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Spatial-Temporal Fish Stock Assessment

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Abstract

This thesis explores an alternative method of assessing the status of commercially exploited fish stocks. Aggregate numerical least-squares regression methods are most often used to estimate fin fish population numbers by age of fish within the stock. These methods, commonly called virtual population analysis (VPA) or cohort analysis, provide single point static estimates of stock size. In this thesis, the state-of-age aggregated stock components are tracked over the course of each season. Data about fish stock spatial-temporal migration dynamics and partial observations from catches by the commercial fishery are used to update stock status estimates over the course of the season. Stock status is described in a probability distribution over discrete stock classes. A Bayesian updating procedure is used to take account of the partially observable catch information. The model requires a probabilistic description of the underlying stock dynamics in the form of a Markovian probability transition matrix, and a reliability measure that explicitly accounts for errors in observation. The spatial-temporal assessment approach is applied to the Scotia-Fundy herring stock in NAFO divisions 4WX. The dynamics of the herring are described and the model is developed for a given season.

Résumé

La viscosité intrinsèque, obtenue à partir des mesures de viscosité des solutions diluées, est souvent utilisée pour déterminer la masse moléculaire moyenne et les dimensions des chaînes moléculaires d'un polymère ainsi que l'interaction entre le polymère et le solvant.

Bien que la mesure de la viscosité d'une solution soit une tâche simple, l'évaluation de la viscosité intrinsèque est, par contre, assujettie à des amplifications des erreurs expérimentales. Ceci est dû au fait que les méthodes traditionnelles d'évaluation de la viscosité intrinsèque se basent sur des extrapolations au-delà de la gamme des données expérimentales. Beaucoup d'efforts et de travaux de recherche sont concentrés sur l'amélioration des méthodes d'extrapolation en raffinant les expressions théoriques associées à de telles extrapolations.

En utilisant trois solutions aqueuses et diluées de polyacrylamides de grades différents, on a évalué une méthode alternative, développée dans notre laboratoire, pour la détermination des viscosités intrinsèques. Cette nouvelle méthode ne comporte aucune extrapolation, donc, elle ne dépend d'aucune expression théorique. En comparant les résultats obtenus par les méthodes traditionnelles à ceux obtenus par la nouvelle méthode, on a conclu que cette dernière possède les capacités nécessaires pour surpasser les difficultés qu'on a éprouvées durant l'utilisation des méthodes traditionnelles.

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Nomenclature

a	Mark-Houwink-Sakurada empirical constant
c	concentration of the polymer solution, g/dL
e	error in the measurement of the specific viscosity
g_i	weight of species i, g
k	Mark-Houwink-Sakurada empirical constant
k_1	hydrodynamic interaction constant
k_2	constant in equation 27
K	Schulz and Blaschke constant
k_H	Huggins constant
k_K	Kraemer constant
M	average molecular weight in Mark-Houwink-Sakurada equation, g/mol
M_i	molecular weight of species i, g/mol
$\overline{M_n}$	number-average molecular weight, g/mol
$\overline{M_w}$	weight-average molecular weight, g/mol
$\overline{M_z}$	z-average molecular weight, g/mol
$\overline{M_v}$	viscosity-average molecular weigh, g/mol
N_i	number of molecules
t	flow time of the polymer solution through a capillary viscometer, s
t_s	flow time of the solvent through a capillary viscometer, s

Greek Letters:

η	viscosity of the polymer solution, Pa.s
$[\eta]$	intrinsic viscosity, dL/g
η_s	viscosity of the solvent, Pa.s
η_{sp}	specific viscosity

Abbreviations:

An-PAAm	anionic polyacrylamide
PAAm	polyacrylamide
ppm	parts per million
N-I PAAm	non-ionic polyacrylamide

Table of Contents

List of Tables

List of Figures

Chapter 1

Introduction

1.1 Introduction

The intrinsic viscosity derived from measurements of dilute solution viscosity can be related to the molecular weight of a polymer using the Mark-Houwink-Sakurada equation, to chain dimensions of a polymer using Flory-Fox equation, and to the interaction between the polymer and the solvent. Intrinsic viscosities may be also used to study the chain branching, the chain stiffness, the polydispersity, as well as the association of the polymer in the solution.

Although the measurement of the viscosity of a solution is a relatively simple task, the evaluation of the intrinsic viscosity is subject to a lot of inaccuracies and error magnifications. Many research efforts have focused on finding a simple and practical method to evaluate accurately the intrinsic viscosity.

In order to determine the intrinsic viscosity, the viscosity of the polymer solution at several dilutions and the viscosity of the solvent are determined. The traditional methods for evaluating the intrinsic viscosity involve an extrapolation of the reduced viscosity, η_{sp} / c, (Huggins, 1942) or the inherent viscosity, $\ln(\eta/\eta_s)/ c$, (Kraemer, 1938) versus the specific viscosity, η_{sp}, or concentration, c, to zero η_{sp} or c. Any error in the quotient caused by an error in measuring the specific viscosity is magnified at low concentrations leading to an inaccurate evaluation of the intrinsic viscosity. Many research works have attempted to improve the extrapolation techniques using elaborate statistical analysis and complicated theoretical equations. In 1996, Kozicki and Kuang proposed an alternative method providing independent evaluations of intrinsic viscosities without the requirement of any extrapolations and/or complicated theoretical equations.

The traditional methods as well as the alternative method for evaluation of the intrinsic viscosity are presented in detail in Chapter 2. The analysis and the computational methods are described in Chapter 3. The properties of the materials used in this work are presented in Chapter 4. This is followed by a description of the equipment used and the experimental procedures. In Chapter 6, the experimental results, the evaluation of the alternative method as well as the comparison between results obtained by this method and the traditional methods are presented. Finally, the conclusions and the recommendations are summarized in Chapter 7 and 8, respectively.

1.2 Scope of Research

The objectives of this work are to test and assess an alternative method for evaluation of intrinsic viscosities. The objectives also include a comparison between the results obtained by the alternative and the traditional methods. The results were carefully analyzed in order to determine the accuracy of the intrinsic viscosities evaluated using the alternative method. The experiments were performed using three different aqueous dilute polyacrylamide solutions.

1.3 Literature Survey

In the late 1930's, intrinsic viscosities were determined by plotting the reduced viscosity, η_{sp} / c, versus the concentration and by fitting the experimental data to a straight line. Then, an extrapolation of this line is involved in order to find the limit of η_{sp} / c as the concentration approaches zero, consistent with the definition of the intrinsic viscosity. In 1938, Kraemer proposed an empirical relationship relating the inherent viscosity, $\frac{\ln(\eta / \eta_s)}{c}$, to the concentration. In 1941, Schulz and Blaschke proposed a relationship relating the reduced viscosity, η_{sp} / c, to the specific viscosity, η_{sp}, because it was found empirically that their experimental data fitted a straight line better in a plot of the reduced viscosity versus the specific viscosity than in the conventional plot. In 1942, Huggins proposed an equation relating the reduced viscosity, η_{sp} / c, to the concentration c. Huggins' equation has been widely used for determination of intrinsic viscosities.

When using these methods, the evaluations of intrinsic viscosities were inaccurate due to the fact that, at low concentrations, any error in the viscosity measurement will be magnified when η_{sp} or ln (η/η_s) is divided by the concentration (Reilly et al., 1979). In 1979, Reilly et al. succeeded in improving the extrapolation techniques associated with Huggins' equation using adjustable parameters. These parameters were determined using detailed statistical analysis and complicated computational methods.

In 1996, Kozicki and Kuang proposed a simplified method for evaluation of intrinsic viscosities. This method does not involve any extrapolation and does not require any theoretical equations. The present work is intended to test and assess this alternative method using three polyacrylamide systems.

Chapter 2

Theoretical Aspects

2.1 Viscosities Commonly Used in Dilute Solutions

a. Viscosity of a Polymer Solution, η

The viscosity of a solution is a measure of the resistance of the solution to flow. It is usually determined by measuring the time of flow through a calibrated capillary at a controlled temperature and relatively low shear rates.

b. Viscosity of the Solvent, η_s

The viscosity of a pure solvent is determined in the same fashion as the solution viscosity. The viscosity of the solvent does not only serve as a factor in subsequent equations, but also may be used as a check on the calibration of the capillary viscometer and the measurement procedures.

c. Specific Viscosity, η_{sp}

The specific viscosity, η_{sp}, is defined as

$$\eta_{sp} = \frac{\eta - \eta_s}{\eta_s} = \frac{t - t_s}{t_s} \qquad (1)$$

where t and t_s are the flow times of the dilute polymer solution and the solvent, respectively.

d. Reduced Viscosity

The ratio of the specific viscosity over the solution concentration, η_{sp} / c, is called the reduced viscosity or the viscosity number.

e. Intrinsic Viscosity, [η]

The intrinsic viscosity, [η], is defined as the limit of η_{sp} / c as the concentration approaches zero

$$[\eta] = \lim_{c \to 0} \left(\frac{\eta_{sp}}{c} \right) = \lim_{c \to 0} \left(\frac{\eta - \eta_s}{\eta_s c} \right) \tag{2}$$

It is also called the limiting viscosity number and expressed in terms of weight per unit volume (often in dL/g). The intrinsic viscosity is a measure of the capacity of a polymer molecule to enhance the viscosity. It is related to the volume the polymer chains occupy in the solution, and is therefore related to their shape and size.

2.2 Methods Used to Determine Intrinsic Viscosities

2.2.a. Traditional Methods

i. Kraemer Method (1938):

Kraemer proposed the following relationship between the viscosity of the polymer solution and the concentration

$$\frac{\ln(\eta / \eta_s)}{c} = [\eta] + k_K [\eta]^2 c \tag{3}$$

where k_k is a constant which nearly always has a negative value. The relationship is linear in c with the intrinsic viscosity as an intercept. If the solution absolute viscosity η is measured at different concentrations, a plot of $\frac{\ln(\eta / \eta_s)}{c}$ versus the concentration can be drawn. The intrinsic viscosity is easily determined by fitting the experimental data to equation 3 and extrapolating the straight line to zero concentration.

ii. Schulz and Blaschke (1941) Method :

Schulz and Blaschke obtained values for the intrinsic viscosity by extrapolation of the plot of the reduced viscosity versus the specific viscosity to zero specific viscosity. These authors found that their data fitted a straight line better in this type of plot than in the plot suggested by Kraemer. They proposed the following linear expression relating the reduced viscosity and specific viscosity

$$\frac{\eta_{sp}}{c} = [\eta] + K\,\eta_{sp} \qquad (4)$$

where K is a constant.

iii. Huggins Method (1942):

Huggins derived an equation by hydrodynamic treatment of a model for randomly kinked polymer chains consisting of strings of sub-molecules. His derivation involved an empirical factor in Stokes relation between the viscosity and the frictional force per submolecule which arises from its flow through the solution. The Huggins equation written in series form is:

$$\frac{\eta_{sp}}{c} = [\eta]\left(1 + \sum_{n=1}^{\infty} k_n [\eta]^n c^n\right) \tag{5}$$

After truncating the summation, we obtain the familiar form of Huggins equation

$$\frac{\eta_{sp}}{c} = [\eta] + k_H [\eta]^2 c \tag{6}$$

The constant k_H is called the Huggins constant which is always positive. Analogously to the previous methods, if the specific viscosity, η_{sp}, is measured at different concentrations, a plot of η_{sp} /c versus the concentration can be drawn. The intrinsic viscosity can therefore be determined directly from a fit of the experimental data to equation 6.

A more general expression for Huggins' relationship is the power series:

$$\frac{\eta_{sp}}{c} = a_1 + a_2 c + a_3 c^2 \tag{7}$$

From the hydrodynamic theory (Eirich and Riseman, 1949),

$$\begin{aligned} a_1 &= [\eta] \\ a_2 &= k_1 [\eta]^2 \end{aligned} \tag{8}$$

where k_1 is the hydrodynamic interaction constant. For dilute solutions of low and moderate molecular weight polymers, k_1 is usually identified with Huggins constant k_H . However, Van Oene and Cragg (1962) have pointed out that chain entanglement may occur in dilute solutions of high molecular weight polymers and contribute to the value of k_H which will then exceed that of k_1. Therefore, k_H should be regarded as an empirical constant obtained by dividing the slope of the plot of η_{sp} /c versus c by $[\eta]^2$, and k_1 as that part of k_H due to the hydrodynamic interaction between separate polymer chains.

When viscosity data are available at only a few concentrations, the Huggins and Kraemer equations are often used together since they are both linear in c and have the same intercept. Even though many methods have been developed to determine intrinsic viscosities, Huggins method is still the most commonly used. Therefore, Huggins method will be used for comparison purposes in this work.

iv. The Error Magnification Problem:

When using the traditional methods, accurate determination of intrinsic viscosities is not always achievable. It should be also noted that Huggins relation, even in its non-truncated form, is based on a simple model and contains a number of assumptions. Furthermore, many studies have shown that equations 4 and 6 are usually inadequate outside of a limited concentration range.

A source of inaccuracies in determining [η] results from the fact that when η_{sp} or ln η_{sp} is divided by the concentration, the error in the quotient caused by the error in the viscosity measurement is magnified at low concentrations (Reilly et al., 1979). Thus, writing

$$\left(\eta_{sp}\right)_{\exp erimental} = \eta_{sp} + e \qquad (9)$$

where e is the error in η_{sp}, and taking the following limit as c → 0, yields

$$\lim_{c\to 0}\left(\frac{\eta_{sp\,(exp)}}{c}\right) = \lim_{c\to 0}\left(\frac{\eta_{sp}+e}{c}\right)$$

$$= \lim_{c\to 0}\frac{\eta_{sp}}{c} + \lim_{c\to 0}\frac{e}{c} \qquad (10)$$

$$= [\eta] + \infty = \infty$$

Hence, the error in the quotient η_{sp} /c due to the error in η_{sp} is magnified by the magnification factor c^{-1}, and approaches infinity as the polymer concentration approaches zero.

Reilly et al. (1979) have rearranged Huggins' equation in such a way that the error magnification could be avoided. They then fitted their experimental data to the rearranged equation using adjustable parameters. When sufficient data are available and with the aid of a computer to apply numerical calculation and regression analysis, these parameters could be determined. It should be noted that Reilly's method has included improvements in the extrapolations techniques, although being based on Huggins' method it nevertheless involved a linear extrapolation.

2.2.b. The New Alternative Method (Kozicki and Kuang, 1996)

This method evolves from the expression defining the intrinsic viscosity

$$[\eta] = \lim_{c\to 0}\left(\frac{\eta_{sp}}{c}\right) = \lim_{c\to 0}\left(\frac{\eta-\eta_s}{\eta_s c}\right) \qquad (11)$$

Applying the l'Hôpital rule to this expression , we obtain

$$[\eta] = \left(\frac{d\eta_{sp}}{dc} \right)_{c=0} \tag{12}$$

This new expression provides an alternative method for evaluation of $[\eta]$ based on the first derivative of the specific viscosity with respect to the concentration at zero concentration. Recalling equation 1,

$$\eta_{sp} = \frac{\eta - \eta_s}{\eta_s} = \frac{t - t_s}{t_s}$$

we know that η_{sp} is zero when the concentration is zero ($\eta = \eta_s$). Hence, the intrinsic viscosity can be determined without the need of extrapolation of the experimental data to zero concentration. Since no extrapolation is involved, one does not require a theoretical relationship to fit the data.

In the determination of the intrinsic viscosity, the solution viscosity must be measured at different concentrations. A plot of the specific viscosity versus the concentration is also needed. Any analytical expression for η_{sp} in terms of c which contains the origin, provides a good fit of the experimental data, and yields a first derivative at zero concentration could be used to determine the intrinsic viscosity.

Since η_{sp} is used in this method instead of η_{sp}/c, no distortion in the error structure associated with the presence of the concentration in the quotient is encountered in this method. The error magnification problem associated with inaccurate evaluations of $[\eta]$ is therefore avoided.

In this work, we provide comparisons of the results obtained by the new method with these yielded by the existing methods.

2.3 Intrinsic Viscosity and Average Molecular Weights

The intrinsic viscosity is of paramount importance because it can be related to the molecular weight. Many other methods are also available for obtaining this property, namely: light scattering, diffusion and sedimentation measurements. Since the intrinsic viscosity can be determined without the requirement of very sophisticated and expensive equipment, it is often found advantageous to use [η] for the determination of molecular weights.

2.3.a. Types of Average Molecular Weights

A monodisperse polymer sample is defined as a polymer in which the molecular weight of all macromolecules is the same. On the other hand, a polydisperse polymer represent a polymer sample containing molecules having a range of molecular weights. Most commercial polymers are polydisperse.

