

User's Guide

VISFIT: a computer tool for the measurement of intrinsic viscosities

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From:

“Multiple Linear Least-Squares Fits with a Common Intercept:
Determination of the Intrinsic Viscosity of Macromolecules in Solution”

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The latest versions of the VISFIT program and related documentation can be found at:

<http://leonardo.fcu.um.es/macromol>

1. Introduction

The intrinsic viscosity, $[h]$, is one of the most useful properties of macromolecules in solution. It can be employed to determine the molecular weight of the macromolecule, provided that the parameters K and a in the Mark-Houwink-Sakurada equation, $[h]=KM^a$ are known. For flexible chain macromolecules, it can provide information on the dimensions of the macromolecular coil and the flexibility of the chain skeleton. In the field of biological macromolecules, it is well known that it depends very sensitively on the overall structure, adopting values for elongated structures that are much larger than those proper of globular shapes.

The increase in the solution viscosity h , with respect to that of the pure solvent h_0 , due to the presence of the macromolecular solute, with concentration c , can be measured by the *relative viscosity*.

$$h_r = \frac{h}{h_0} \quad (1)$$

or by the *specific viscosity*

$$h_{sp} = \frac{h - h_0}{h_0} = h_r - 1 \quad (2)$$

The intrinsic viscosity $[h]$ is defined as the ratio of specific viscosity to concentration in the limit of infinite dilution:

$$[h] = \lim_{c \rightarrow 0} \frac{h_{sp}}{c} = \lim_{c \rightarrow 0} \frac{h - h_0}{h_0 c} = \lim_{c \rightarrow 0} \frac{h_r - 1}{c} \quad (3)$$

The dependence of solution viscosity on solute concentration at the infinite dilution limit can be expressed in several ways. At infinite dilution, h_{sp}/c equals $[h]$, and for moderately diluted solution the concentration dependence can be expressed in a linear form, the Huggins equation

$$\frac{h_{sp}}{c} = [h] + k_H [h]^2 c \quad (4)$$

so that $[h]$ could be obtained by extrapolation to zero concentration of data for h_{sp}/c at varying concentration. Typically, this would be done by a least-squares fitting, in which the intercept is $[h]$ and the slope is $k_H [h]^2$

It can be shown that $[h]$ is also the zero-concentration limit of $\ln h_t/c$. Then, Kraemer proposed to express the concentration dependence of this quantity as:

$$\frac{\ln(h_t)}{c} = [h] - k_K [h]^2 c \quad (5)$$

Thus, the Kraemer extrapolation has the same intercept $[h]$ as the Huggins equation. It can be shown that

$$k_H + k_K = 1/2 \quad (6)$$

This relationship comes from purely mathematical arguments and must hold for any polymer / solvent system.

Rather than doing a separate linear least-squares extrapolation for each of the two relationships, eqs. 4 and 5, we propose to fit simultaneously both equations. We have devised a least-squares procedure which takes into account that the two series of data have the same abscissas and a common intercept. The mathematical details (described in our above cited paper) were implemented in a computer program, VISFIT, which is intended for handling the experimental viscosity-concentration data in the determination of the intrinsic viscosity.

2. Experimental procedure and VISFIT operating modes.

The determination of concentration-dependent solution viscosities is most easily carried out using a dilution Ubbelohde viscosimeter, which differs from the classical Ostwald viscosimeter in having a third arm employed to add amounts of pure solvent, so that change in concentration can be made *in situ*. The viscosity is determined from the time, t , required for a given volume of solution to flow falling through a capillary. First of all, a measurement of the falling time of the pure solvent, t_0 , is done. Then, putting in the viscosimeter a volume V_1 of a solution of concentration c_1 , the falling time t_1 is measured. Afterwards, a series of new measurements is done adding a volume d_i of pure solvent and obtaining the new falling time t_i , which corresponds to a concentration related to the previous one by $c_i = c_{i-1} V_{i-1} / V_i = c_{i-1} V_{i-1} / (V_{i-1} + d_i)$. Thus the primary set of data is a series of pairs of values (d_i, t_i) .

