” constant is close to 0.75 or higher for these “good” solvents. In a “poor” solvent, which shows a positive heat of mixing; segments of a polymer molecule attract each other in solution more strongly than they attract the surrounding solvent molecules. The polymer molecule assumes a tighter configuration, and the solution has a lower intrinsic viscosity. The M-H “ $a$ ” constant is close to 0.5 in “poor” solvents, while for a rigid or rod-like polymer molecule that is greatly extended in solution, the M-H “ $a$ ” constant approaches a value of 2.0 [14].

#### 1.4.1. Iterative Method

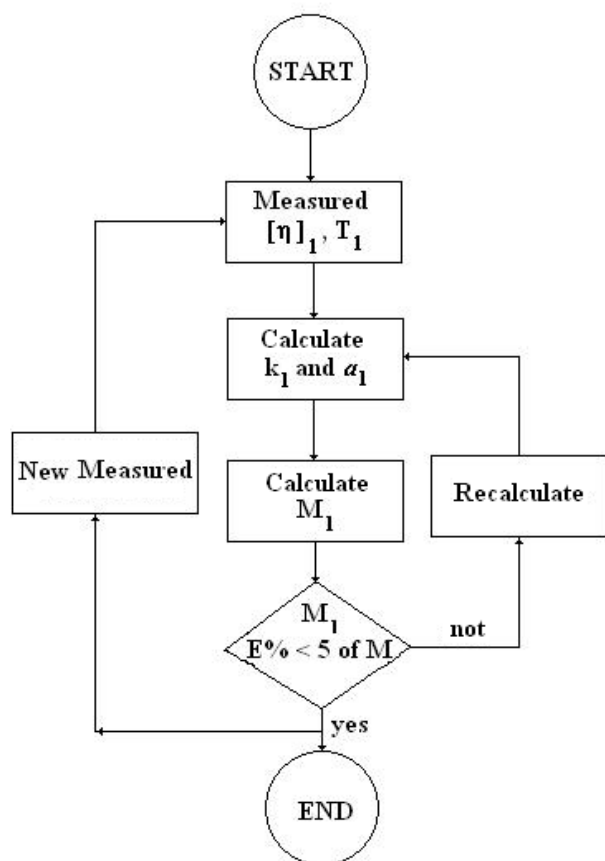


Figure 1. Schematic diagram of the iteration process

After obtaining, the Mark-Houwink parameters are established by fixing molecular weight ( $M$ ), and the intrinsic viscosity  $[\eta]$  was measured at each temperature and these Mark-Houwink parameters are calculated. In the case of a protein, the  $M_0$  is the molecular weight representative of the amino acid monomers (calculated according to their percentage in the macromolecule). The  $a$  and  $k$  values are iterated and re-calculated, and a new molecular weight  $M_1$  is calculated. This procedure is repeated until the value of this molecular weight  $M_1$  is

very similar to  $M$  and with an error less than 5% or less than 1%. This procedure is then repeated for each temperature, and data is thus obtained the Mark-Houwink parameters with respect to the standard molecular weight ( $M$ ). An illustration of this process is seen in Table 1 and Figure 1.  $M$  is calculated from the Mark-Houwink parameters standard at 25°C and are obtained from literature (polyvinylalcohol-co-vinylacetate [24] and xanthan gum [25] and from previous works pectin [14] and gelatin B [26]).

Table 1. Iterative calculation procedure,  $M$  is standard at 25°C

$T_1$				
$[\eta]_1$	$k_1$	$a_1$	$M_1$	$M_1 \text{ RE\%} < 5\% M$
	$k_{1i}$	$a_{1i}$	$M_{1i}$	“
	$k_{1ii}$	$a_{1ii}$	$M_{1ii}$	“
	$k_{1i...}$	$a_{1i...}$	$M_{1i...}$	$M_{1i...} \text{ RE\%} < 1\% M$
$T_2$				
$[\eta]_2$	$k_2$	$a_2$	$M_2$	$M_2 \text{ RE\%} < 5\% M$
	$k_{2i}$	$a_{2i}$	$M_{2i}$	“
	$k_{2ii}$	$a_{2ii}$	$M_{2ii}$	“
	$k_{2i...}$	$a_{2i...}$	$M_{2i...}$	$M_{2i...} \text{ RE\%} < 1\% M$

## 2. Materials and Methods

### 2.1. Sample Preparation

Pectin from citrus peel was supplied by Sigma (Galacturonic acid  $\geq 74.0\%$ , methoxyl groups 6.7%). Five grams of biopolymer powder was dissolved in 250 mL of pure water deionized and stirred gently at temperature 40°C for 2 h. Finally, pectin was diluted in distilled water to prepare solutions of 1.0, 0.75, 0.5, 0.25, and 0.15% wt. in 0.01M of NaCl.