The molecular weight distribution is an important piece of information in determining many physical and rheological properties of a polymer. This molecular weight distribution can be described by various molecular weight averages: the number-average molecular weight, the weight-average molecular weight, the z-average-molecular weight, and the viscosity-average molecular weight.

i. Number-Average Molecular Weight

The number-average molecular weight, $\overline{M_n}$, is defined as

$$\overline{M_n} = \frac{\sum_i N_i M_i}{\sum_i N_i} \tag{13}$$

where N$_i$ is the number of molecules of the species i and M$_i$ is the molecular weight. The number-average molecular weight is determined from the boiling point, freezing point, vapor pressure, osmotic pressure and end group analysis (Tobolsky and Mark, 1971).

ii. Weight-Average Molecular Weight

The weight-average molecular weight, $\overline{M_w}$, is defined as

$$\overline{M_w} = \frac{\sum_i g_i M_i}{\sum_i g_i} \tag{14}$$

where g$_i$ is the weight of species i and M$_i$ is the molecular weight. The weight-average molecular weight is determined using light scattering, diffusion, and ultra-centrifugation techniques (Tobolsky and Mark, 1971).

iii. Z-Average Molecular Weight

The z-average-molecular weight, $\overline{M_z}$, is defined as

$$\overline{M_z} = \frac{\sum_i N_i M_i^3}{\sum_i N_i M_i^2} \tag{15}$$

where N$_i$ is the number of molecules of the species *i* and M$_i$ is the molecular weight. The z-average-molecular weight is determined by ultra-centrifugation techniques (Smith, 1968).

iv. Viscosity-Average Molecular Weight

The viscosity-average molecular weight, $\overline{M_v}$, is defined as

$$\overline{M_v} = \left[\frac{\sum_i N_i M_i^{a+1}}{\sum_i N_i M_i}\right]^{1/a} \tag{16}$$

where N_i is the number of molecules of the species *i*, *a* an empirical constant, and M_i is the molecular weight. The viscosity of a polymer solution depends on the temperature, the nature of the solvent and polymer, the polymer concentration, and the sizes of the polymer molecules. Because of the last dependence and the simplicity of measuring the viscosity of a solution, the viscosity-average molecular weight is widely used for the characterization of the molecular weight distribution of a polydisperse polymer. This average molecular weight can be easily obtained from viscosity measurements on dilute solutions by applying the Mark-Houwink-Sakurada equation

$$[\eta] = \mathrm{kM}^{a} \tag{17}$$

where k and *a* are empirical constants that depend on the solvent and the temperature. With polydisperse samples, M is equal to the viscosity-average molecular weight $\overline{M_v}$. It is known that $\overline{M_v}$ lies between the number-average molecular weight, $\overline{M_n}$, and the weight-average molecular weight, $\overline{M_w}$, and is closer to $\overline{M_w}$ (Smith, 1968; Williams, 1971).

Chapter 3

Methodology

Three different polyacrylamide samples were used: two non-ionic polyacrylamide samples having different molecular weights (5-6×10^6 and 18×10^6) and one anionic partially hydrolyzed polyacrylamide sample. Stock aqueous polyacrylamide solutions were prepared and then diluted to the desired concentrations. A wide range of solution concentrations was prepared (5 ppm to 400ppm). The flow times of these solutions and the solvent (water) were measured using a Canon-Fenske routine viscometer. The specific viscosity at each solution concentration was evaluated using equation 1,

$$\eta_{sp} = \frac{\eta - \eta_s}{\eta_s} = \frac{t - t_s}{t_s}$$

The Huggins and the alternative methods were used to determine the intrinsic viscosity. Plots of the reduced viscosity versus the concentration and of the specific viscosity versus the concentration were constructed.

When using the alternative method, two analytical expressions were used to represent the experimental data. These expressions have the following forms:

$$\eta_{sp} = ac + bc^d \qquad (18)$$

$$\eta_{sp} = a_1c + a_2c^2 + a_3c^3 \qquad (19)$$

The parameters a, b and d in equation 18, and a_1, a_2, and a_3 in equation 19 were determined by least squares fitting of the analytical expressions to the experimental data.

The curve fittings were done using three software packages : MAPLE-V, Sigma Plot 4.0, and Microsoft Excel 7.0. The true curves were then plotted in the η_{sp} versus c plot. Then, the specific viscosities determined at different concentrations using equation 19 were divided by the corresponding concentrations, and then plotted in a Huggins plot (reduced viscosity versus concentration plot) in order to visualize the error magnification occurring when using Huggins' method. The experimental errors, the error in the quotient η_{sp} /c, and the error in η_{sp} /c were calculated using the following equations:

In the alternative method's plot (η_{sp} versus c),

$$\text{Experimental Error} = \eta_{sp}(\text{true curve}) - \eta_{sp}(\text{experimental}) \qquad (20)$$

Since the error in the quotient η_{sp} /c is magnified by c^{-1},

$$\underset{(\text{due to the error in } \eta_{sp})}{\text{Error in quotient } \frac{\eta_{sp}}{c}} = \text{Experimental Error} \times \left(\frac{1}{c}\right) \qquad (21)$$

And, in Huggins plot (η_{sp} /c versus c),

$$\text{Error in } \eta_{sp}/c = \eta_{sp}/c\ (\text{fitted curve}) - \eta_{sp}/c\ (\text{experimental}) \qquad (22)$$

$$\text{Error in } \eta_{sp}/c = \text{Error in quotient } \eta_{sp}/c \qquad (23)$$

Recalling the new expression for the intrinsic viscosity, equation 12

$$[\eta]=\left(\frac{d\eta_{sp}}{dc}\right)_{c=0}$$

The intrinsic viscosity can therefore be determined by evaluating the derivative of η_{sp} with respect to the concentration at c = 0. So, if equation 18 is used to fit the experimental data, $[\eta]$ would be equal to the parameter a. And, if equation 19 is used to fit the experimental data, $[\eta]$ would be equal to the parameter a_1.

The intrinsic viscosity obtained for each solution was also used to calculate the average molecular weight of the polyacrylamide sample. This molecular weight was compared to the one supplied by the manufacturer. The Mark-Houwink-Sakurada equation (equation 17) was used to determine the average molecular weights. For the polyacrylamide solutions used in this work, equation 17 has the following forms:

Non-ionic sample (5-6×10^6): $$[\eta] = 1\times10^{-2}\,\overline{M}_w^{\,0.755} \tag{24}$$

Non-ionic sample (18×10^6): $$[\eta] = 6.9\times10^{-3}\,\overline{M}_n^{\,0.83} \tag{25}$$

where $\overline{M_w}$ is assumed to be $\approx 2\times\overline{M_n}$.

For the anionic sample: $$[\eta] = 3.13\times10^{-3}\,\overline{M}_w^{\,0.77} \tag{26}$$

Kulicke et al. (1982) have established equation 24 for aqueous non-ionic polyacrylamide solutions at 25 °C and of a molecular weight range of 0.4 - 90 × 10^5. Equation 25 was proposed by Klein and Conrad (1978) for aqueous non-ionic polyacrylamide solutions at 25 °C and of a molecular weight range of 10 - 150 × 10^5. Cohen (1981) have established equation 26 for anionic polyacrylamide which is 20% hydrolyzed and of a molecular weight range of 1-3 ×10^6.

Comparisons between the intrinsic viscosities, Huggins constants and the molecular weights obtained by Huggins method and the new alternative method were also performed. The viscosity data were taken from a study done by James and McLaren (1975). The purpose of this investigation is to corroborate the viability and utility of the alternative method using comparisons with the traditional methods used for determination of intrinsic viscosities.

Chapter 4

Properties of Materials

4.1 Acrylamide Polymers

The industrial use of acrylamide polymers has grown significantly in the last twenty years. These polymers are mainly used in water treatment, mining, and paper manufacture. The production of copolymers includes cationic and anionic comonomers and on polymer modification through controlled methylolation, hydrolysis, and the Mannich reaction.

Properties of acrylamides are widely present and reviewed in the literature and much useful information is provided by the manufacturers of monomers and polymer. Acrylamide, $H_2C{=}CHCONH_2$ (2-propenamide), is a white, crystalline solid. It exhibits good thermal stability and long shelf life when it is not exposed to light, air, high temperatures, and vibrations. In table 4.1 some physical properties of acrylamide relevant to our work are presented. Three different high molecular weight polyacrylamide samples were used in this work. The properties of these samples are presented in detail in the following sections.

Table 4.1: Some Physical Properties of Acrylamide (Ref. Encyclopedia of Polymer Science and Engineering).

Property	Value
Molecular Weight	71.08
Melting Point, °C	84.5 ± 0.3
Vapor Pressure	
Solid, Pa	
25 °C	0.9
40 °C	4.4
50 °C	9.3
Liquid, Pa	
87 °C	0.27
103 °C	0.67
116.5 °C	1.4
136 °C	3.3
Density, g/mL at 30 °C	1.122
Solubility at 30 °C, g/100mL	
in heptane	0.0068
in benzene	0.346
in acetone	63.1
in ethanol	86.2
in water	215.5

4.2 Types of Polyacrylamide Used

Three commercial grades of polyacrylamide were used in the present work: two non-ionic polyacrylamides with different molecular weights and one anionic polyacrylamide. The purpose of using the non-ionic and the anionic polymers is to determine the effect of the surface charge on the application of the alternative method for determination of intrinsic viscosities. The polyacrylamides used are linear and polydisperse polymers. The main source of information of the polymer is the technical literature of the manufacturer. For commercial reasons, the manner by which the polymer is produced and the molecular distribution are not available.

4.2.1 Advantages of Using High Molecular Weight Polyacrylamide (PAAm):

One of the main reasons for using high molecular weight polyacrylamide in this work is its ability to produce viscoelastic effects when dilute aqueous solutions of this polymer flow through constricted geometries (Marshall and Metzner, 1967; Durst et al., 1982; Haas and Durst, 1982; Kulicke and Haas, 1984; Odell et al., 1988). Polyacrylamide is soluble in water over a wide range of concentration and has no upper or lower temperature limits. Under normal conditions, aqueous polyacrylamide solutions are usually stable. Furthermore, polyacrylamide is non-toxic (Teot, 1978) and non-irritating to skin under normal use conditions.

4.2.2 Disadvantages of Using High Molecular Weight Polyacrylamide (PAAm): Shear Rate Dependency

The observed viscosity of aqueous polyacrylamide solutions depends not only on concentration, molecular weight, and temperature, but also on shear rate (Ferry, 1982). Therefore, the measurement techniques can play an important role. At very low shear rates, the viscosity is independent of shear rate, but if the rate increased beyond a certain point, a drop in the viscosity is observed. This phenomenon is called shear thinning. At a given temperature, the upper limit of the very low shear rates range decreases with molecular weight and also with polymer concentration. Figure 4.2.2 is a typical plot.

The shear thinning effect of highly dilute polyacrylamide solution having ultrahigh molecular weight is not negligible. To avoid the shear thinning effect, low-shear viscometer should be used to determine the viscosity of the polymer solution (Kulicke et al., 1982). However, Kulicke and Haas (1984) stated that at the low concentrations used in their study, which are close to the concentrations used in the present work, no shear thinning could be observed using either a low-shear rotational or a multibulb-capillary viscometer. A capillary viscometer ordinarily measures at shear rates of several hundreds up to 3000 s^{-1}. A disagreement with this statement is presented in our work, since the shear thinning effect is suspected to be responsible for an anomalous behavior of the polyacrylamide solution. These complexities and contradictions make it difficult to assess literature reports and to compare one set of results with another.

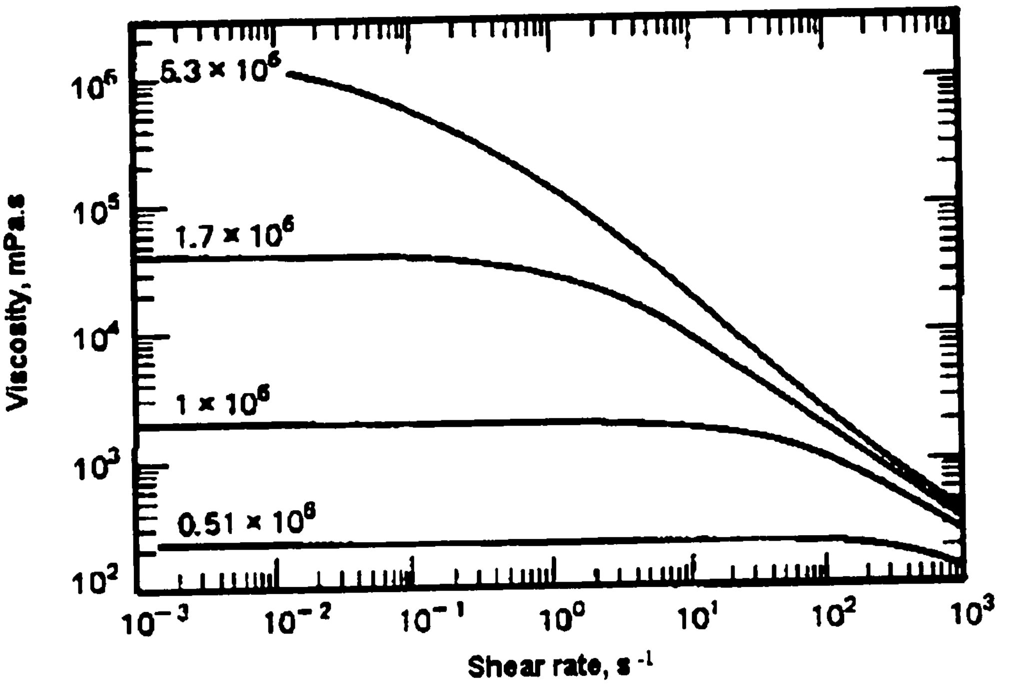


Figure 4.2.2: Effect of Shear Rate on Viscosity; Polyacrylamides of Varying Molecular Weight at 5 % Concentration in Water at 25 °C (Pergamon Press, Ltd).

Solution Aging

The stability of polyacrylamide solutions is a very desirable property and is adequate for many applications. This property can be lost however when physical stress is applied to the solution. This results in a decrease in the viscosity of the solution with time. This phenomenon is called solution "aging" and is related to the disentanglement or the disaggregation of the polymer molecules (Molyneux, 1984). The physical stress includes exposure to light, air, vibration, high temperatures ($T > 70\ ^{o}C$), and shear stress.

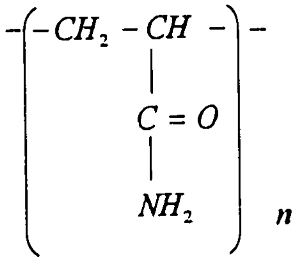
To minimize the effects of solution aging, the stock polymer solution is prepared according to particular instructions presented in the experimental section of this thesis, and then stored in a tightly-capped, brown glass bottle in a cupboard in the laboratory.

Formation of Aggregates

Large, sometimes fibrous aggregates have been observed in dilute aqueous solutions of ultrahigh molecular weight polyacrylamide (Boyadjan et al., 1976). The presence of these aggregates increases with the molecular weight of the polymer. The aggregation problem can affect the dependence of the intrinsic viscosity on the temperature and can be responsible for anomalous behaviors of polyacrylamide solutions. This effect is discussed in detail in the results and discussion section of this work.

4.2.3 Non-Ionic Polyacrylamide (N-I PAAm)

Non-ionic polyacrylamide (or unhydrolyzed polyacrylamide) is a homopolymer of acrylamide (2-propenamide).



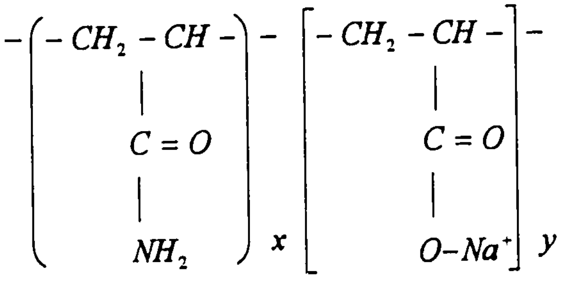
$$-\left(-CH_2-\underset{\begin{array}{c}|\\ C=O\\ |\\ NH_2\end{array}}{CH}-\right)_n-$$

Two non-ionic polyacrylamide samples were used in this work. The first has a molecular weight equal to 5 to 6 × 10^6 , and the second has a molecular weight equal to 18 × 10^6. Only the molecular weights were supplied by the manufacturer. Both samples were supplied by Polysciences, Inc. of Warrington, Pennsylvania. The chemical reaction of this polymer in an aqueous solution is the hydrolysis of the amide groups. However, this reaction occurs at temperatures above 67 °C (Silberberg et al., 1957). Since the operating temperature used in this work is 25 °C, it is unlikely that the amide groups underwent any chemical reaction or that the polymer gained a surface charge during the experiments of this study (Slegr, 1992).

The purpose of using two non-ionic polyacrylamide samples having different molecular weight is to determine whether this property has an effect on the application of the alternative method for determination of intrinsic viscosities.

4.2.4 Anionic Polyacrylamide (An-PAAm)

The anionic polyacrylamide, also called partially hydrolyzed polyacrylamide, is a modified form of the non-ionic polyacrylamide. It is a copolymer of 2-propenamide and the sodium salt of 2-propenoic acid.



$$-\left(-CH_2-\underset{\substack{|\\ C=O\\ |\\ NH_2}}{CH}-\right)_x-\left[-CH_2-\underset{\substack{|\\ C=O\\ |\\ O-Na^+}}{CH}-\right]_y-$$

The anionic polyacrylamide sample was also supplied by Polysciences, Inc. of Warrington, Pennsylvania. The molecular weight provided by the manufacturer is: $M_w > 10 \times 10^6$. From the literature supplied by the manufacturer, this sample is 40% hydrolyzed. This polyacrylamide is called anionic because of the presence of a net negative charge.

