A Novel Method of Extracting Mark-Hauwink-Sakurada Parameters from Viscosity Data

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Abstract -- **Mark–Hauwink–Sakurada parameters are calculated by measuring viscosity of solution of polymers of known molecular weight. The molecular weight is generally determined by an independent method like light scattering or gel permeation chromatography. In this paper a new method of measurement of these parameters is discussed which rely solely on viscosity data and does not need the measurement of molecular mass as a prerequisite.**

Keywords: *Mark-Hauwink-Sakurada Parameters, Permeation Chromatography, Molecular Weight.*

Figure 1. Fluid motion.

I. INTRODUCTION

MOLECULAR weight is an important parameter characterizing a polymer sample. The molecular weight can be determined by chemical or physical analysis which include functional group analysis, by measurement of the colligative properties, light scattering, ultracentrifugation or measurement of viscosity of dilute solution. All methods except the last one are absolute. The viscosity method is an indirect method but its value lies in its simplicity and that it can be applicable to a large group of polymer systems. All the physical methods require solubility of the polymer and extrapolation to infinite dilution [1].

The solution viscosity as a measure of polymer molecular weight is recognized as early as 1930 by Staudinger. Solution viscosity is the measure of size or extension in space of a polymer molecule. Viscosity measurements are simple and they are extremely useful in correlating molecular weights that they have become a valuable tool for molecular characterization of polymers.

II. THEORY

When adjacent layers of a fluid move with relative velocity, forces known as viscous forces come into play to reduce their relative motion. When we consider a fluid whose upper layer is moving with a velocity *u* in a fixed direction then a state will be reached when the lower most layer is at rest and the intermediate layers move with velocity less than *u* as shown in Figure 1.
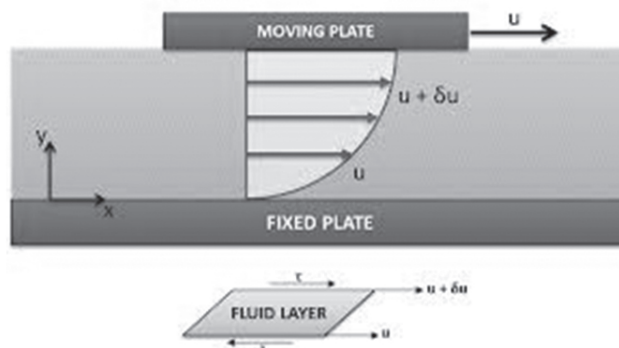
The force F acting at area at right angle to the diagram and parallel to u is proportional to the area and the velocity gradient.

$$F \propto A \times (vel.gradient)$$

Or:

$$F = \eta A \frac{\partial u}{\partial y}$$

Where η is a constant for the liquid and is called the coefficient of viscosity.

When the determination of molecular weight is required another related quantity called the intrinsic viscosity is brought into picture. The intrinsic viscosity is a quantity which is independent of concentration of the solution but is the function of the solvent used. The intrinsic viscosity is defined as:

$$[\eta] = [\frac{\frac{\eta}{\eta_o}-1}{c}]_{c=0}$$

Where η/η_o is the viscosity ratio and c is the concentration. The Mark–Houwink equation, also known as the Mark–Houwink–Sakurada equation or the Kuhn–Mark–Houwink–Sakurada equation gives a relation between intrinsic viscosity [η]and molecular weight M:

$$[\eta]=KM^a$$

From this equation the molecular weight of a polymer can be determined from data on the intrinsic viscosity and vice versa. The values of the Mark–Houwink parameters, a and K, depend on the particular polymer-solvent system. For solvents, a value of a=0.5 is indicative of a theta solvent. A value of a=0.8 is typical for good solvents.

III. CALCULATION

Ref [2], [3] and [4] were taken as a base for the following calculations. Part of the data of the three references were taken and values of the parameters were calculated by applying the formulae developed in the appendix.

A) Measurement of a.
The data is taken from [2] where the Mark-Hauwink-Sakurada parameters for Poly (Methyl Methacrylate) are evaluated.