Transparent liquid adhesive polyvinylalcohol-co-vinylacetate (PVA-co-VAC) (Bologoma®, Akapol SA, Argentina, with a molecular weight of 47,000 g/mol and 12% vinylacetate) was weighed 15 g, and allowed to dry at 60°C for 24hs. After fully dried 2.75 g of gum remained, with 2.0 grams of this then dissolved with 200 ml distilled water. This solution was used to prepare solutions of 1.0, 0.5, and 0.25% wt. in 0.01M of NaCl.

As of 0.27 g of xanthan gum (Parafarm, Argentina) were dissolved in 200 ml of 0.01M of NaCl solution, from this were prepared solution of 0.1 and 0.075% wt.

The gelatin was dried in zip plastic bags in desiccators. Samples of the gelatin B (from cow bone with an isoelectric point of 5.10, supplied by Britannia Lab, Argentina) were dissolved in 0.01M of NaCl in order to prepare solutions of 1.0, 0.75, 0.5, and 0.25% wt.

### 2.2. Density Measurement

The densities of the solution and solvent were measured with an Anton Paar DMA5N densimeter.

### 2.3. Capillary Viscometry

Solutions and reference solvents were analyzed using an Ubbelohde 1B viscometer (IVA), under precise temperature control using a thermostatic bath (Haake 1C). Measurements were performed using 25 ml aliquots of the sample solutions, again with measurement of the flow time.

### 2.3.1. Viscometer Calibration

This process should be performed as follows: after cleaning the viscometer with cleaning solution, rinse with distilled water. Add a 10 ml aliquot of water and let it come to thermal equilibrium with the thermostat. Both fiducially marks should be below the water level of the thermostat. Using a rubber bulb, pull the water in the viscometer above the upper fiducially mark and measure the time required the water to flow from the upper to the lower mark. Repeat this process to determine the uncertainty in the time measurement. The flow time for the water, along with its density at 25°C (0.99777 g/cm<sup>3</sup>) and viscosity (0.8937 cP) are used with Equation 1 to determine the viscosities of the solvent and the sample solution. Next, drain the water from the viscometer. Rinse it first with a few milliliters of solvent (distilled water), then with acetone and dry. Add a 10 ml aliquot of distilled water, and after the viscometer and water are at thermal equilibrium, measure the flow time as before. To correct errors in the viscosity measurements the Hagenbach-Couette method of time correction was employed, where the  $t_H$  calculated was 0.82 sec.

While the polymer is dissolving, clean the viscometer with cleaning solution. If this is not available, prepare a cleaning solution by dissolving 12 g sodium dichromate (Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, Carlo Erba) in 12–15 ml hot water. Cautiously, slowly, and while stirring, add 25 ml concentrated sulfuric acid. Store this solution in a 250 ml bottle with a glass stopper. Use carefully on glassware that has been previously cleaned with detergent and water. Do not dispose of this cleaning solution in the sink. Once the viscometer is clean and the initial water flow measurements can be repeated, proceed to take the measurements of the samples. Record the temperature using a CHECKTEMP digital thermometer.

## 3. Results and Discussion

The Huggins method was used to calculate the intrinsic viscosity for study of the four macromolecules, and the standard Mark-Houwink parameters were calculated at 25°C. The range of temperatures used were 20–50°C for pectin; 25–50°C for xanthan gum; 20–37.4°C for gelatin B; and 25–60°C for polyvinylalcohol-co-vinylacetate.