A major difference between the non-ionic and the anionic polyacrylamide is the arrangement of the molecular chain. In the first polymer, the molecule are randomly coiled, hence, the molecular chain is easily deformed under stress. For the anionic polymer, because of the repulsion between neighboring identically charged groups on the main chain, the random coils form a semi-stiff rod rendering the structure of this polymer more rigid than the structure of the non-ionic sample (Merrill et al., 1967).

4.2.5 Concentrations of Polyacrylamide Solutions Used

Stock polymer solutions of each polyacrylamide sample were prepared according to particular instructions explained in detail in the experimental section. A concentration of the stock polymer solutions of $0.5\%\frac{w}{w}$ polyacrylamide proved to be suitable since the solutions were not too viscous for measuring a specific quantity necessary for further dilution (Slegr, 1992). The concentration range used in this work was from 5 ppm to 400 ppm, and it was obtained by diluting the stock solutions to the desired concentrations.

4.2.6 Distilled Water

The distilled water used in the aqueous polymer solutions was double-distilled tap water from the distillation unit located in the pilot plant of the chemical engineering department. The resistivity of the distilled water varied between 17.5 and 17.9 mΩ.cm. This water is considered to be pure enough for the purpose of this study.

Chapter 5

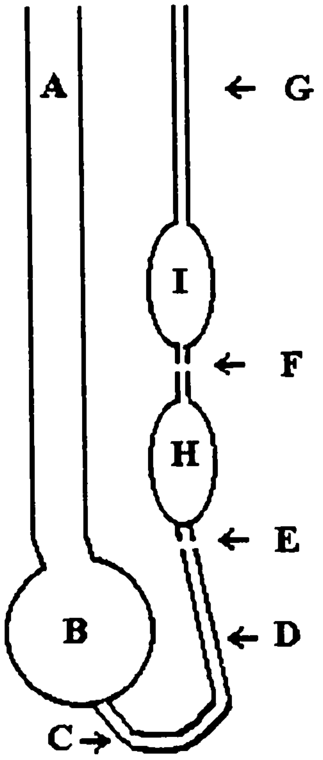
Experimental Aspects

5.1 The Cannon-Fenske Routine Viscometer for Transparent Liquids

The specific viscosity was measured using a Cannon-Fenske routine viscometer for transparent liquids. Two sizes of this viscometer were used:

A size 50 was used when the flow time of the solution through the capillary viscometer was lower than 6 minutes. However, the size 100 was used for solutions having a flow time higher than 6 minutes when using the size 50 viscometer.

A diagram of a typical Cannon-Fenske viscometer is represented in figure 5.1. During the viscosity measurements, the viscometer was immersed in a constant temperature bath at 25 ± 1 °C (GCA Precision Scientific Tem-Trol Viscosity bath) which was covered in order to avoid any degradation of the polymer caused by an exposure to light.



LEGEND:

A	*Mounting Tube*
B	*Lower Reservoir*
C	*Connecting Tube*
D	*Capillary Tube*
E and F	*Timing Marks*
G	*Arm*
H	*Timing Reservoir*
I	*Upper Reservoir*

Figure 5.1: Schematic Diagram Depicting a Typical Cannon-Fenske Viscometer for Transparent liquid (International Research Glassware, Kenilworth, NJ)

5.2 Viscosity Measurements

The procedure for measuring the viscosity conformed to ASTM Standards (Standard Specification for Kinematic Glass Viscometers ASTM Designation: D 2515-66; and Standard Method for Test for Viscosity of Transparent and Opaque Liquids ASTM Designation: D 445-65, 1995):

1. The sample was charged into the viscometer by inverting the instrument and applying suction to tube A, immersing tube G in the solution, and drawing the liquid sample to mark E.
2. The arm G was wiped, and the instrument was turned to its normal vertical position.
3. The viscometer was then placed and aligned vertically in the constant temperature bath.
4. Ten minutes were allowed for the sample to come to the temperature of the bath.
5. By applying suction to tube G, the liquid sample was drawn slightly above the mark F.
6. The efflux time was measured by allowing the liquid sample to flow freely down past the mark F and measuring the time for the meniscus to pass from mark F to mark E.

After each viscosity measurement, the viscometer was washed thoroughly with distilled water and acetone, and was then air-dried to remove the final traces of solvents. Periodically (almost on a monthly basis), traces of organic deposits were removed with chromic acid.

5.3 Density Measurements

Density was measured at 25 °C using a DMA 48 Digital Density Meter (Anton Paar Co., Graz, Austria). The procedure for measuring the density of the sample followed the manufacturer's directions. The accuracy of the density reading (listed in the operating manual) was ± 1×10^{-4} g/cm^3. The density meter was cleaned after each measurement using distilled water and acetone, and was then air-dried to remove the final traces of solvents.

5.4 Preparation of Stock Polymer Solutions

The aqueous stock polyacrylamide solutions were prepared as a concentrate of 0.5% polyacrylamide in distilled water. These stock solutions were then diluted to the desired concentrations (concentration range: 5 to 400 ppm). The procedure for preparation of the aqueous polyacrylamide solutions followed the instructions supplied by Dow Chemical Company of Midland, Michigan (Slegr, 1992).

An appropriate amount of distilled water was put into a 1.0 L beaker. A magnetic stirrer was used and the speed was adjusted in such a way that the bottom of the water vortex was thirty to fifty percent the diameter of the beaker. Then, the polymer crystals were poured just below the curve of the water vortex for a period of fifty to sixty seconds (See figure 5.4). When all the polymer crystals were added, the speed of the magnetic stirrer was adjusted to the lowest possible speed. Then, the beaker containing the solution was covered to prevent any possible degradation due to an exposure to light and air. The solution was stirred for a period of three hours, and then filtered through a 75 µm sieve. The solution was stored at room temperature in a tightly-capped, brown glass bottle placed in a closed and dark cupboard. A fresh stock polymer solution was prepared every two to three weeks.

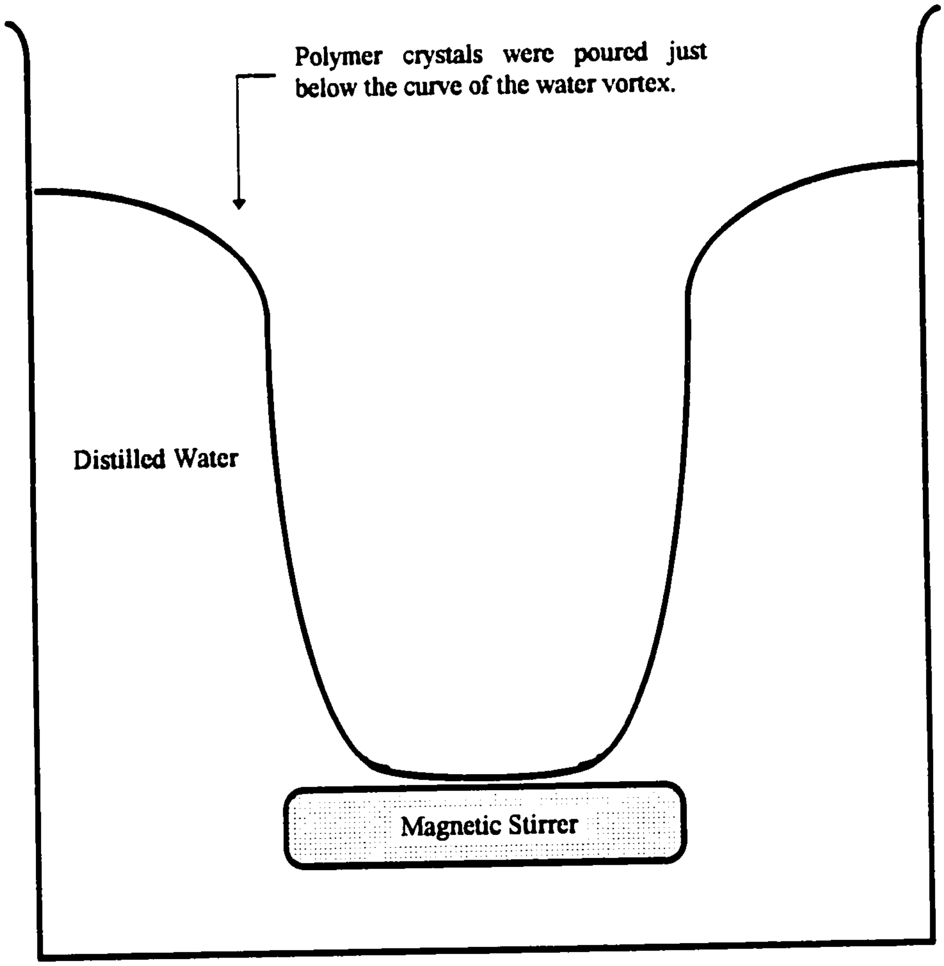


Figure 5.4: Schematic Diagram Depicting the Addition of Polymer Crystals to a Beaker Containing Distilled Water.

Chapter 6

Results and Discussions

6.1 The New Alternative Method

Figures 6.1, 6.2 and 6.3 depict the plots of the specific viscosity versus the polymer concentration for the three polyacrylamide samples which are based on the new alternative method. The smooth curves that are included in these figures represent equations 18 and 19. Since η_{sp} is zero when the concentration is zero, the origin is a point on the true curve.

The experimental and the calculated values of the specific viscosities at different concentrations are summarized in Table 6.1. For each polymer sample, two runs were performed to confirm the reproducibility of the data. The results of the second runs are summarized in Appendix A. It was found that the results were consistent in both runs. Equations 18 and 19 fitted to the experimental data of each polyacrylamide sample are tabulated in Table 6.2. The variances between the specific viscosities obtained by equations 18 and 19 and the experimental values are included in Table 6.3.

In Figures 6.1, 6.2 and 6.3, we notice that the smooth curves represent all experimental data over a wide concentration range. This is an important finding because all experimental data points could be used for the determination of the intrinsic viscosity, which enables one to place greater confidence in the evaluation of the intrinsic viscosity. Furthermore, from Figures 6.1, 6.2 and 6.3, and the variances in Table 6.3, both smooth curves are found to fit very well the experimental values. Since the variances between the specific viscosities obtained by equations 18 and 19 and the experimental values are too small and close to each other, we can use either equations for further calculations. In this work, the polynomial equation, i.e. equation 19, will be used in subsequent discussions.

As mentioned earlier in this work, the parameters in equations 18 and 19 were determined by least squares fitting of these equations to the experimental data. The parameters of equation 18 were obtained using MAPLE V and Sigma Plot packages. The results obtained by each software are very close. The input and output files generated by the two software packages are shown in Appendix B. On the other hand, the parameters of equation 19 were obtained using Sigma Plot and Microsoft Excel. This was done by fitting the experimental data to a third order polynomial equation. The results generated by each software are very close and are represented in Appendix B.

The intrinsic viscosity is obtained directly in the parameter evaluation as the parameter a when using equation 18 and the parameter a_1 when using equation 19. The intrinsic viscosity for each polyacrylamide sample is tabulated in Table 6.4.

It should be emphasized that the differences between the molecular weights and the surface charges of the three polyacrylamide samples have no effect on the application of the alternative method for the evaluation of intrinsic viscosities.

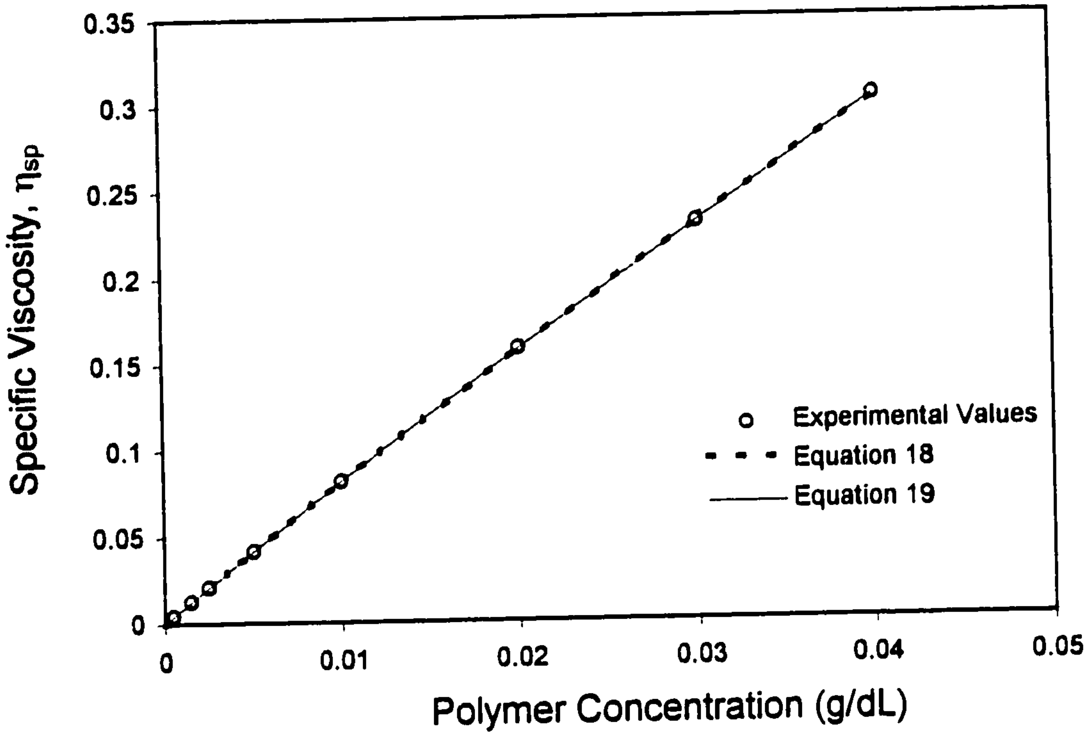


Figure 6.1: Specific Viscosity Versus Polymer Concentration for Non-Ionic Polyacrylamide (Mw = 5-6 x 10^6) at 25 °C.

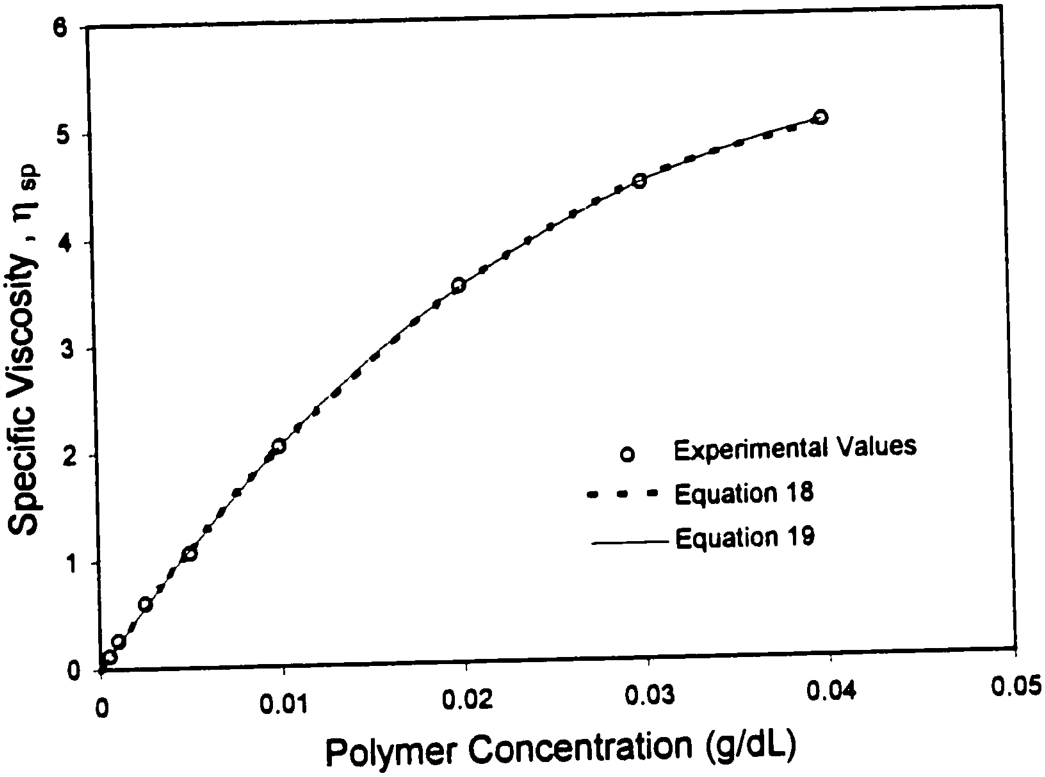


Figure 6.2: Specific Viscosity Versus Polymer Concentration for Non-Ionic Polyacrylamide (Mw = 18 × 10^6) at 25 °C.

