

Intrinsic Viscosity Analysis of Polyethylene Oxide in DI Water using m-VROC II

- **Key Words:** viscosity, polyethylene oxide, intrinsic viscosity, hydrodynamic radius, molecular weight, Mark-Houwink-Sakurada equation, dilute polymer solution
 - **Goal:** We conducted an intrinsic viscosity analysis on a series of diluted polyethylene oxide (PEO) solutions in deionized water. The intrinsic viscosity obtained from this analysis was utilized to estimate the hydrodynamic radius of PEO. Furthermore, the molecular weight was estimated using the Mark-Houwink-Sakurada coefficients found in the Polymer Handbook, and this value was compared to the molecular weight reported by the manufacturer.

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Introduction

Intrinsic viscosity is a property that characterizes how a polymer solution affects the viscosity of a solvent. It specifically measures the relative increase in viscosity caused by the presence of polymer macromolecules dissolved in a solvent, under conditions where the pair interactions are minimal. In other words, it reflects the characteristics of individual macromolecules in a particular solvent. Factors that influence the intrinsic viscosity

of a polymer solution include molecular weight, polymer chain structure (e.g., linear, branched, coiled), and polymer-solvent interaction. It is common to use intrinsic viscosity analysis to estimate molecular weight for a specific polymer-solvent system. In addition, intrinsic viscosity is related to the hydrodynamic radius of the polymer. The hydrodynamic radius provides a measure of the spatial dimensions of the polymer chain in solution, whereas intrinsic viscosity gives insight into the contribution of the polymer to solution viscosity.

Intrinsic viscosity is typically measured at very low concentrations of polymer, for which the solution is in the dilute regime and the polymer chains do not significantly interact with each other. This allows intrinsic viscosity to be primarily influenced by the size and shape of individual polymer molecules and their interactions with the solvent molecules. This application note details the intrinsic viscosity of polyethylene oxide (PEO) in DI water. Additionally, further analysis was conducted to determine the molecular weight and hydrodynamic radius.

Experiment

Polyethylene oxide with an average molecular weight of 100 kDa was sourced from Sigma Aldrich. A stock solution was prepared in DI water and was diluted to prepare a concentration series appropriate for the intrinsic viscosity analysis. This series included concentrations of 8, 10, 12.5, 15, and 20 mg/mL. The viscosities of the polymer solutions and DI water were measured on the **m-VROC**[®] II with a B05 chip (depth = 50 μ m, P_{max} = 42K Pa) at 25°C using a flow rate of 1200 μ L/min (shear rate = 22,970 sec⁻¹). The loaded volume for each sample was approximately 80 μ L and twenty-five measurements were made for each with the retrieval feature activated. The use of VROC technology ensures high repeatability of the data, crucial for accurate intrinsic viscosity determination.



Viscosity Data, Analysis, and Discussion

Figure 1 shows viscosity (η) as a function of polymer concentration (c). Each data point represents the average of twenty-five measurements. To conduct an analysis of intrinsic viscosity, it is crucial to rescale the data correctly. We will now present the relevant equations to clarify the rescaling process and explain the significance of the parameters obtained.



Figure 1. Absolute viscosity (η) versus polymer concentration (c).

Two empirical equations, Huggins and Kraemer, are utilized for this analysis. Here is a step-by-step guide on how to calculate intrinsic viscosity:

1- Reduced viscosity (η_{red}) is determined using the equation:

$$\eta_{red} = \frac{\left(\frac{\eta}{\eta_{solvent}} - 1\right)}{c} \tag{1}$$

where $\eta_{solvent}$ is the viscosity of solvent or DI water, and c is the concentration of the polymer solution. The parameters characterizing the individual polymers and their interactions are shown in the Taylor series expansion below of the relative viscosity in terms of concentration applicable in the dilute regime.

$$\frac{\eta}{l_{solvent}} = 1 + [\eta]c + k_H[\eta]^2 c^2 + \mathcal{O}(c^3)$$

In this equation, the coefficient of the first-order term represents the intrinsic viscosity, $[\eta]$, which measures the increase in viscosity per unit concentration of the polymer. The second-order coefficient, $k_{H}[\eta]^{2}$, includes the Huggins constant, k_{H} , which quantifies interactions between adjacent polymer molecules.