**Table 2. Hydrodynamic data for PVA-co-VAc as a function of temperature**

T (°C)	[ $\eta$ ] (cm <sup>3</sup> /g)	k (cm <sup>3</sup> /g)	<i>a</i>	M	RE%
25.0	43.74	0.04910	0.6319	46,620	0.2580
30.0	55.43	0.05120	0.6500	46,627	0.2731
35.0	61.34	0.05210	0.6581	46,409	0.1957
40.0	66.43	0.05234	0.6649	46,550	0.1075
45.0	73.88	0.05253	0.6744	46,586	0.1849
50.0	79.21	0.05260	0.6809	46,523	0.0494
55.0	94.27	0.05280	0.6966	46,587	0.1871
60.0	99.79	0.05310	0.7014	46,560	0.1290

As with most macromolecules, the intrinsic viscosity decreases with temperature, or in other words, there is a decrease in the hydrodynamic radius of the macromolecule due to the effect of its compaction, which translates to a decrease in viscosity. A unique phenomenon occurs with PVA-co-VAc since an increase in temperature causes an increase in the intrinsic viscosity [21,22,23], and therefore in the hydrodynamics of this

macromolecule. This phenomenon is due to an increase in the hydrophobicity, which is expressed as a macromolecular expansion (Table 2).

The molecular weight of PVA-co-VAc is 46,500 g/mol and the MH parameters used were those published by Misra and Mukherjee [24], with these data being consistent with those shown in this work. The conformation acquired by this macromolecule in an aqueous solution is random-coil, and as the temperature increases, the polymer expands. This contradicts the behavior of many polymers and biopolymers, which tend to pack regardless of their conformation. This is explained by a change in the affinity of the polymer caused by water, which makes it more hydrophobic as the temperature increases, although even with this phenomenon the PVA-co-VAc remains in solution.

**Table 3. Mark-Houwink parameters obtained for pectin. Data provided courtesy of Elsevier (Masuelli, M. Viscometric study of pectin. Effect of temperature on the hydrodynamic properties. International Journal of Biological Macromolecules 2011; 48: 286-291) [15]**

T (K)	[ $\eta$ ] (cm <sup>3</sup> /g)	k (cm <sup>3</sup> /g)	<i>a</i>	M (g/mol)	RE%
22.2	502.12	0.0242	0.8232	176,510	2.6221
26.6	462.35	0.0234	0.8221	168,749	1.8901
29.6	450.33	0.0226	0.8215	173,117	0.6404
34.9	444.36	0.0222	0.8213	171,333	0.3878
37.0	430.24	0.0219	0.8208	170,889	0.6459
39.9	410.07	0.0217	0.8180	169,008	1.7395
44.8	403.11	0.0215	0.8169	170,685	0.7645
49.8	386.15	0.0213	0.8129	173,788	1.0395

Pectin acquires a rod-like conformation with M of 172,000 g/mol, and it tends towards compaction with increasing temperature. These data are supported by a decrease in the hydration value [15]. With the method used in the cited work, the percentage of relative error in the calculation of the molecular weight of pectin can be improved even further with RE% becoming less than 1%, but in the present work these values range from 1–5.33% (see Table 3).

For xanthan gum, the value of "*a*" decreases as temperature increases. This phenomenon is not very marked compared to the rest of the macromolecules and can be explained by the weak influence of temperature in gum and by its low levels of thermodynamic change. In other words, this macromolecule is almost inert to temperature changes in this range of temperatures (see Table 4). Molecular weight calculated for xanthan gum is 1,675,000 g/mol from the Mark-Houwink parameters for each temperature. Mark-Houwink parameters used are "*k*" = 2.79 x 10<sup>-3</sup> cm<sup>3</sup>/g and "*a*" = 1.2754 at 25°C, data obtained from Tinland and Rinaudo [25] (Dependence of the Stiffness of the Xanthan Chain on the External Salt Concentration. Macromolecules 1989; 22: 1863-1865).

**Table 4. Intrinsic viscosity and Mark-Houwink parameters of xanthan gum at different temperatures**

T (°C)	[ $\eta$ ] (cm <sup>3</sup> /g)	k (cm <sup>3</sup> /g) x 10 <sup>3</sup>	<i>a</i>	M (g/mol)	RE%
25.0	24.20	2.7900	1.2754	1,675,310	0.0006
30.0	23.72	2.7911	1.2741	1,672,944	0.1406
35.0	23.45	2.8122	1.2727	1,674,373	0.0553
40.0	22.67	2.8135	1.2704	1,672,622	0.1598
45.0	21.77	2.8145	1.2675	1,673,535	0.1053
50.0	22.31	2.8959	1.2671	1,675,812	0.0306

In the case of gelatin B the value of "*a*" shows a sharper change than in xanthan gum, covering a range of T<sub>g</sub> from 26–30°C, and therefore as in other proteins the



conformation changes in this macromolecule are highly influenced by temperature. This is due to the sol-gel transition and thermal denaturation.