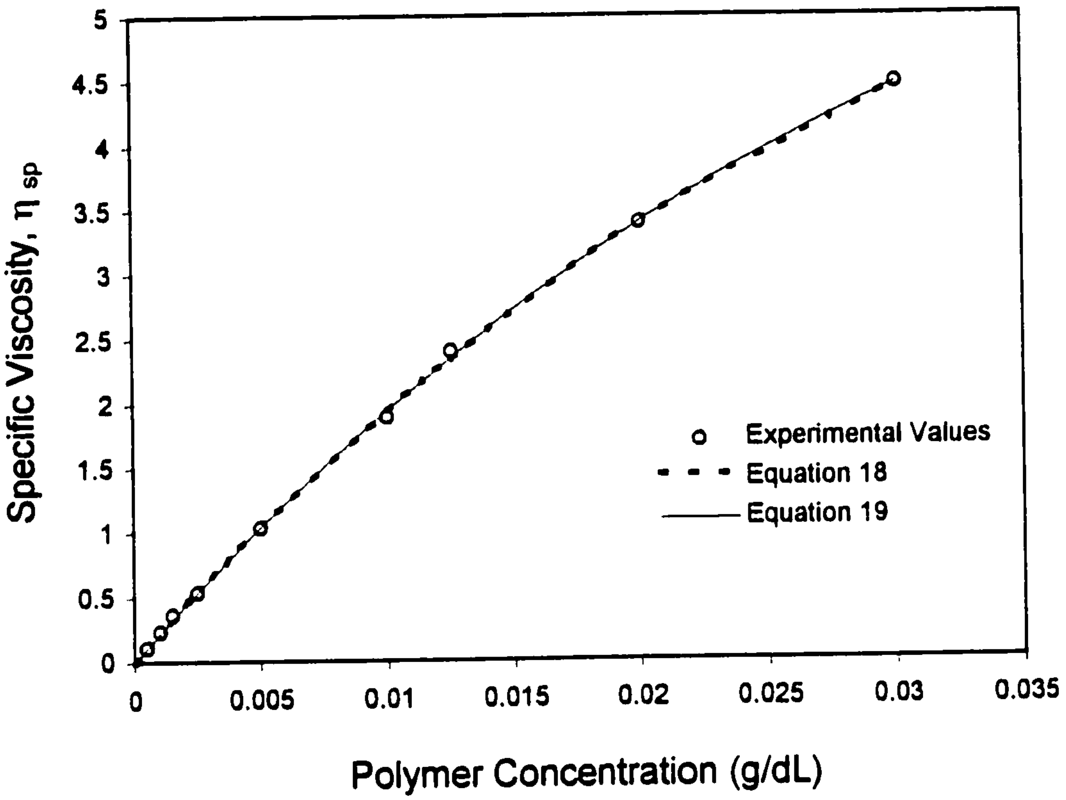


Figure 6.3: Specific Viscosity Versus Polymer Concentration for Anionic Polyacrylamide ($M_w > 10 \times 10^6$) at 25 °C.

Table 6.1: Viscosity Measurements

Non-ionic Polyacrylamide (Mw = 5-6 $\times 10^6$)

ppm	*t (s)*	*c (g/dL)*	η_{sp}	η_{sp} *(eq. 18)*	η_{sp} *(eq. 19)*
5	250.01	0.0005015	0.004540	0.004397	0.004248
15	252.08	0.001505	0.01286	0.01293	0.01269
25	254.13	0.002508	0.02109	0.02128	0.02106
50	259.25	0.005015	0.04167	0.04172	0.04166
100	269.14	0.01003	0.08140	0.08138	0.08168
200	288.25	0.02006	0.1582	0.1577	0.1579
300	306.35	0.03009	0.2309	0.2315	0.2311
400	324.4	0.04012	0.3034	0.3032	0.3034

Non-ionic Polyacrylamide (Mw = 18 $\times 10^6$)

ppm	*t (s)*	*c (g/dL)*	η_{sp}	η_{sp} *(eq. 18)*	η_{sp} *(eq. 19)*
5	278.63	0.0005015	0.1195	0.1211	0.1179
10	313.74	0.001003	0.2606	0.2392	0.2342
25	399.80	0.002508	0.6064	0.5797	0.5728
50	514.27	0.005015	1.066	1.108	1.104
100	175.73	0.01003	2.049	2.042	2.048
200	260.10	0.02006	3.513	3.496	3.502
300	314.05	0.03009	4.449	4.466	4.456
400	346.01	0.04012	5.004	4.999	5.002

Anionic Polyacrylamide (Mw > 10 $\times 10^6$)

ppm	*t (s)*	*c (g/dL)*	η_{sp}	η_{sp} *(eq. 18)*	η_{sp} *(eq. 19)*
5	276.23	0.0005015	0.1086	0.1125	0.1102
10	307.34	0.001003	0.2335	0.2225	0.2190
15	338.68	0.001505	0.3593	0.3306	0.3264
25	382.57	0.002508	0.5354	0.5413	0.5367
50	144.21	0.005015	1.032	1.041	1.038
100	205.05	0.01003	1.890	1.940	1.943
125	241.36	0.01254	2.401	2.346	2.349
200	311.59	0.02006	3.391	3.402	3.400
300	388.22	0.03009	4.471	4.470	4.470

Table 6.2: The Equations of the Fitted Smooth Curves for Each Polyacrylamide Sample.

Polymer Sample	Equation 18	Equation 19
N-I PAAm (Mw = 5-6 × 10^6)	$\eta_{sp} = 9.239\,c - 4.274\,c^{1.29}$	$\eta_{sp} = 8.490\,c - 38.43\,c^2 + 380.7\,c^3$
N-I PAAm (Mw = 18 × 10^6)	$\eta_{sp} = 245.9\,c - 1397.2\,c^{1.76}$	$\eta_{sp} = 236.9\,c - 3412.4\,c^2 + 15359\,c^3$
An-PAAm (Mw > 10 × 10^6)	$\eta_{sp} = 227.8\,c - 1135.8\,c^{1.76}$	$\eta_{sp} = 221.2\,c - 2906.5\,c^2 + 16369\,c^3$

Table 6.3: Variances Between the Specific Viscosities Obtained by Equations 18 and 19 and the Experimental Values

	N-I PAAm ($Mw = 5\text{-}6 \times 10^6$)	N-I PAAm ($Mw = 18 \times 10^6$)	An-PAAm ($Mw > 10 \times 10^6$)
Variance (Equation 18)	8.82×10^{-8}	5.11×10^{-4}	7.49×10^{-4}
Variance (Equation 19)	4.15×10^{-8}	4.91×10^{-4}	8.62×10^{-4}

Note :

$$Variance = (m-1)^{-1}\sum_{i=1}^{m}\left(y(x_i) - y_i\right)^2$$

Table 6.4: The Intrinsic Viscosities for the Three Polyacrylamide Samples

	[η] (dL/g) Using Equation 18	[η] (dL/g) Using Equation 19
N-I PAAm (Mw = 5-6 × 10^6)	9.329	8.490
N-I PAAm (Mw = 18 × 10^6)	245.9	236.9
An-PAAm (Mw > 10 × 10^6)	227.8	221.2

6.2 Huggins Method

The data shown in figures 6.1, 6.2, and 6.3 are respectively re-plotted in Figures 6.4, 6.5, and 6.6, as reduced viscosity versus the polymer concentration. These figures represent typical Huggins plots.

In Figure 6.4, the data show an exponential increase in the reduced viscosity with a decrease in polymer concentration below 25 ppm and a marked deviation from a preceding near linear behavior. However, in Figure 6.5 and 6.6, the data show an increase in η_{sp}/c with a decrease in the concentration until 10 ppm in the first figure and 15 ppm in the second, then, a sudden decrease in the reduced viscosity. This could be due to a measurement error or to a possible degradation of the polymer. A negative slope of the plots of the reduced viscosity versus the polymer concentration was reported at 42.5 °C by Silberberg et al. (1957). Slegr (1992) also reported a negative slope at an operating temperature equal to 25 °C. Such a reduction in the reduced viscosity with increase in concentration in the case of polyacrylamide could conceivably be the result of aggregation if the aggregates formed are more compact or more spherical than the individual molecule (Silberberg et al., 1957). Some of the peculiarities of the reduced viscosity against the concentration curves may be due to shear dependence. Beside the shear thinning effect occurring at high shear rates, the viscosity at 25 °C increases appreciably as the rate of shear is lowered in the case of polyacrylamide solutions (Silberberg et al., 1957). However, we mentioned earlier in this work that at the low concentrations used in our study, no shear thinning effect should be present. These contradictions make it difficult to single out the main reason for this anomalous behavior of the polyacrylamide solutions.

As the concentration approaches zero, the deviation from smooth behavior is attributed to the error magnification in the quotient η_{sp} /c due to the presence of c in the quotient. The values of the error magnification are calculated using equations 20, 21 and 22, and tabulated in Table 6.5.

The requirement of an extrapolation beyond the available experimental data and the uncertainty of the data points in the proximity of zero polymer concentration typifies the difficulties with intrinsic viscosity determinations when using the traditional methods (Kozicki and Kuang, 1996). The smooth curves in Figures 6.4, 6.5, and 6.6 represent the specific viscosities determined by equation 19 divided by the concentrations. It is obvious from Figures 6.4, 6.5, and 6.6 that the true curve representing the experimental data points is not a straight line. This typifies the inferiority of the traditional methods for determination of intrinsic viscosities which rely on fitting the experimental data points to a straight line and extrapolating to zero concentration.

If we compare the first two points in Figures 6.1 and 6.4, we notice a slight deviation from the true curve in the first figure but an exponential rise relative to other points in the Huggins plot. This is due to the fact that the error in the quotient η_{sp} /c due to the error in the specific viscosity is magnified by the magnification factor c^{-1}. The displacements in the first and second points in Figure 6.4 from the true curve are also quantitatively consistent with the magnification of errors in η_{sp} at these points (check Table 6.5). These displacements are also discernible if a comparison is made between the Figures 6.2 and 6.5, and Figures 6.3 and 6.6.

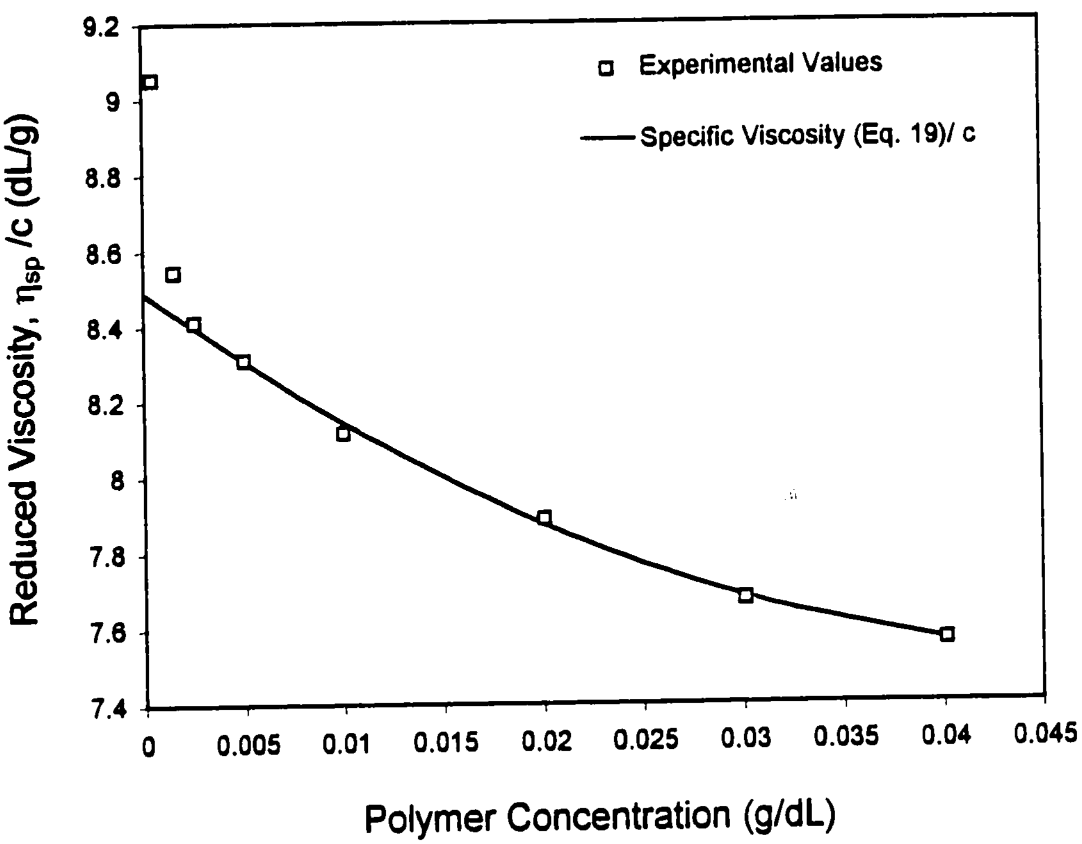


Figure 6.4: Reduced Viscosity Versus Polymer Concentration for Non-Ionic Polyacrylamide (Mw = 5-6 x 10^6) at 25 °C (Huggins Plot).

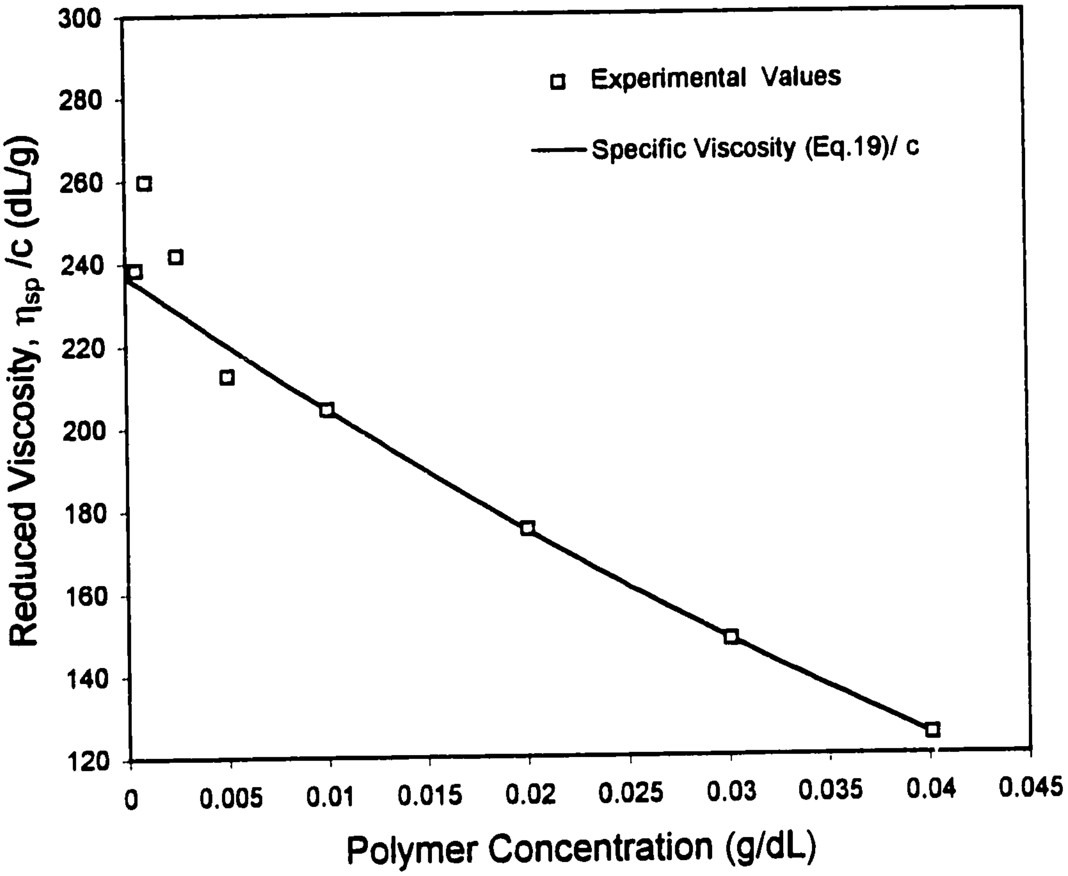


Figure 6.5: Reduced Viscosity Versus Polymer Concentration for Non-Ionic Polyacrylamide (Mw = 18 × 10^6) at 25 °C (Huggins Plot).