The flow rate across the capillary is governed by the Hagen-Poiseuille law, which states that the flow time (for a given volume) is proportional to the density of the fluid, r and inversely proportional to its viscosity h . Accordingly, the viscosity can be written as $h = A r t$, where A is an instrumental constant depending on construction details of the viscosimeter. This is approximately valid, but a better description is achieved taking into account end effects arising from the fact that the velocity profile at the extremities of the capillary is not Pouiseuillean. Then, the viscosity is given by

$$h = r(A t - B / t) \quad (7)$$

where B is another instrumental constant. The viscosimeter can be calibrated, determining the values of A and B from a series of measurements of flow time for pure liquids of known density and viscosity, at the same temperature as the solution measurements.

2.a. VISFIT (simple) mode 1

Our VISFIT computer program for the determination of the intrinsic viscosity has two operational modes. In the approximate (but still acceptably precise) *mode 1*, end corrections (the B constant) is neglected, and furthermore the solution density is supposed to be the same as that of the pure solvent (the latter approximation is quite accurate for the usual, quite dilute solutions employed in the experiment). Therefore, we are in the case when $h = A r t$. As all we need are values of h_r (or $h_{sp}=h_r-1$), they can be simply calculated as the ratio of flow times, $h_r = t / t_0$, where t_0 is the flow time of the pure solvent. Thus in this mode neither densities nor the A and B constants are needed.

2.b. VISFIT (advanced) mode 2

In the more rigorous *mode 2* of VISFIT, both the density variation and the capillary end effects are taken into account. The latter are represented by the viscosimeter constants A and B, obtained from a separate, previous experiment in which the viscosimeter was calibrated as mentioned above. For the concentration-dependent density, a linear relationship is assumed to be valid in dilute solution. If r_1 is the solution density (determined apart, for instance by picnometry) at concentration c_1 (which could be that of the initial, most concentrated solution), and r_0 is the density of pure solvent, then at any concentration c the density of the solution can be estimated as $r = r_0 + c(r_1 - r_0)/c_1$. In this version of VISFIT, the program will need data of A and B , r_0 , r_1 and c_1 . The instrumental correction may be more important than that from the change in density. If one would like to include the former, ignoring the latter (thus avoiding the measurements of density), this could be done giving r_0 for r_1 (indeed the value given will be irrelevant; it will cancel out in the evaluation of H_r). Similarly, one could neglect the calibration correction, still including the densities; this is done setting $B = 0$ and giving any arbitrary value to A .

3. Running VISFIT

The input data for VISFIT can be either (a) given from the keyboard, following the program's prompts, or (b) supplied in an input file. In the latter case, the only line to be typed is that with the name of the input file. The data set contains:

- Name of the output results file (*)
- Name of the output graphics file (*)
- Title of the case (e.g., polymer/solvent/temperature) (*)
- Flow time for the pure solvent
- Concentration of the initial solution (before dilution)
- Volume of the initial solution
- Flow time of the initial solution
- Operating mode (1-basic, 2-advanced).

If mode is 2, advanced, three more lines will follow:

- Values (comma separated) of the constants A and B (comma separated) of the capillary viscometer (in cgs units)
- Solvent density
- Density of the initial solution

Finally there will be a series of lines, one for each flow time measurements, giving

- Values (comma separated) of added solvent volume and resulting flow time
- Values (comma separated) of added solvent volume and resulting flow time
- ... etc
- -1., -1. Indicates end of data set

(*) In the input data file, these three names will have 30 characters, so add the needed spaces after the last letter of the name

An example of the input file is presented below. VISFIT will generate a main results file, also given below. Finally, the program produces a file intended to be exported to a graphics tool (we employ SigmaPlot). This file contains, first, three columns with the experimental values of c , \mathbf{h}_{sp}/c and $\ln \mathbf{h}_{rel}/c$, which define the two sets of data points :

(a) $(c, \mathbf{h}_{sp}/c)$, (b) $(\ln \mathbf{h}_{rel}/c)$

Similarly, the other three columns contain two lines with c , \mathbf{h}_{sp}/c and $\ln \mathbf{h}_{rel}/c$ values. The first line is for $c = 0$, and the two accompanying numbers are the same as the intrinsic viscosity. The other line correspond to a concentration slightly larger than the initial one, and correspond to points $(c, \mathbf{h}_{sp}/c)$, $(\ln \mathbf{h}_{rel}/c)$, that when joined with the common intercept give the two fitted straight lines.