The data is summarized in table 1.

TABLE 1 -- VALUES OF AVERAGE VALUES OF A AND INTRINSIC VISCOSITY OF POLY(METHYL METHACRYLATE) [2]

Type of solvent	Average value of a	Limiting viscosity $[\eta_1]$ for MW=10^5	Limiting viscosity $[\eta_2]$ for MW=10^6	Limiting viscosity $[\eta_3]$ for MW=1.8×10^5
Benzene	0.76	35 ml/g	200 ml/g	70 ml/g
Toluene	0.72	30 ml/g	155 ml/g	58 ml/g
Acetone	0.73	25 ml/g	150 ml/g	60 ml/g

Using equation (6) of the appendix one calculates a and and the result is presented in table 2.

TABLE 2 -- COMPARISON OF EXPERIMENTAL VALUES OF A WITH THOSE CALCULATED FROM EQUATION (6)

Solvent	Experimental	Calculated
Benzene	0.76	0.80
Toluene	0.72	0.77
Acetone	0.73	0.78

B) Measurement of K
The data presented in ref[4] is used to verify equation (14) of the appendix which is meant to calculate K. The table of ref [4] which is used in the following calculation is reproduced here.

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)

T (K)	$[\eta]$ (cm^3/g)	k (cm^3/g)	a	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

Using the values of intrinsic viscosity of the solution at different temperatures and the values of a from table 3 we calculates the values of K from equation (14) of the appendix. The experimental data is compared with that calculated from equation (14) is presented in table 4.

TABLE 4 -- COMPARISON OF EXPERIMENTAL K WITH CALCULATED K.

Temperature	K Experimental	K Calculated
22.2	0.0242	0.0250
26.6	0.0234	0.0240
29.6	0.0226	0.0235
34.9	0.0222	0.0230
37.0	0.0219	0.0225
39.9	0.0217	0.0224
44.8	0.0215	0.0220

IV. CONCLUSION

It has been shown that the new method of measuring the Mark-Hauwink parameters yields results close to the values obtained by other methods. The method described in this paper has a positive future in context of determining the molecular mass of a given polymer which is important as a quality control in various polymer industries.

V. ACKNOWLEDGEMENTS

VI. REFERENCES

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VII. APPENDIX

The derivation of important formulae which extract the Mark Hauwink parameters from viscosity data alone:

Section a) The Mark Hauwink equation relates the intrinsic viscosity of a polymer solution with its average molecular mass through a set of parameters (a and K) which are dependent on the nature of the polymer and the solvent. The Mark Hauwink equation reads:

$$[\eta] = KM^a$$

The quantity on the left hand side is called the intrinsic viscosity and M on the right hand side is the average molecular mass of the given sample of polymer. K and a are the Mark Hauwink parameters.

To derive the parameters a and K one takes the polymer solution by dissolving a known mass of polymer sample in the given solvent. The viscosity of the solution is measured at different concentrations by the method described in the proposal. The intrinsic viscosity is extracted from this data by taking the limit to zero concentration. Let us call this as intrinsic viscosity $[\eta_1]$.

$$[\eta_1] = KM_1^a$$

Now the solution is masticated for some given time so that the polymer in the solution breaks down and its average molecular mass reduces. Let the reduced average molecular mass be called M_2. The intrinsic viscosity of the masticated solution is also extracted in the same way by experimenting on the new solution. Let the new viscocity be called $[\eta_2]$. Then from the Mark Hauwink equation:

$$[\eta_2] = KM_2^a$$

The original solution is made in duplicate. Now the two solutions (Original +Masticated) are mixed together. Let the total mass of the polymer before dissolution be TM. Then the average molecular mass of the polymer in the solution is TM divided by the no. of polymer molecules. Thus:

$$[\eta_1] = K\left(\frac{TM}{N_1}\right)^a \tag{1}$$

And
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$$[\eta_2] = K\left(\frac{TM}{N_2}\right)^a \tag{2}$$