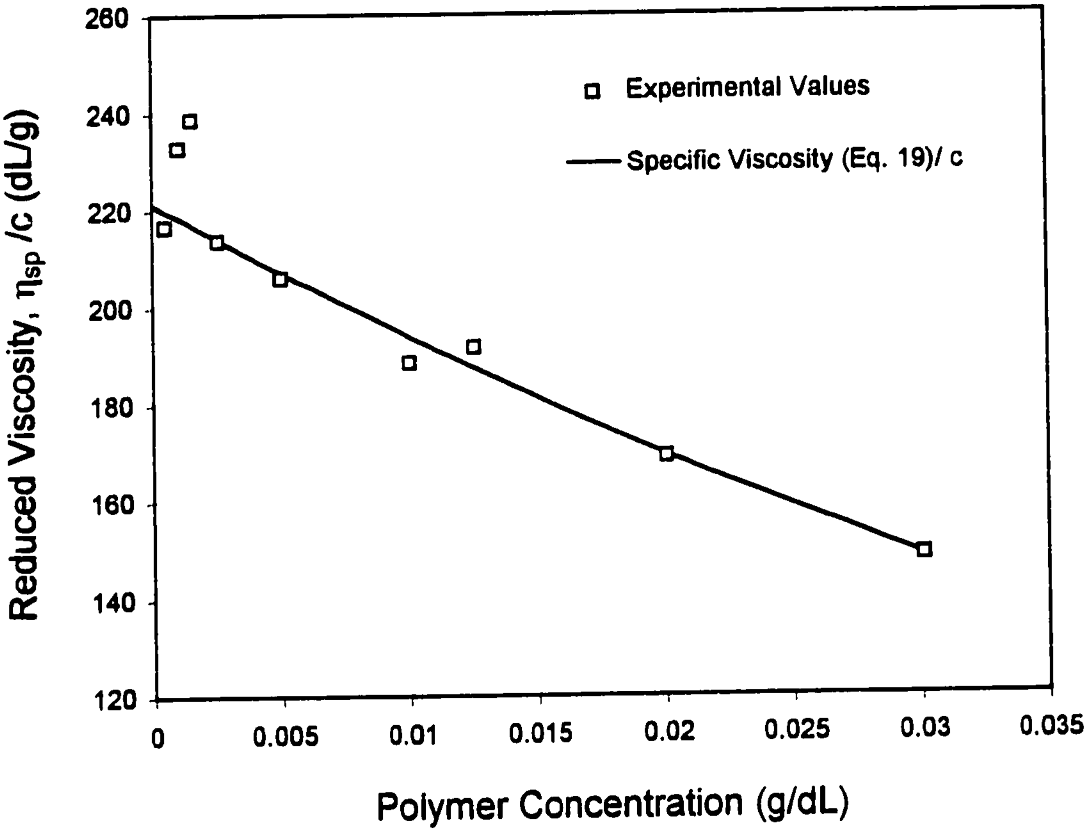


Figure 6.6: Reduced Viscosity Versus Polymer Concentration for Anionic Polyacrylamide (Mw > 10 × 10^6) at 25 °C (Huggins Plot).

Table 6.5: Error Magnifications

Non Ionic Polyacrylamide (Mw = 5 - 6 × 10^6)

c *(g/dL)*	η_{sp}	η_{sp} *(eq. 19)*	η_{sp}/c *(dL/g)*	η_{sp}*(eq. 19) / c* *(dL/g)*	**Experimental Error**	**Error in quotient** η_{sp}/c	**Error in** η_{sp}/c
0.0005015	0.004540	0.004248	9.053	8.471	-0.000292	-0.5823	-0.5820
0.001505	0.01286	0.01269	8.545	8.432	-0.00017	-0.11296	-0.113
0.002508	0.02109	0.02106	8.409	8.397	-0.00003	-0.01196	-0.012
0.005015	0.04167	0.04166	8.309	8.307	-0.00001	-0.00199	-0.002
0.01003	0.08140	0.08168	8.116	8.144	0.00028	0.0279	0.028
0.02006	0.1582	0.1579	7.886	7.871	-0.0003	-0.01496	-0.015
0.03009	0.2309	0.2311	7.674	7.680	0.0002	0.007	0.006
0.04012	0.3034	0.3034	7.562	7.562	0	0	0

Table 6.5, continued

Non Ionic Polyacrylamide (Mw = 18 × 10^6)

c *(g/dL)*	*η sp*	*η_{sp}* *(eq. 19)*	*η_{sp} / c* *(dL/g)*	*η_{sp}(eq. 19) / c* *(dL/g)*	***Experimental Error***	***Error in quotient η_{sp} /c***	***Error in η_{sp} /c***
0.0005015	0.1195	0.1179	238.3	235.1	-0.0016	-3.19	-3.20
0.001003	0.2606	0.2342	259.8	233.5	-0.0264	-26.32	-26.30
0.002508	0.6064	0.5728	241.8	228.4	-0.0336	-13.397	-13.40
0.005015	1.066	1.104	212.6	220.1	0.038	7.58	7.50
0.01003	2.049	2.048	204.3	204.2	-0.001	-0.0997	-0.1
0.02006	3.513	3.502	175.1	174.6	-0.011	-0.55	-0.50
0.03009	4.449	4.456	147.9	148.1	0.007	0.23	0.20
0.04012	5.004	5.002	124.7	124.7	-0.002	-0.05	0

Table 6.5, continued

Anionic Polyacrylamide (Mw > 10 × 10^6)

c (g/dL)	η_{sp}	η_{sp} (eq. 19)	η_{sp}/c (dL/g)	η_{sp}(eq. 19) / c (dL/g)	Experimental Error	Error in quotient η_{sp}/c	Error in η_{sp}/c
0.0005015	0.1086	0.1102	216.6	219.7	0.0016	3.19	3.10
0.001003	0.2335	0.2190	232.8	218.3	-0.0145	-14.46	-14.50
0.001505	0.3593	0.3264	238.7	216.9	-0.0329	-21.86	-21.80
0.002508	0.5354	0.5367	213.5	214.0	0.0013	0.52	0.50
0.005015	1.032	1.038	205.8	207.0	0.006	1.196	1.20
0.01003	1.890	1.943	188.4	193.7	0.053	5.28	5.30
0.01254	2.401	2.349	191.5	187.3	-0.052	-4.15	-4.20
0.02006	3.391	3.400	169.0	169.5	0.009	0.45	0.50
0.03009	4.471	4.470	148.6	148.6	-0.001	-0.03	0

6.3 Molecular Weight Determination

The intrinsic viscosities determined using the new alternative method were used to determine the average molecular weights of the corresponding polymers using the relationships between the intrinsic viscosity and the average molecular weight (i.e. equations 24, 25, and 26). The calculated molecular weights as well as the ones supplied by the manufacturer (Polysciences, Inc. of Warrington, Pennsylvania) are tabulated in Table 6.6.

The calculated molecular weight for the non ionic polyacrylamide sample, with a $Mw = 5\text{-}6 \times 10^6$, is relatively close to the value supplied by the manufacturer. However, the calculated molecular weights for the second non ionic sample ($Mw = 18 \times 10^6$) and the anionic sample are different from the supplied values.

This discrepancy between the calculated and the supplied molecular weights is suspected to be due to the anomalous behavior of the polyacrylamide solutions when they are exposed to high shear rates. No real explanation could be found for this peculiar behavior since there are a lot of contradictions, with regards to the shear thinning effect at low concentrations, in the literature.

Furthermore, since the negative slopes in Huggins plots were also reported in other studies (Silberberg et al., 1957; Slegr, 1992), we did not suspect that the behavior of the polyacrylamide solutions would possess any abnormalities. Unfortunately, the peculiar behavior of the polyacrylamide solutions was detected at a late stage of this study and no further investigations could have been done to draw a final conclusion regarding the shear thinning effect on such solutions. However, it should be emphasized that the alternative

Table 6.6: Determination of Average Molecular Weights

Polyacrylamide Sample	***[η] (cm³/g)***	***Mw (supplied by Manufacturer)****	***Calculated*** $\overline{M_w}$
Non-ionic	849	$5\text{-}6 \times 10^6$	3.38×10^6
Non-ionic	23690	18×10^6	150×10^6
Anionic	22120	$> 10 \times 10^6$	785×10^6

* Molecular weights are supplied by Polysciences, Inc. of Warrington, Pennsylvania.

method provided us with the necessary tools to determine accurately the intrinsic viscosity. This will be proven in the next section where a comparison between the intrinsic viscosities determined by the alternative and the traditional methods is presented.

6.4 Comparison Between the Intrinsic Viscosities Obtained by the Alternative and Huggins Methods Based on James and McLaren Data

The viscosity data used in the following comparison were taken from a study done by James and McLaren (1975). In this study, James and McLaren determined the intrinsic viscosity and Huggins constant of a WSR-301 solution using Huggins method. The typical Huggins plot (reduced viscosity versus polymer concentration) used for the determination of $[\eta]$ is depicted in Figure 6.7. A straight line was fitted to the experimental data and then extrapolated to zero concentration in order to determine the intrinsic viscosity from the value of the intercept. As shown in Figure 6.7, in order to fit the experimental data to the straight line, the points close to the origin must be disregarded. This represents a weakness of Huggins method since three out of eight data points were ignored when determining the intrinsic viscosity.

The same viscosity data were re-plotted in Figure 6.8 as specific viscosity versus polymer solution in accordance with the alternative method proposed for intrinsic viscosity evaluation. The smooth curve included in this figure represents a plot of equation 19. All experimental data points were utilized in the fitting of equation 19. Thus, this true curve should yield a more accurate intrinsic viscosity than the one yielded by a curve based on only selected points. The intrinsic viscosity determined from the parameter a_1 of equation

19 as well as the one determined by James and McLaren using Huggins method are tabulated in Table 6.7.

James and McLaren determined in their work the weight average molecular weight of WSR-301 using Shin's correlation

$$[\eta] = 1.03 \times 10^{-4} \overline{M}_w^{0.78}$$

This correlation was also used in the present work to determine the average molecular weight using the value of the intrinsic viscosity obtained by the alternative method. The average molecular weights are summarized in Table 6.7.

Using equation 6, James and McLaren calculated Huggins constant, k_H. However, we calculated Huggins constant from the parameters of equation 19 as follows:

Recalling equation 7 and 8 and assuming $k_1 = k_H$ for dilute solutions, we get

$$\eta_{sp} = [\eta]c + k_H[\eta]^2 c^2 + k_2[\eta]^3 c^3 \tag{27}$$

Using equation 19:

$$\eta_{sp} = a_1 c + a_2 c^2 + a_3 c^3$$

Hence,

$$k_H = \frac{a_2}{[\eta]^2} = \frac{a_2}{a_1^2} \tag{27}$$

The values of Huggins constant, k_H, calculated using Huggins equation and the parameters of equation 19 are tabulated in Table 6.7.

The smooth curve in Figure 6.9 represents the specific viscosity determined by equation 19 divided by the concentration. From this figure, it is obvious that the computed true curve derived from the experimental data points in this plot is not linear. Furthermore, if we compare the first four points in Figures 6.8 and 6.9, we notice a slight negative deviation of the first three points and a slight positive deviation of the fourth point from the true curve in Figure 6.8, but a large deviation of all four points from the true curve in Huggins plot (Figure 6.9). This is seen to result from the error magnification when the concentration approaches zero.

It is interesting to note that the values of the intrinsic viscosity determined using the alternative and Huggins methods are close (check Table 6.7). Since the experimental values close to the origin were not reliable, James and McLaren had to use additional experimental data points at higher concentrations in order to obtain more reliable estimates of the intrinsic viscosity. There is some deviation in the values of Huggins constant obtained by the two methods. The agreement between the molecular weights could be considered fortuitous since a linear extrapolation was used, whereas the behavior exhibited by the curve in Figure 6.9 is seen to be non-linear.

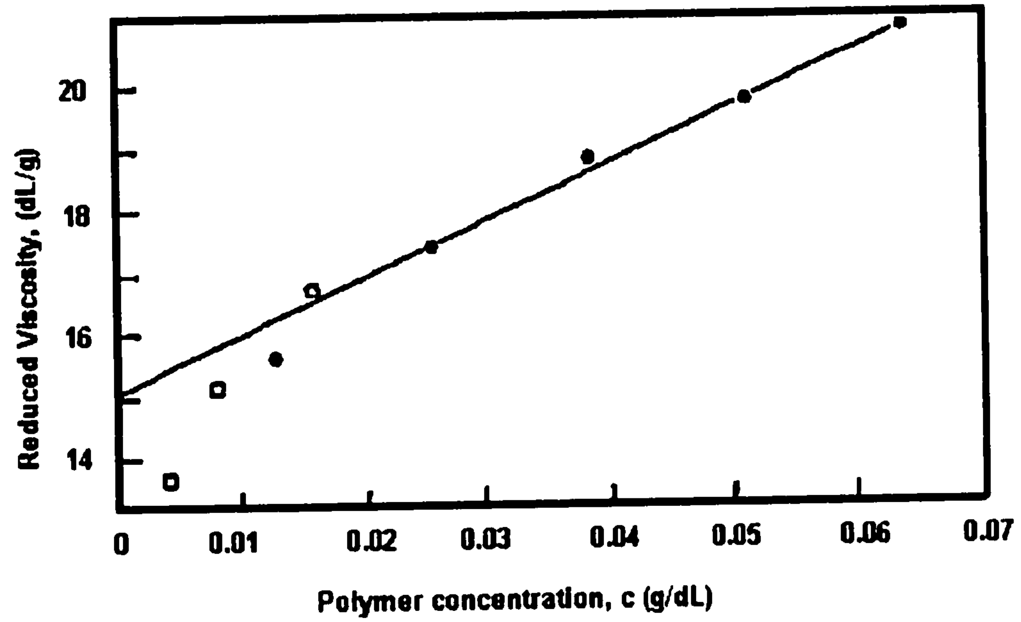


Figure 6.7: Viscometric Data for WSR-301 Solutions at T = 25 °C. •, Solutions Prepared for Intrinsic Viscosity Analysis; □, Solutions Used in Porous-Media Tests (James and McLaren, 1975).

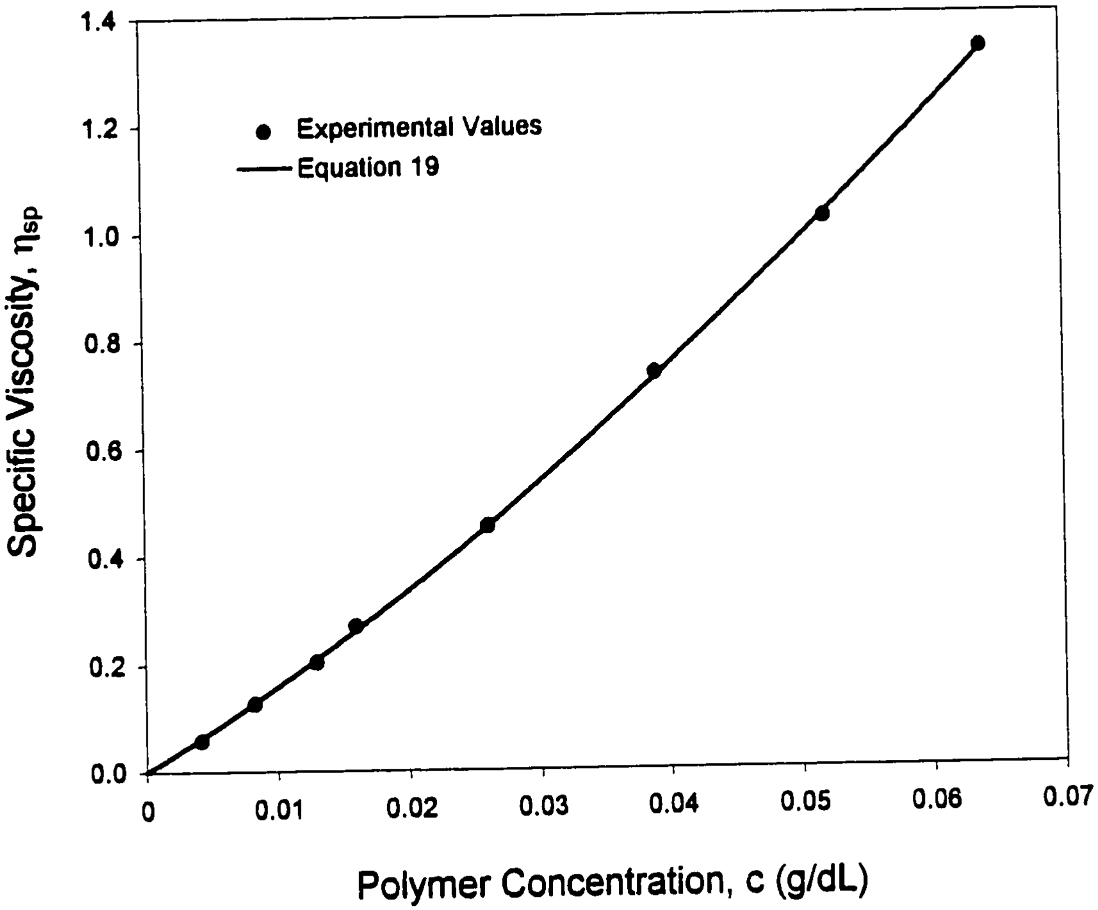


Figure 6.8: Specific Viscosity Versus Polymer Concentration for WSR-301 at 25 °C. Viscosity Measurements Done by James and McLaren (1975).