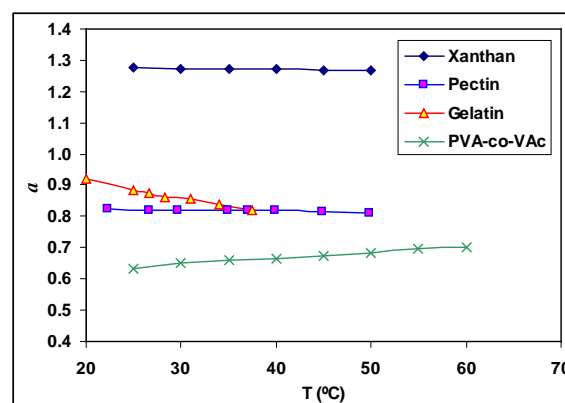
**Table 5. Data obtained for intrinsic viscosity and Mark-Houwink parameters of gelatin B at different temperatures**

T (°C)	$[\eta]$ (cm <sup>3</sup> /g)	k (cm <sup>3</sup> /g)	$a$	M (g/mol)	RE%
20.00	62.12	0.1681	0.9211	67,452	0.0702
25.00	48.65	0.1660	0.8850	67,442	0.0849
26.60	44.46	0.1631	0.8737	67,449	0.0744
28.30	41.15	0.1626	0.8621	67,462	0.0558
31.00	39.28	0.1621	0.8554	67,429	0.1051
34.00	35.53	0.1618	0.8400	67,457	0.0626
37.40	31.12	0.1614	0.8198	67,425	0.1104

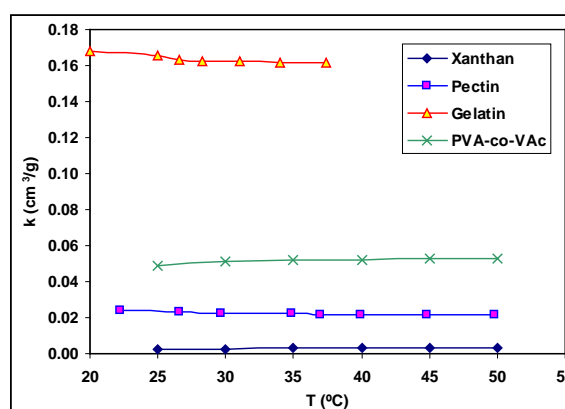
The molecular weight calculated for gelatin is 67,500 g/mol (Table 5). Pouradier & Venet [27] shown that an equation of the type  $[\eta] = 0.166 (M/M_0)^{0.885}$  exists between the intrinsic viscosity and molecular weight of gelatin, where  $M_0$  is the molecular weight of the repeating unit, where is  $M_0 = 110$  [28], calculated from percent of aminoacid content [29]. The work of reference [26] falls into the error of assessment of  $M_0$  must therefore be corrected to the value of  $M_0 = 110$  g/mol. Bohidar [28] studied the aggregation properties of gelatin chains in neutral aqueous solutions, reported in the temperature range of 35–60°C. The data measured in the cited study at 35°C were intrinsic viscosity  $[\eta] = 384$  cm<sup>3</sup>/g; diffusion coefficient  $D = 1.12 \times 10^{-7}$  cm<sup>2</sup>/s; molecular weight  $M_w = 410,000$  g/mol; and hydrodynamic radius of  $R_H = 28$  nm. The Mark-Houwink equation for  $[\eta] = 0.328 n^{0.69}$ , with a monomer molecular weight of 110 g/mol for the repeating unit and  $n$  values of 3727. Bohidar concluded that the intermolecular interaction was repulsive and showed significant decrease as the temperature was reduced, and that random coil shape was confirmed by the data obtained. Bohidar [28] not consider that the molecular weight does not change with temperature, so if changes are the hydrodynamic properties of the system, except that bond breaks occur (the molecular weight decreases) or aggregation of macromolecules (molecular weight increases); in the temperature range studied in this work neither of these phenomena does not occur. However, it is very likely that this author worked with other types of gelatin or at least with a different type of hydrolysis, leading to different values of " $a$ " and " $k$ ". Also, whereas  $a$  and  $k$  were each found to be the same for alkali-processed gelatins, they were different for an acid-processed gelatin (Zhao [30]).