4. Example

The following is an example of the input file of VISFIT in the advance mode, taken from a laboratory experiment. Polystyrene (Aldrich, 43,010-2), was dissolved in toluene (Fluka, 89675). Chemicals were used without further purification. Solution and solvent were filtered through a filter funnel. The viscosity measurements were determined using an Ubbelhode viscosimeter constructed in our glass-blowing shop, immersed in a home-made thermostated bath of transparent polymethylmethacrylate walls, with a temperature control precise within $\pm 0.05^\circ\text{C}$. The measurement of the falling time was done with an inexpensive digital stopwatch. The input file for VISFIT is listed in Figure 1.

```

outputres-2.txt          !Name of results file (30 char.)
outputgra-2.txt          !Name of file for graphics (30 char.)
Polystyrene/Toluene/25.0 C !Title for experiment (30 char.)
41.2                      !Flow time of pure solvent (s)
0.0162                    !Concentration of initial solution (g/cm^3)
15.                        !Volume of initial solution (cm^3)
76.30                      !Flow time of initial solution (s)
2                           !MODE: 1-Elementary 2-Advanced
0.000177 , 0.029          !Viscosimeter constants, A (cm^2 s^-2), B (cm^2)
0.8623                     !Solvent density (g/cm^3)
0.8544                     !Initial solution density (g/cm^3)
1.0 , 73.77                !Added volume of solvent (cm^3), and flow time (s)
3.1 , 67.60                !Added volume of solvent (cm^3), and flow time (s)
2.9 , 63.46                !Added volume of solvent (cm^3), and flow time (s)
8.0 , 56.73                !Added volume of solvent (cm^3), and flow time (s)
10. , 52.32                !Added volume of solvent (cm^3), and flow time (s)
-1., -1.                   !End of data

```

Figure 1. Input data file for VISFIT in the advanced mode.

If we had operated in the simplest *mode 1*, which do not require a previous calibration and the concentration dependence of density, then in the input file the lines with A , B , \mathbf{r}_0 , \mathbf{r}_1 and c_1 would be missing.

VISFIT produces a main output file, displayed in Figure 2, with the results of the fit, including the intermediate calculations for each concentration, and the results of the

double least-squares fit. The values of the intrinsic viscosity and the Huggins and Kraemer constants are finally reported.

```
Title: Polystyrene/Toluene/25.0 C
Name of output graphics file:outputgra-2.txt
Flow time for solvent (s): 41.20
Concentration of initial solution (g/cm3): 0.016200
Volume of initial solution (cm3): 15.000
Flow time of initial solution (s): 76.30
Viscosimeter constants A (cm^2 s^-2) and B (cm^2): 1.77E-04 2.90E-02
Solvent density (g/cm^3) : 0.8623
Solvent viscosity (poise): 0.00568
Solution density (g/cm^3) at concentracion c1 (g/cm^3) : 0.8544 at 0.00000

V Add      time      conc      dens      eta      etarel      Y      YCAL      Z      ZCAL
 0.00    76.30  0.016200  0.8544  0.011214  1.9739   60.11   60.47   41.97   42.11
 1.00    73.77  0.015188  0.8549  0.010827  1.9056   59.63   59.67   42.46   42.46
 3.10    67.60  0.012723  0.8561  0.009876  1.7384   58.04   57.72   43.46   43.30
 2.90    63.46  0.011045  0.8569  0.009234  1.6253   56.61   56.40   43.97   43.88
 8.00    56.73  0.008100  0.8583  0.008180  1.4398   54.30   54.07   45.00   44.89
10.00    52.32  0.006075  0.8593  0.007482  1.3169   52.17   52.47   45.31   45.59

Common Intercept = 47.68
Slope (Y) = 7.90E+02     Slope (Z) = -3.44E+02

Intrinsic viscosity: 47.68 cm^3/g
Huggins const. k_H: 0.347     Kraemer const. k_K: 0.151
Sum of constants k_H+k_K: 0.499
```