Equation (2) is rearranged into the Huggins equation:

$$k_{ed} = [\eta] + k_H [\eta]^2 c$$

 $\eta_{r_{\ell}}$ This equation can be linearly fit to the viscosity vs concentration data to determine the intrinsic viscosity.

2- Inherent viscosity (η_{inh}) is calculated using the equation:

$$\eta_{inh} = \frac{\ln\left(\frac{\eta}{\eta_{solvent}}\right)}{c}$$

The Kraemer method relies on the Kraemer equation, which gives the linear relationship between inherent viscosity and concentration in the dilute regime.

$$\eta_{inh} = [\eta] - k_K [\eta]^2 c$$

(4)

(3)

(5)

(2)

In this equation, k_K represents Kraemer constant, which quantifies interactions between adjacent polymer molecules. The fit of this equation to the viscosity vs concentration data allows one to alternatively determine the intrinsic viscosity.

3- η_{red} and η_{inh} versus *concentration (c)* are plotted and fitted with a linear function. The intercept provides the intrinsic viscosity [η]. Figure 2 shows the rescaled viscosity data for the PEO solution, which had been fitted with equations (3) and (5).



Figure 2. Reduced viscosity (η_{red}) and inherent viscosity (η_{inh}) versus polymer concentration. Intercept determines the intrinsic viscosity [η].

4- Further analysis can be conducted on the data to gain more insights into the polymer solution. The hydrodynamic radius of the polymer can be determined using the intrinsic viscosity data as follows:

$$r_h = \left(\frac{3M_w[\eta]}{10\pi N_A}\right)^{1/3} \tag{6}$$

 N_A , M_w , and r_h are Avogadro's number, the polymer molecular weight, and the hydrodynamic radius, respectively. The hydrodynamic radius derived from intrinsic viscosity provides an estimate of the polymer's size in solution when the molecular weight is known,

5- The final analysis is the Mark-Houwink-Sakurada equation, which relates the intrinsic viscosity to the polymer molecular weight.

$$[\eta] = \kappa M_w^{\ \alpha}$$

The pre-factor κ and exponent a can be sourced from literature like the Polymer Handbook for widely studied synthetic polymer-solvent combinations. These parameters vary based on factors such as the specific polymer-solvent system, temperature, and the molecular weight range. For less common systems, it is



necessary to determine these values beforehand before equation (7) can be used to estimate molecular weight from intrinsic viscosity measurements.

According to the Polymer Handbook, the pre-factor κ is 0.0125 mL/g and the exponent a is 0.78 for polyethylene oxide (PEO) dissolved in deionized water. The calculated values for $[\eta]$, M_w , and r_h are presented in **Table 1**. As stated in the experimental section, the PEO vendor specified the molecular weight of PEO as 100 kDa. Our calculations based on intrinsic viscosity closely align with the manufacturer's reported molecular weight.

It is worth mentioning that the entire intrinsic viscosity analysis, from start to finish, can be conducted with RheoSense Analysis Software, **Clariti®**. For more detailed information, please refer to the <u>Intrinsic Viscosity Standard Operating Procedure (SOP)</u>.

 Table 1: Parameters extracted from the intrinsic viscosity analysis for the PEO studied.

method	[η] (mL/g)	r _h (nm)	Mw (kDa)	R ²
Huggins	98.1	15.6	98.3	0.998
Kraemer	96.3	15.4	95.7	0.991

Concluding Remarks

In this application note we presented a method to make reliable and accurate intrinsic viscosity measurement with **m-VROC®** II for polyethylene oxide (PEO) dissolved in DI water. Intrinsic viscosity offers a practical method to characterize individual molecules in the solution by providing an estimate of their hydrodynamic radius or molecular weight. Our VROC technology enables highly accurate and reproducible measurements of solutions in the dilute regime, which is crucial for intrinsic viscosity analysis. Our results consistently demonstrate reliability in estimating parameters such as molecular weight and hydrodynamic radius, aligning closely with values reported by manufacturer.

References

J. Brandrup, E.H. Immergut, E.A. Grulke, *Polymer Handbook*, Fourth Edition, Volume 2, 1999.

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