The Mark-Houwink parameters for gelatin B determined in this work are very similar to those from Pouradier & Venet [27], since the macromolecule is more rod-like than random-coil (see Figure 2). This can be verified by calculating the Perrin and Simha numbers, with  $P > 5$  and  $v_{a/b}$  14.6, which confirms that gelatin in an aqueous solution is a biopolymer with a rod-like

conformation and with a tendency towards compaction with increasing temperature ( $R_H$  decreases).



**Figure 2.** Values for " $a$ " as a function of T (°C)



**Figure 3.** Values for " $k$ " as a function of T (°C)

Hydrodynamic properties of polysaccharides at different temperatures in aqueous solution has been carried out by Guner [9,10] for dextran and by Kasaii [11] and Tsai [12,13] for chitosan, but the methods used by these authors are more difficult since they require measurement of the intrinsic viscosity at a variety of molecular weights and temperatures.

Figure 2 shows a slight decrease in " $a$ " when plotted in terms of temperature. This is due to a positive thermodynamic level, which is in turn due to the affinity of the macromolecule to the solvent, as it becomes more hydrophilic ( $R_H$  decreases). However, for PVA-co-VAc the opposite occurs, in other words, this affinity for the solvent is lacking and therefore its hydrophobicity increases ( $R_H$  increases).

Figure 3 shows that there is very little change in the values of " $k$ " in relation to temperature, and in fact it could be said that " $k$ " should be independent of T, although both PVA-co-VAc and gelatin present deviations from this trend.

**Table 6. Arrhenius plot of  $a$  and  $k$  with the respective standard deviations**

Biopolymer	$a$	$\sigma^2$	$k$ (cm <sup>3</sup> /g)	$\sigma^2$
Xanthan gum	$a = 1.2849e^{-3 \times 10^{-4} T}$	0.9721	$k = 0.0027e^{0.0012 T}$	0.9681
Pectin	$a = 0.8321e^{-4 \times 10^{-4} T}$	0.9645	$k = 0.0262e^{-0.0051 T}$	0.9518
Gelatin	$a = 1.0407e^{-6 \times 10^{-3} T}$	0.9848	$k = 0.1751e^{-0.0021 T}$	0.9804
PVA-co-VAc	$a = 0.5933e^{2.8 \times 10^{-3} T}$	0.9809	$k = 0.0471e^{0.0024 T}$	0.9734

Qing Shen et al. [31] evaluated solvent polarity parameters and plotted them with the  $k$  coefficient of the Mark-Houwink equation. These presented good linear fits, and they suggested that a method of extrapolation could be applied to obtain similar polarity parameters for polymers. Since the polarity parameters for polymers are dependent on temperature,  $k$  also depends on the temperature, and with increasing temperature gelatin becomes much more polarized and PVA-co-VAc becomes slightly polarized (see Figure 3).

Table 6 shows the details related to the functionality of the  $a$  and  $k$  parameters with temperature, with this being the typical Arrhenius equation. Although these are empirical equations, they can be interpreted as representing the relation between the conformational energies exerted by macromolecules in relation to a given solvent, within the temperature range studied. Good standard deviations are seen for both  $a$  and  $k$  functions, although the  $\sigma^2$  values are lower.

## 4. Conclusions

The iterative method for calculation of Mark-Houwink parameters is very useful for determining the molecular weight and hydrodynamics of a macromolecule at different temperatures, for cases where these parameters are known only for a single temperature. The criterion for applicability is that the molecular weight does not change with temperature (within a discrete range), in other words, that no bond breaking or bond formation occurs, although changes in hydrodynamics are permissible.

In this work, the Mark-Houwink parameters were determined for PVA-co-VAc, gelatin B, pectin, and xanthan gum. The molecular weights obtained showed a RE% of less than 5%, which establishes that this can be a good method for solving this type of experimental problem.

In all cases, the value of " $a$ " was found to decrease with increases in temperature, and this is consistent with the thermodynamic changes seen in most biopolymers in an aqueous solution. In other words, increasing temperature causes a decrease in the intrinsic viscosity and hydrodynamic radius [32-36]. The exceptional case was found to be with PVA-co-VAc, since its solubility decreases with increasing temperature.

## Acknowledgments

The author thanks Universidad Nacional de San Luis Projects 2-1712 and 2-2414 for their financial support.

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