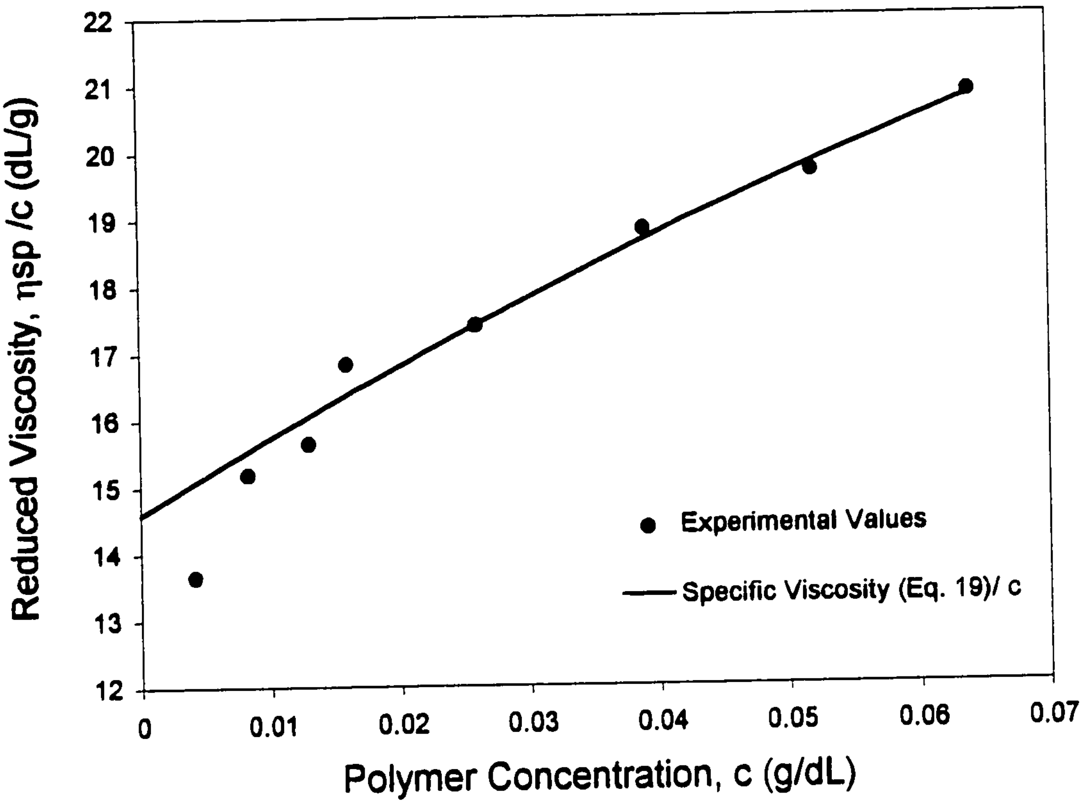


Figure 6.9: Reduced Viscosity Versus Polymer Concentration for WSR-301 at 25 °C. Viscosity Measurements Done by James and McLaren (1975).

Table 6.7: The Intrinsic Viscosities, Huggins Constants and Weight Average Molecular Weights for WSR-301 Solutions.

	James & McLaren	New Method
Intrinsic Viscosity (dL/g)	15	14.59
k_H	0.4	0.54
Average Molecular Weight	4.2×10^6	4.02×10^6

Note: Equation 19 Fitted to the Experimental Data is:

$$\eta_{sp} = -296.36\, c^3 + 115.97\, c^2 + 14.59\, c$$

Chapter 7

Conclusions

1. A new method for evaluation of intrinsic viscosities developed in this laboratory was tested using measurements collected with polyacrylamide solutions and compared with traditional methods.

2. The alternative method offers a number of advantages:

   - It provides independent evaluation of intrinsic viscosities.
   - Since it does not involve extrapolation, it does not require a theoretical equation in the evaluation of the intrinsic viscosity.
   - Any analytical expression containing the point $\eta_{sp}=0$ at zero concentration, providing a good fit of the experimental data, and yielding a first derivative at $c=0$ can be used for an independent evaluation of $[\eta]$.
   - It does not suffer from a magnification of error at low concentrations and is therefore not restricted to limited concentration range.
   - All experimental data points are considered when evaluating $[\eta]$.

3. The alternative method is simple and practical, and does not require complicated theoretical equations and associated computations

4. Anomalous behavior was encountered with the polyacrylamide solutions which was responsible for discrepancies in the molecular weights determined from the intrinsic viscosities for the anionic sample and the non-ionic sample having a $Mw = 18 \times 10^6$.

5. By comparing the results obtained by the traditional methods and the new alternative method, we are able to conclude that the latter is a superior method.

Chapter 8

Recommendations

1. A thorough study should be done in order to determine the shear thinning effect on low concentrations polyacrylamide solutions, since a lot of contradictions and ambiguity are present in the literature with regards to this subject.

2. In order to avoid any peculiarity in the behavior of the polyacrylamide solutions it is recommended to use a low-shear rotational viscometer for the evaluation of the viscosity of even highly dilute polyacrylamide solutions.

3. Another polymer less problematic than the polyacrylamide should be used to valorize the superiority of the new alternative method over the traditional methods for determination of intrinsic viscosities.

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Appendix A

Results of the Second Run for Each Polyacrylamide Solution Concentration. (These were conducted on separately prepared solutions using a newly prepared stock solution.)

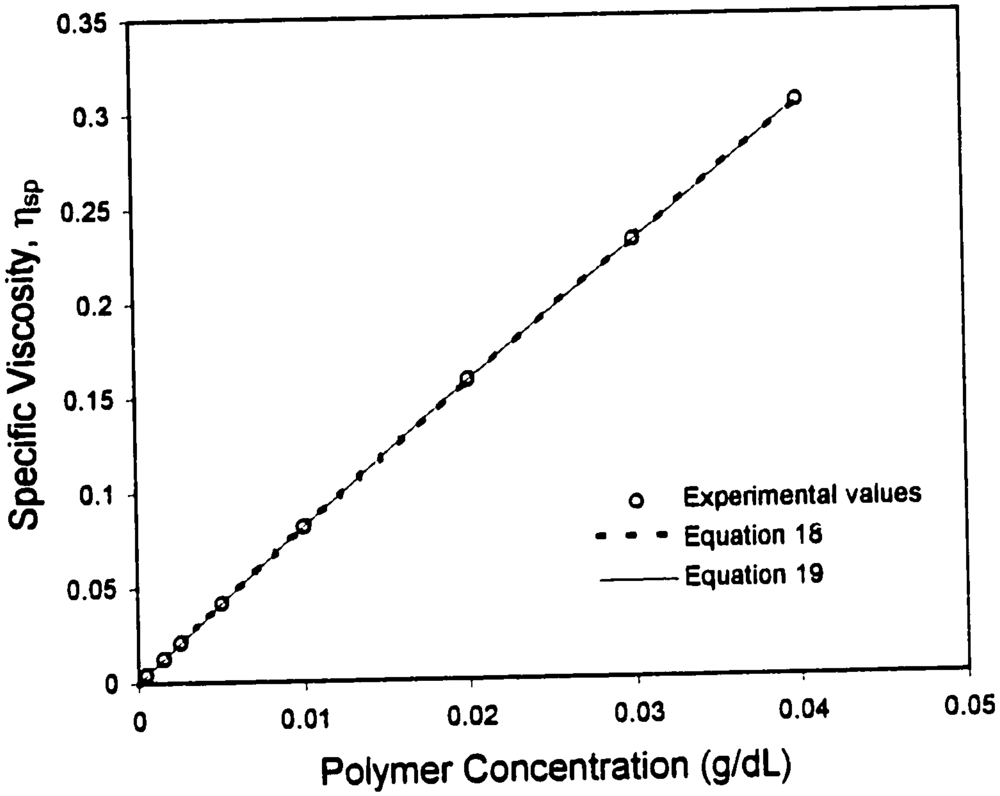


Figure A.1: Specific Viscosity Versus Polymer Concentration for Non-Ionic Polyacrylamide (Mw = 5-6 × 10^6) at 25 °C.

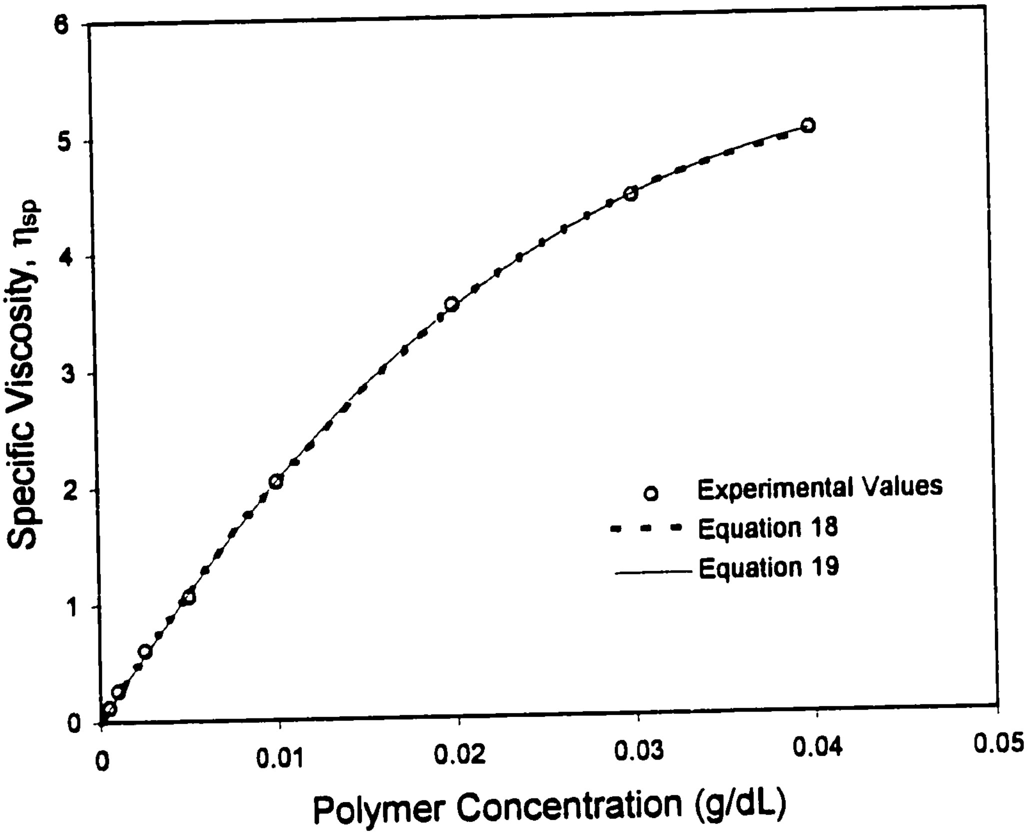


Figure A.2: Specific Viscosity Versus Polymer Concentration for Non-Ionic Polyacrylamide (Mw = 18 × 10^6) at 25 °C.

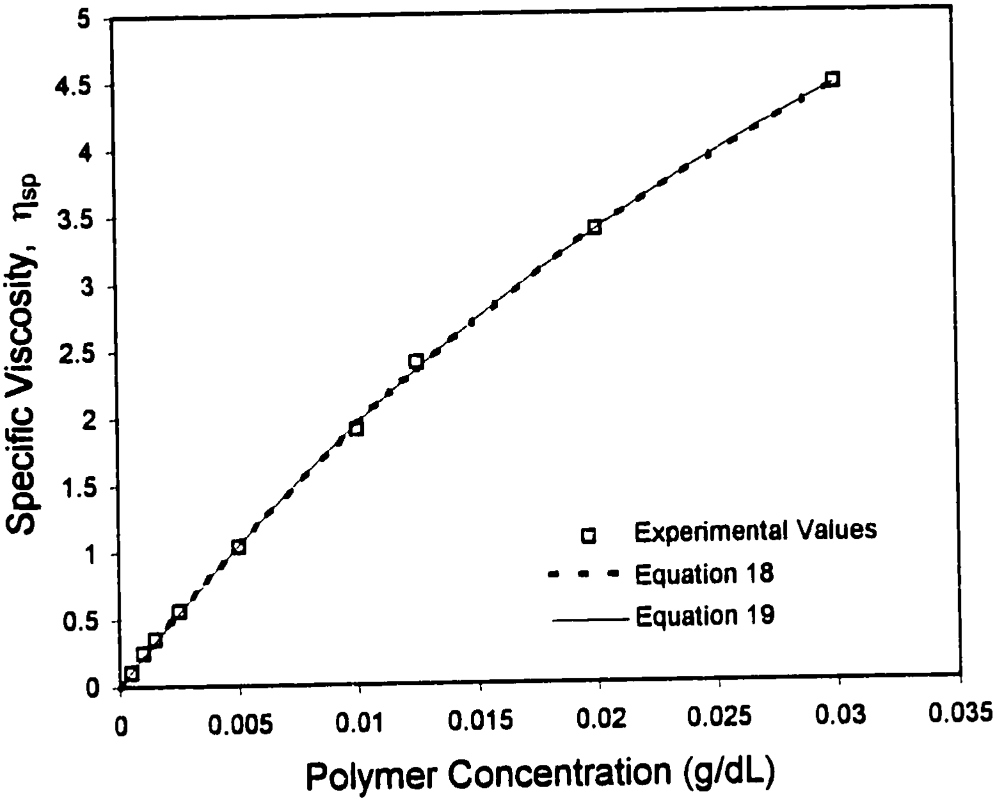


Figure A.3: Specific Viscosity Versus Polymer Concentration for Anionic Polyacrylamide (Mw > 10 × 10^6) at 25 °C.

Table A.1: Viscosity Measurements

Non-Ionic Polyacrylamide (Mw = 5-6 × 10^6)

ppm	*t (s)*	*c (g/dL)*	η_{sp}	η_{sp} *(eq. 18)*	η_{sp} *(eq. 19)*
5	249.96	0.0005015	0.004339	0.004405	0.004261
15	252.04	0.001505	0.01270	0.01295	0.01273
25	254.16	0.002508	0.02122	0.02132	0.02111
50	259.27	0.005015	0.04175	0.04178	0.04176
100	269.19	0.01003	0.08161	0.08148	0.08182
200	288.28	0.02006	0.1583	0.1579	0.1581
300	306.38	0.03009	0.2310	0.2316	0.2312
400	324.45	0.04012	0.3036	0.3034	0.3036

Non-Ionic Polyacrylamide (Mw = 18 × 10^6)

ppm	*t (s)*	*c (g/dL)*	η_{sp}	η_{sp} *(eq. 18)*	η_{sp} *(eq. 19)*
5	278.12	0.0005015	0.1175	0.1211	0.1180
10	313.78	0.001003	0.2608	0.2393	0.2343
25	400.70	0.002508	0.6100	0.5801	0.5732
50	514.56	0.005015	1.068	1.109	1.105
100	175.30	0.01003	2.042	2.047	2.051
200	261.35	0.02006	3.535	3.505	3.512
300	314.20	0.03009	4.452	4.476	4.467
400	346.34	0.04012	5.010	5.004	5.006

Anionic Polyacrylamide (Mw > 10 × 10^6)

ppm	*t (s)*	*c (g/dL)*	η_{sp}	η_{sp} *(eq. 18)*	η_{sp} *(eq. 19)*
5	274.92	0.0005015	0.1034	0.1167	0.1127
10	310.91	0.001003	0.2478	0.2297	0.2237
15	337.15	0.001505	0.3531	0.3400	0.3331
25	388.81	0.002508	0.5605	0.5536	0.5467
50	508.12	0.005015	1.039	1.055	1.053
100	724.60	0.01003	1.908	1.948	1.955
125	847.56	0.01254	2.402	2.349	2.356
200	310.84	0.02006	3.380	3.392	3.387
300	387.82	0.03009	4.465	4.462	4.464

Table A.2: The Equations of the Fitted Smooth Curves for Each Polyacrylamide Sample.