Where N_1 and N_2 are the no. of polymer molecules in the

original and Masticated solution respectively. The Mark Houwink equation for the mixture(Original +Masticated) will read:

$$[\eta_3] = K\left(\frac{2TM}{N_1+N_2}\right)^a \tag{3}$$

Dividing (1) by (2) we get:

$$\frac{[\eta_1]}{[\eta_2]} = \left(\frac{N_2}{N_1}\right)^a \tag{4}$$

And dividing (3) by (1) we get:

$$\frac{[\eta_3]}{[\eta_1]} = \left(\frac{2}{1+\frac{N_2}{N_1}}\right)^a \tag{5}$$

Taking the value of N_2/N_1 from (4) and substituting in (5)

$$\frac{[\eta_3]}{[\eta_1]} = \left(\frac{2}{1+\left(\frac{[\eta_1]}{[\eta_2]}\right)^{1/a}}\right)^a \tag{6}$$

(6) becomes our governing equation to determine the parameter a.

Section b) To find K we determine the intrinsic viscosity of a given sample at two nearby temperatures.

Let the two temperatures be T_1 and T_2 and the corresponding viscosities be $\eta(T_1)$ and $\eta(T_2)$. Let us now differentiate the Mark Houwink equation with respect to temperature. We get:

$$d[\eta(T)] = M^a dK + Kd(M^a)$$
$$= d[\eta] = M^a dK + KM^a \ln(M)\, da \tag{7}$$

Let the values of a and K at temperature T_1 and T_2 be a1, a_2, K_1 and K_2 respectively.

Then from (7):

$$[\eta(T_2)] - [\eta(T_1)] = M^{a_1}(K_2 - K_1) + K_1 M^{a_1} \ln(M)\,(a_2 - a_1) \tag{8}$$

Since from the Mark Hauwink equation we get:

$$\frac{[\eta(T_1)]}{[\eta(T_2)]} = \frac{K_1}{K_2}(M^{a_1-a_2}) \tag{9}$$

We can get K_2-K_1 from the above equation (8).

$$K_2 = K_1(M^{a_1-a_2})\frac{[\eta(T_2)]}{[\eta(T_1)]} \qquad (10)$$

And so:

$$K_2 - K_1 = K_1(M^{a_1-a_2})\frac{[\eta(T_2)]}{[\eta(T_1)]} - K_1 \qquad (11)$$

Substituting (11) for K_2-K_1 and and using Mark Houwink equation for M viz:

$$M = \left(\frac{[\eta(T_1)]}{K_1}\right)^{1/a_1} \qquad (12)$$

We get equation for K:

$$[\eta(T_2)] - [\eta(T_1)] = M^{a_1}(K_1(M^{a_1-a_2})\frac{[\eta(T_2)]}{[\eta(T_1)]} - K_1) + K_1 M^{a_1} \ln(M)(a_2 - a_1)$$

And:

$$[\eta(T_2)] - [\eta(T_1)] = \left(\frac{[\eta(T_1)]}{K_1}\right)(K_1\left(\frac{[\eta(T_1)]}{K_1}\right)^{\frac{a_1-a_2}{a_1}} \times \frac{[\eta(T_2)]}{[\eta(T_1)]} - K_1) + K_1\left(\frac{[\eta(T_1)]}{K_1}\right)\ln\left(\left(\frac{[\eta(T_1)]}{K_1}\right)^{1/a_1}\right)(a_2 - a_1)$$

$$(13)$$

Which gives on simplification :

$$[\eta(T_2)] - [\eta(T_1)] = [\eta(T_1)]\{\left(\frac{[\eta(T_1)]}{K_1}\right)^{\frac{a_1-a_2}{a_1}} \times \frac{[\eta(T_2)]}{[\eta(T_1)]} - 1\} + ([\eta(T_1)])\ln\left(\left(\frac{[\eta(T_1)]}{K_1}\right)^{1/a_1}\right)(a_2 - a_1)$$

$$(14)$$

Equation (14) becomes the master equation for determining K. The viscosities are measured and from it, the a's are calculated in the manner described in previous section.

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