Figure 2. Output data file for VISFIT in the advanced mode, produced by the input data in Figure 1.

VISFIT generates also a file with (a) the experimental values of c_i , y_i and z_i and (b) two pairs of points, $(0,[\mathbf{h}])$ and (c_h,y_h) , and $(0,[\mathbf{h}])$ and (c_h,z_h) , where c_h is a value somewhat higher than the highest concentration, and y_h and z_h are the values calculated for c_h with the least-squares equations. Each pair of points defines one or the straight lines.

0.00608	52.17	45.31		
0.00810	54.30	45.00		
0.01105	56.61	43.97		
0.01272	58.04	43.46		
0.01519	59.63	42.46		
0.01620	60.11	41.97		
			0.00000	47.68
			0.02025	63.67
				40.72

Figure 3. The second output data file for VISFIT, intended for input of a graphics program

This second file (Figure 3) is intended to be imported by graphics program in order to produce a plot of the double-extrapolation. For the data used here as example, we obtain the plot displayed in Figure 4.

Polystyrene / Toluene / 25 °C

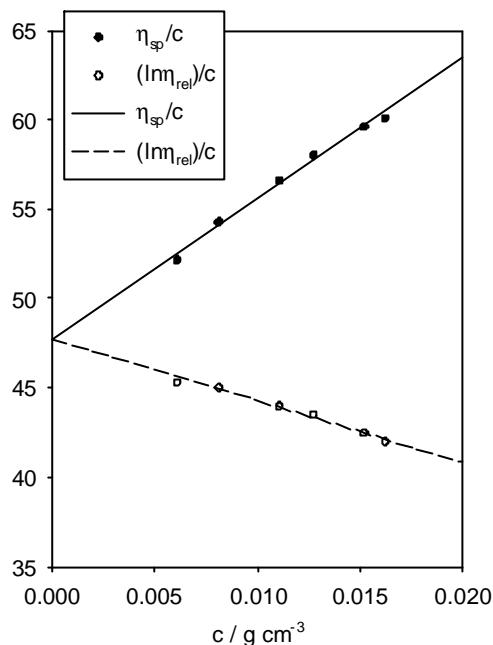


Figure 3. Plot of the double extrapolation, showing the experimental data and the extrapolating straight lines.

The intrinsic viscosity of this polystyrene in toluene at 25 °C was found to be $[\mathbf{h}] = 47.7 \text{ cm}^3/\text{g}$. Using the Mark-Houwink-Sakurada equation for this polymer/solvent system, $[\mathbf{h}] = 9.77 \times 10^{-3} \text{ M}^{0.73}$, the result for viscous-average molecular weight of the polystyrene sample is $M = 1.1 \times 10^5$. The quality of the results is assured by the excellent agreement of the sum of the Huggins and Kraemer constants, $k_H + k_K = 0.499$, with the exact result in eq. 6.

5. Availability

The latest version of this program VISFIT program can be found and freely downloaded from our Web site: <http://leonardo.fcu.um.es/macromol>

Executable files for MS DOS (running in the command mode or under MS Windows), and for Linux will be available, along with sample input and output files in the two operating modes of the program. The names of the executables are **visfit_x-msd.exe**, for MS DOS, and **visfit_x-lnx.exe**, for Linux, where x is the number of the present version.

6. Release notes

This is the first version of the program, submitted along with the final version of the paper in *J. Chem. Ed.* In future versions this section will contain a description of the modifications introduced in the most recent version.