Polymer Sample	Equation 18	Equation 19
N-I PAAm (Mw = 5-6 × 10^6)	$\eta_{sp} = 9.261\ c - 4.318\ c^{1.29}$	$\eta_{sp} = 8.516\ c - 39.86\ c^2 + 403.5\ c^3$
N-I PAAm (Mw = 18 × 10^6)	$\eta_{sp} = 245.6\ c - 1438.1\ c^{1.77}$	$\eta_{sp} = 236.9\ c - 3373.5\ c^2 + 14421\ c^3$
An-PAAm (Mw > 10 × 10^6)	$\eta_{sp} = 239.3\ c - 856.8\ c^{1.64}$	$\eta_{sp} = 226.4\ c - 3418.4\ c^2 + 27422\ c^3$

Table A.3: Standard Deviations Between the Specific Viscosities Obtained by Equations 18 and 19 and the Experimental Values

	N-I PAAm ($Mw = 5\text{-}6 \times 10^6$)	N-I PAAm ($Mw = 18 \times 10^6$)	An-PAAm ($Mw > 10 \times 10^6$)
Standard Deviation Equation 18	77×10^{-8}	5.13×10^{-4}	5.56×10^{-4}
Standard Deviation Equation 19	16×10^{-8}	4.81×10^{-4}	5.83×10^{-4}

Table A.4: The Intrinsic Viscosities for the Three Polyacrylamide Sample

	$[\eta]$ (dL/g) Using Equation 18	$[\eta]$ (dL/g) Using Equation 19
N-I PAAm (Mw = 5-6 × 10^6)	9.261	8.516
N-I PAAm (Mw = 18 × 10^6)	245.6	236.9
An-PAAm (Mw > 10 × 10^6)	239.3	226.4

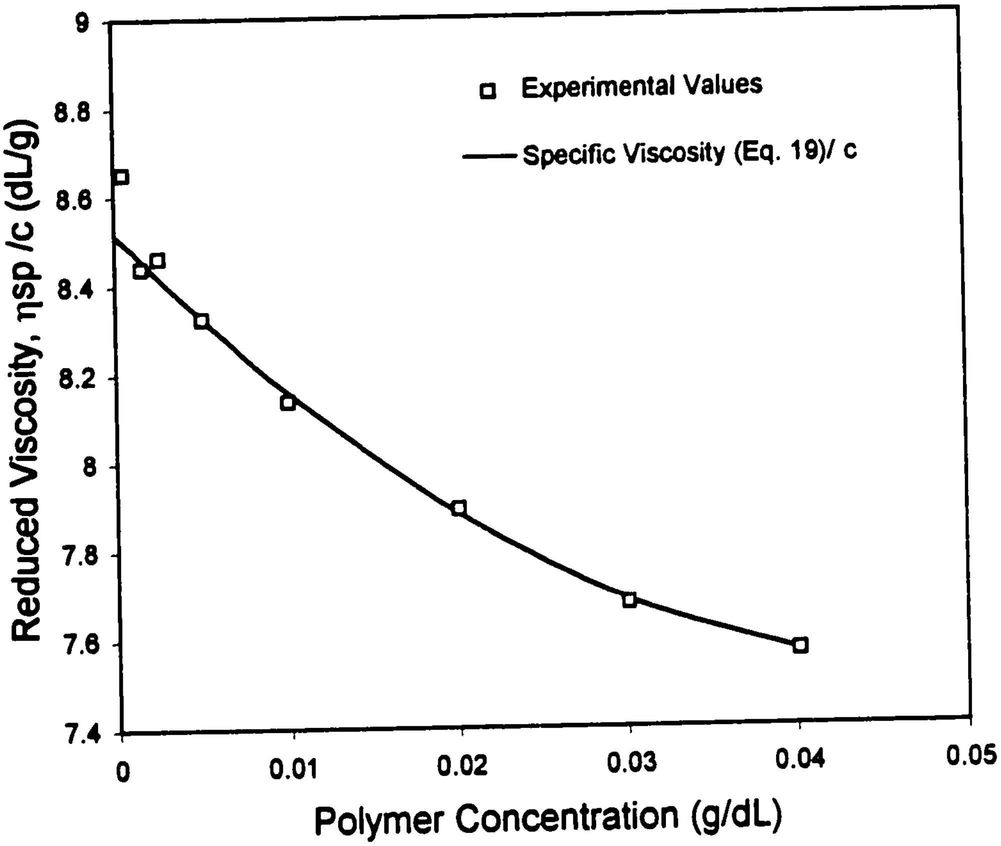


Figure A.4: Reduced Viscosity Versus Polymer Concentration for Non-Ionic Polyacrylamide (Mw = 5-6 × 10^6) at 25 °C (Huggins Plot).

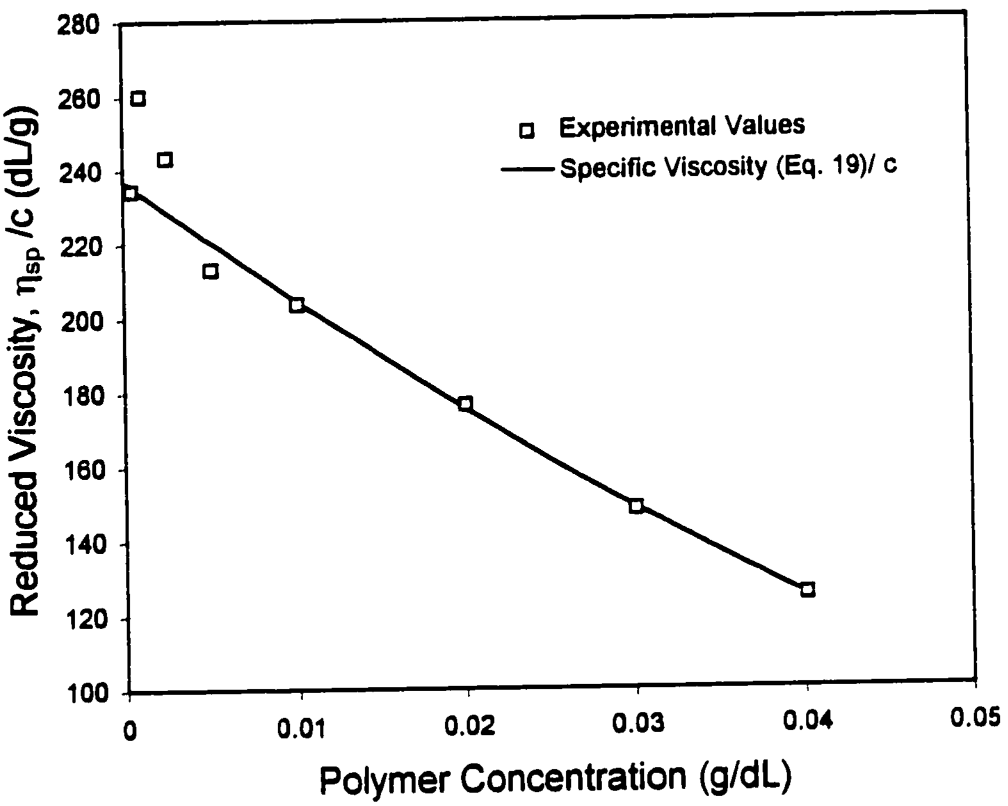


Figure A.5: Reduced Viscosity Versus Polymer Concentration for Non-Ionic Polyacrylamide (Mw = 18 × 10^6) at 25 °C (Huggins Plot).

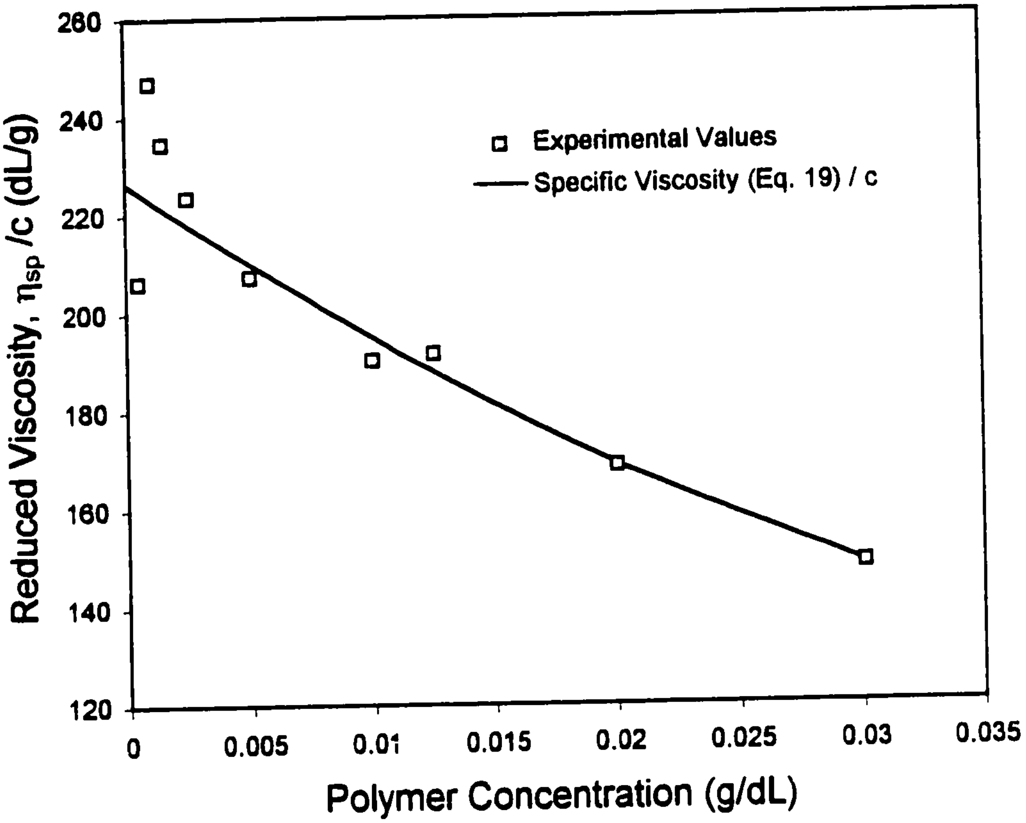


Figure A.6: Reduced Viscosity Versus Polymer Concentration for Non-Ionic Polyacrylamide (Mw > 10 × 10^6) at 25 °C (Huggins Plot).

Table A.5: Error Magnifications

Non-Ionic Polyacrylamide (Mw = 5-6 × 10^6).

c (g/dL)	η_{sp}	η_{sp} (eq. 19)	η_{sp}/c (dL/g)	η_{sp} (eq. 19) / c (dL/g)	Experimental Error	Error in quotient η_{sp}/c	Error in η_{sp}/c
0.0005015	0.004339	0.004261	8.652	8.497	-0.000078	-0.156	-0.155
0.001505	0.01270	0.01273	8.439	8.458	0.00003	0.0199	0.0190
0.002508	0.02122	0.02111	8.461	8.417	-0.00011	-0.0439	-0.044
0.005015	0.04175	0.04176	8.325	8.327	0.00001	0.00199	0.002
0.01003	0.08161	0.08182	8.137	8.158	0.00021	0.0209	0.021
0.02006	0.1583	0.1581	7.891	7.881	-0.0002	-0.00997	-0.01
0.03009	0.2310	0.2312	7.677	7.684	0.0002	0.0066	0.007
0.04012	0.3036	0.3036	7.567	7.567	0	0	0

Table A.5, continued

Non-Ionic Polyacrylamide ($M_w = 18 \times 10^6$).

c (g/dL)	η_{sp}	η_{sp} (eq. 19)	η_{sp} / c) (dL/g)	η_{sp}(eq. 19) / c (dL/g)	Experimental Error	Error in quotient η_{sp}/c	Error in η_{sp}/c
0.0005015	0.1175	0.1180	234.3	235.3	0.0005	0.997	1
0.001003	0.2608	0.2343	260.0	233.6	-0.0265	-26.42	-26.40
0.002508	0.6100	0.5732	243.2	228.5	-0.0368	-14.67	-14.70
0.005015	1.068	1.105	213.0	220.3	0.037	7.38	7.30
0.01003	2.042	2.051	203.6	204.5	0.009	0.897	0.90
0.02006	3.535	3.512	176.2	175.1	-0.023	-1.15	-1.10
0.03009	4.452	4.467	148.0	148.5	0.015	0.499	0.50
0.04012	5.010	5.006	124.9	124.8	-0.004	-0.0997	-0.10

Table A.5, continued

Anionic Polyacrylamide ($Mw > 10 \times 10^6$).

c (g/dL)	η_{sp}	η_{sp} (eq. 19)	η_{sp}/c (dL/g)	η_{sp} (eq. 19) $/c$ (dL/g)	Experimental Error	Error in quotient η_{sp}/c	Error in η_{sp}/c
0.0005015	0.1034	0.1127	206.2	224.7	0.0093	18.54	18.50
0.001003	0.2478	0.2237	247.1	223.0	-0.0241	-24.03	-24.10
0.001505	0.3531	0.3331	234.6	221.3	-0.02	-13.29	-13.30
0.002508	0.5605	0.5467	223.5	218.0	-0.0138	-5.502	-5.50
0.005015	1.039	1.053	207.2	210.0	0.014	2.79	2.80
0.01003	1.908	1.955	190.2	194.9	0.047	4.69	4.70
0.01254	2.402	2.356	191.5	187.9	-0.046	-3.67	-3.60
0.02006	3.380	3.387	168.5	168.8	0.007	0.35	0.30
0.03009	4.465	4.464	148.4	148.4	-0.001	-0.03	0

Table A.6: Determination of Average Molecular Weights

Polyacrylamide Sample	***[η] (cm³/g)***	***Mw (supplied by Manufacturer)****	***Calculated*** $\overline{M_w}$
Non-ionic	851.6	$5\text{-}6 \times 10^6$	3.39×10^6
Non-ionic	23692	18×10^6	150×10^6
Anionic	22640	$> 10 \times 10^6$	810×10^6

* Molecular weights are supplied by Polysciences, Inc.of Warrington, Pennsylvania

Appendix B

- Input and Output Files Generated by Sigma Plot 4.0 for Equation 18 and 19.
- Input and Output Files Generated by Maple V for Equation 18.
- Input and Output Files Generated by Microsoft Excel 7.0 for Equation 19.

B.1 Input and Output Files Generated by Sigma Plot Using Equation 18 for Non-Ionic Polyacrylamide (Mw = 5-6 × 10^6).

Input File:

c (g/dL)	ηsp
0,0005015	0,004540
0,001505	0,01286
0,002508	0,02109
0,005015	0,04167
0,01003	0,08140
0,02006	0,1582
0,03009	0,2309
0,04012	0,3034

```
Nonlinear Regression

[Variables]
x=col(1)
y=col(2)
'Automatic Initial Parameter Estimate Functions
F(q)=ape(x;y;2;0;1)

[Parameters]
a=F(0)[1] "Auto"
b=F(0)[2] "Auto"
c=F(0)[3] "Auto"

[Equations]
f=a*x+b*x^c
fit f to y

[Constraints]
c>1.01

[Options]
tolerance=0,000100
stepsize=100
iterations=100
```

Output File:

```
R = 0,99999650  Rsqr = 0,99999301        Adj Rsqr = 0,99999021

Standard Error of Estimate = 0,0004

        Coefficient  Std. Error    t            P
a       9,2225       0,5252        17,5585      <0,0001
b       -4,2802      0,2744        -15,5997     <0,0001
c       1,2936       0,1120        11,5491      <0,0001
```

```
Analysis of Variance:
            DF    SS        MS        F              P
Regression  2     0,0882    0,0441    357396,4746    <0,0001
Residual    5     0,0000    0,0000
Total       7     0,0882    0,0126

PRESS = 0,0000

Durbin-Watson Statistic = 3,0186

Normality Test:  Passed  (P = 0,6069)

Constant Variance Test:  Passed  (P = 0,1597)

Power of performed test with alpha = 0,0500: 1,0000

Regression Diagnostics:
Row   Predicted   Residual   Std. Res.   Stud. Res.   Stud. Del. Res.
1     0,0044      0,0001     0,4146      0,4257       0,3879
2     0,0129      -0,0001    -0,1817     -0,2000      -0,1796
3     0,0213      -0,0002    -0,5385     -0,6249      -0,5821
4     0,0417      -0,0000    -0,1281     -0,1561      -0,1400
5     0,0814      0,0000     0,0484      0,0589       0,0527
6     0,1577      0,0005     1,2863      1,8451       2,9213
7     0,2315      -0,0006    -1,5794     -2,1131      -5,7796
8     0,3032      0,0002     0,5806      1,9281       3,4049

Influence Diagnostics:
Row   Cook's Dist. Leverage   DFFITS
1     0,0033       0,0513     0,0902
2     0,0028       0,1750     -0,0827
3     0,0451       0,2574     -0,3428
4     0,0039       0,3266     -0,0975
5     0,0006       0,3250     0,0366
6     1,2001       0,5140     3,0042
7     1,1758       0,4413     -5,1370
8     12,4241      0,9093     10,7815

95% Confidence
Row   Predicted   Regression 5%   Regression 95% Population 5%   Population 95%
1     0,0044      0,0042          0,0046         0,0035          0,0053
2     0,0129      0,0125          0,0133         0,0119          0,0139
3     0,0213      0,0208          0,0217         0,0203          0,0223
4     0,0417      0,0412          0,0422         0,0407          0,0428
5     0,0814      0,0809          0,0819         0,0803          0,0824
6     0,1577      0,1571          0,1584         0,1566          0,1589
7     0,2315      0,2309          0,2321         0,2304          0,2325
8     0,3032      0,3023          0,3041         0,3019          0,3044
```

B.2 Input and Output Files Generated by Sigma Plot Using Equation 19 for Non-Ionic Polyacrylamide Sample (Mw = 5-6 $\times 10^6$)

Input File:

```
c (g/dL)        ηsp

0,0005015       0,004540
0,001505        0,01286
0,002508        0,02109
0,005015        0,04167
0,01003         0,08140
0,02006         0,1582
0,03009         0,2309
0,04012         0,3034
```

```
Nonlinear Regression

[Variables]
x=col(1)
y=col(2)
'Automatic Initial Parameter Estimate Functions
F(q)=ape(x;y;3;0;1)

[Parameters]
y0=F(0)[1] "Auto
a=F(0)[2] "Auto
b=F(0)[3] "Auto
c=F(0)[4] "Auto

[Equations]
f=y0+a*x+b*x^2+c*x^3
fit f to y

[Constraints]
y0=0

[Options]
tolerance=0,000100
stepsize=100
iterations=100
```

Ouput File:

```
R = 0,99999651  Rsqr = 0,99999302        Adj Rsqr = 0,99998779

Standard Error of Estimate = 0,0004

        Coefficient  Std. Error    t           P
y0      -0,0000      0,0003        -0,0000     1,0000
a       8,4335       0,0973        86,7185     <0,0001
b       -35,3801     6,0685        -5,8301     0,0043
c       336,2931     98,7607       3,4051      0,0271
```

```
Analysis of Variance:
             DF      SS            MS            F              P
Regression   3       0,0882        0,0294        191147,8741    <0,0001
Residual     4       0,0000        0,0000
Total        7       0,0882        0,0126

PRESS = 0,0003

Durbin-Watson Statistic = 1,1112

Normality Test:  Passed   (P = 0,6198)

Constant Variance Test:  Passed   (P = 0,6620)

Power of performed test with alpha = 0,0500: 1,0000

Regression Diagnostics:
Row        Predicted   Residual     Std. Res.     Stud. Res.    Stud. Del. Res.
1          0,0042      0,0003       0,8145        1,1174        1,1669
2          0,0126      0,0002       0,6287        0,7510        0,7017
3          0,0209      0,0002       0,3979        0,4523        0,4021
4          0,0414      0,0002       0,5697        0,6703        0,6161
5          0,0814      0,0000       0,0817        0,1196        0,1038
6          0,1577      0,0005       1,3938        1,9187        5,8859
7          0,2309      0,0000       0,0201        0,0394        0,0341
8          0,3031      0,0003       0,7131        5,4131        >1e20

Influence Diagnostics:
Row        Cook's Dist. Leverage    DFFITS
1          0,2754       0,4687      1,0959
2          0,0602       0,2991      0,4583
3          0,0149       0,2260      0,2173
4          0,0431       0,2775      0,3818
5          0,0041       0,5334      0,1110
6          0,8236       0,4723      5,5680
7          0,0011       0,7404      0,0576
8          414,7356     0,9826      >1e20

95% Confidence
Row        Predicted   Regression 5%  Regression 95% Population 5%  Population 95%
1          0,0042      0,0035         0,0050         0,0029         0,0055
2          0,0126      0,0120         0,0132         0,0114         0,0139
3          0,0209      0,0204         0,0215         0,0197         0,0221
4          0,0414      0,0409         0,0420         0,0402         0,0427
5          0,0814      0,0806         0,0822         0,0800         0,0827
6          0,1577      0,1569         0,1584         0,1563         0,1590
7          0,2309      0,2300         0,2318         0,2295         0,2323
8          0,3031      0,3020         0,3042         0,3016         0,3047
```

B.3 Input and Output Files Generated by Sigma Plot Using Equation 18 for Non-Ionic Polyacrylamide (Mw = 18 × 10^6).

Input File:

c(g/dL)	η_{sp}
0,0005015	0,1195
0,001003	0,2606
0,002508	0,6064
0,005015	1,066
0,01003	2,049
0,02006	3,513
0,03009	4,449
0,04012	5,004

```
Nonlinear Regression

[Variables]
x = col(1)
y = col(2)
'Automatic Initial Parameter Estimate Functions
F(q)=ape(x;y;2;0;1)

[Parameters]
a=.01
b=.01
c=1.01

[Equations]
f=a*x+b*x^c
fit f to y

[Constraints]
c>1.01

[Options]
tolerance=0,000100
stepsize=100
iterations=100
```

Output File:

```
R = 0,99993274   Rsqr = 0,99986548        Adj Rsqr = 0,99981168

Standard Error of Estimate = 0,0268

            Coefficient  Std. Error     t            P
a           246,3023     8,9508         27,5173      <0,0001
b           -1384,1208   267,3386       -5,1774      0,0035
c           1,7560       0,0813         21,6007      <0,0001
```

```
Analysis of Variance:
               DF      SS          MS          F              P
Regression     2       26,6111     13,3055     18582,5338     <0,0001
Residual       5       0,0036      0,0007
Total          7       26,6147     3,8021
PRESS = 0,0170

Durbin-Watson Statistic = 2,6216

Normality Test:  Passed   (P = 0,5239)

Constant Variance Test:  Passed   (P = 0,6620)

Power of performed test with alpha = 0,0500: 1,0000

Regression Diagnostics:
Row       Predicted    Residual     Std. Res.     Stud. Res.    Stud. Del. Res.
1         0,1213       -0,0018      -0,0672       -0,0678       -0,0607
2         0,2395       0,0211       0,7872        0,8098        0,7771
3         0,5802       0,0262       0,9791        1,0896        1,1160
4         1,1085       -0,0425      -1,5884       -1,9743       -3,7609
5         2,0425       0,0065       0,2448        0,3137        0,2834
6         3,4953       0,0177       0,6610        0,9310        0,9159
7         4,4652       -0,0162      -0,6042       -0,8974       -0,8763
8         4,9992       0,0048       0,1798        0,7874        0,7524

Influence Diagnostics:
Row       Cook's Dist. Leverage     DFFITS
1         0,0000       0,0178       -0,0082
2         0,0128       0,0551       0,1877
3         0,0944       0,1925       0,5450
4         0,7080       0,3527       -2,7763
5         0,0211       0,3914       0,2273
6         0,2843       0,4959       0,9085
7         0,3237       0,5467       -0,9623
8         3,7579       0,9479       3,2086

95% Confidence
Row       Predicted    Regression 5%  Regression 95% Population 5%  Population 95%
1         0,1213       0,1121         0,1305         0,0519         0,1907
2         0,2395       0,2234         0,2557         0,1689         0,3102
3         0,5802       0,5500         0,6104         0,5051         0,6553
4         1,1085       1,0677         1,1494         1,0285         1,1885
5         2,0425       1,9994         2,0855         1,9613         2,1236
6         3,4953       3,4469         3,5438         3,4112         3,5794
7         4,4652       4,4143         4,5160         4,3796         4,5507
8         4,9992       4,9322         5,0662         4,9032         5,0952
```

B.4 Input and Output Files Generated by Sigma Plot Using Equation 19 for Non-Ionic Polyacrylamide (Mw = 18 × 10^6).

Input File:

```
c(g/dL)         ηsp

0,0005015       0,1195
0,001003        0,2606
0,002508        0,6064
0,005015        1,066
0,01003         2,049
0,02006         3,513
0,03009         4,449
0,04012         5,004

Nonlinear Regression

[Variables]
x=col(1)
y=col(2)
'Automatic Initial Parameter Estimate Functions
F(q)=ape(x;y;3;0;1)

[Parameters]
y0=F(0)[1] "Auto
a=F(0)[2] "Auto
b=F(0)[3] "Auto
c=F(0)[4] "Auto

[Equations]
f=y0+a*x+b*x^2+c*x^3
fit f to y

[Constraints]
y0=0

[Options]
tolerance=0,000100
stepsize=100
iterations=100
```

Output File:

```
R = 0,99990395  Rsqr = 0,99980792        Adj Rsqr = 0,99966386

Standard Error of Estimate = 0,0357

              Coefficient  Std. Error      t              P
y0            -0,0000      0,0265          -0,0000        1,0000
a             232,8111     8,5776          27,1417        <0,0001
b             -3196,2373   540,0604        -5,9183        0,0041
c             12217,1070   8832,7386       1,3832         0,2388
```

```
Analysis of Variance:
               DF        SS            MS             F              P
Regression     3         26,5477       8,8492         6940,1441      <0,0001
Residual       4         0,0051        0,0013
Total          7         26,5528       3,7933

PRESS = 1,2138

Durbin-Watson Statistic = 1,5929

Normality Test:  Passed   (P = 0,5287)

Constant Variance Test:   Passed   (P = 0,7941)

Power of performed test with alpha = 0,0500: 1,0000

Regression Diagnostics:
Row        Predicted   Residual      Std. Res.     Stud. Res.    Stud. Del. Res.
1          0,1160      0,0035        0,0993        0,1318        0,1144
2          0,2303      0,0303        0,8484        1,0472        1,0645
3          0,5640      0,0424        1,1880        1,3471        1,5784
4          1,0887      -0,0227       -0,6358       -0,7517       -0,7025
5          2,0259      0,0231        0,6475        0,9439        0,9271
6          3,4826      0,0304        0,8504        1,1677        1,2456
7          4,4442      0,0048        0,1337        0,2606        0,2276
8          4,9846      0,0194        0,5426        4,0813        >1e20

Influence Diagnostics:
Row        Cook's Dist. Leverage     DFFITS
1          0,0033      0,4315        0,0996
2          0,1436      0,3437        0,7704
3          0,1297      0,2223        0,8438
4          0,0562      0,2846        -0,4430
5          0,2505      0,5294        0,9833
6          0,3018      0,4696        1,1720
7          0,0475      0,7367        0,3807
8          231,4262    0,9823        >1e20

95% Confidence
Row        Predicted   Regression 5%  Regression 95% Population 5%  Population 95%
1          0,1160      0,0508        0,1811        -0,0027       0,2346
2          0,2303      0,1722        0,2884        0,1154        0,3452
3          0,5640      0,5172        0,6107        0,4544        0,6736
4          1,0887      1,0358        1,1416        0,9763        1,2011
5          2,0259      1,9537        2,0980        1,9033        2,1485
6          3,4826      3,4147        3,5506        3,3624        3,6028
7          4,4442      4,3591        4,5293        4,3136        4,5749
8          4,9846      4,8864        5,0829        4,8450        5,1242
```

B.5 Input and Output Files Generated by Sigma Plot using Equation 18 for Anionic Polyacrylamide (Mw > 10×10^6).

Input File:

c (g/dL)	ηsp
0,0005015	0,1086
0,001003	0,2335
0,001505	0,3593
0,002508	0,5354
0,005015	1,032
0,01003	1,890
0,01254	2,401
0,02006	3,391
0,03009	4,471

```
Nonlinear Regression

[Variables]
x=col(1)
y=col(2)
'Automatic Initial Parameter Estimate Functions
F(q)=ape(x;y;2;0;1)

[Parameters]
a=.01
b=.01
c=1.01

[Equations]
f=a*x+b*x^c
fit f to y

[Constraints]
c>1.01

[Options]
tolerance=0,000100
stepsize=100
iterations=100
```

Output File:

```
R = 0,99982558  Rsqr = 0,99965119          Adj Rsqr = 0,99953492

Standard Error of Estimate = 0,0335

          Coefficient  Std. Error    t           P
a         227,6369     14,2907       15,9291     <0,0001
b         -1142,7125   628,3416      -1,8186     0,1188
c         1,7623       0,2056        8,5724      0,0001
```

```
Analysis of Variance:
              DF        SS          MS          F             P
Regression    2         19,3125     9,6562      8597,6523     <0,0001
Residual      6         0,0067      0,0011
Total         8         19,3192     2,4149

PRESS = 0,0154

Durbin-Watson Statistic = 2,8247

Normality Test:  Passed   (P = 0,2409)

Constant Variance Test:   Passed   (P = 0,9129)

Power of performed test with alpha = 0,0500: 1,0000

Regression Diagnostics:
Row        Predicted   Residual      Std. Res.     Stud. Res.    Stud. Del. Res.
1          0,1124      -0,0038       -0,1137       -0,1152       -0,1053
2          0,2224      0,0111        0,3317        0,3452        0,3183
3          0,3305      0,0288        0,8605        0,9239        0,9106
4          0,5411      -0,0057       -0,1692       -0,1928       -0,1766
5          1,0404      -0,0084       -0,2507       -0,3059       -0,2815
6          1,9399      -0,0499       -1,4891       -1,7613       -2,3135
7          2,3457      0,0553        1,6501        2,0219        3,2698
8          3,4018      -0,0108       -0,3229       -0,5186       -0,4844
9          4,4701      0,0009        0,0276        0,1743        0,1595

Influence Diagnostics:
Row        Cook's Dist. Leverage     DFFITS
1          0,0001      0,0263        -0,0173
2          0,0033      0,0768        0,0918
3          0,0434      0,1324        0,3557
4          0,0037      0,2296        -0,0964
5          0,0153      0,3285        -0,1969
6          0,4126      0,2852        -1,4615
7          0,6834      0,3340        2,3155
8          0,1416      0,6123        -0,6088
9          0,3932      0,9749        0,9940

95% Confidence
Row        Predicted   Regression 5%  Regression 95% Population 5%  Population 95%
1          0,1124      0,0991         0,1257         0,0293         0,1955
2          0,2224      0,1997         0,2451         0,1373         0,3075
3          0,3305      0,3006         0,3603         0,2432         0,4177
4          0,5411      0,5018         0,5804         0,4501         0,6320
5          1,0404      0,9934         1,0874         0,9459         1,1349
6          1,9399      1,8961         1,9837         1,8469         2,0329
7          2,3457      2,2983         2,3931         2,2510         2,4404
8          3,4018      3,3377         3,4660         3,2977         3,5059
9          4,4701      4,3891         4,5510         4,3548         4,5853
```

B.6 Input and Output Files Generated by Sigma Plot using Equation 19 for Anionic Polyacrylamide (Mw > 10 × 10^6).

Input File:

c (g/dL)	ηsp
0,0005015	0,1086
0,001003	0,2335
0,001505	0,3593
0,002508	0,5354
0,005015	1,032
0,01003	1,890
0,01254	2,401
0,02006	3,391
0,03009	4,471

```
Nonlinear Regression

[Variables]
x=col(1)
y=col(2)
'Automatic Initial Parameter Estimate Functions
F(q)=ape(x;y;3;0;1)

[Parameters]
y0=F(0)[1] "Auto
a=F(0)[2] "Auto
b=F(0)[3] "Auto
c=F(0)[4] "Auto

[Equations]
f=y0+a*x+b*x^2+c*x^3
fit f to y

[Constraints]
y0=0

[Options]
tolerance=0,000100
stepsize=100
iterations=100
```

Output File:

```
R = 0,99977510  Rsqr = 0,99955026        Adj Rsqr = 0,99928041

Standard Error of Estimate = 0,0416

        Coefficient  Std. Error    t          P
y0      -0,0000      0,0304        -0,0000    1,0000
a       215,7553     13,3690       16,1385    <0,0001
b       -2493,7542   1183,7793     -2,1066    0,0890
c       8046,9491    26316,9767    0,3058     0,7721
```

```
Analysis of Variance:
             DF     SS          MS          F           P
Regression   3      19,2600     6,4200      3704,1641   <0,0001
Residual     5      0,0087      0,0017
Total        8      19,2687     2,4086

PRESS = 17,0530

Durbin-Watson Statistic = 2,2311

Normality Test:  Passed   (P = 0,2119)

Constant Variance Test:  Passed   (P = 0,6434)

Power of performed test with alpha = 0,0500: 1,0000

Regression Diagnostics:
Row     Predicted   Residual    Std. Res.   Stud. Res.  Stud. Del. Res.
1       0,1076      0,0010      0,0246      0,0313      0,0280
2       0,2139      0,0196      0,4708      0,5547      0,5121
3       0,3191      0,0402      0,9658      1,0940      1,1219
4       0,5256      0,0098      0,2365      0,2628      0,2367
5       1,0203      0,0117      0,2808      0,3416      0,3091
6       1,9213      -0,0313     -0,7511     -0,9656     -0,9575
7       2,3293      0,0717      1,7224      2,1414      6,6532
8       3,3895      0,0015      0,0357      0,0958      0,0858
9       4,4534      0,0176      0,4218      6,4665      >1e20

Influence Diagnostics:
Row     Cook's Dist. Leverage   DFFITS
1       0,0002      0,3806      0,0219
2       0,0299      0,2797      0,3191
3       0,0847      0,2206      0,5968
4       0,0041      0,1904      0,1148
5       0,0140      0,3241      0,2141
6       0,1521      0,3949      -0,7735
7       0,6255      0,3530      4,9147
8       0,0142      0,8610      0,2135
9       2446,5997   0,9957      >1e20

95% Confidence
Row     Predicted   Regression 5%  Regression 95% Population 5%  Population 95%
1       0,1076      0,0415      0,1736      -0,0182     0,2333
2       0,2139      0,1573      0,2705      0,0928      0,3350
3       0,3191      0,2688      0,3693      0,2009      0,4373
4       0,5256      0,4789      0,5723      0,4088      0,6423
5       1,0203      0,9594      1,0812      0,8972      1,1435
6       1,9213      1,8540      1,9885      1,7949      2,0477
7       2,3293      2,2657      2,3929      2,2048      2,4538
8       3,3895      3,2902      3,4888      3,2435      3,5355
9       4,4534      4,3467      4,5602      4,3023      4,6046
```

B.7 Input and Output Files Generated by Maple V Using Equation 18 For Non-Ionic Polyacrylamide (Mw = 5-6*10^6)

Input File:

```
> restart;
> Y[1]:=0.004540;
> Y[2]:=0.01286;
> Y[3]:=0.02109;
> Y[4]:=0.04167;
> Y[5]:=0.0814;
> Y[6]:=0.1582;
> Y[7]:=0.2309;
> Y[8]:=0.3034;
> with(stats):
> Xvalues:=[.0005015,.001505,.002508,.005015,.01003,.02006,.03009,0.0402];
> Yvalues:=[0.004540,0.01286,0.02109,0.04167,0.08140,0.1582,0.2309,0.304];
> eq_fit:=fit[leastsquare[[x,y],y=a*x+b*x^1.29,{a,b}]]([Xvalues,Yvalues]);
> x:=.0005015;
> eta[1]:=solve(eq_fit);
> x:=.001505;
> eta[2]:=solve(eq_fit);
> x:=.002508;
> eta[3]:=solve(eq_fit);
> x:=.005015;
> eta[4]:=solve(eq_fit);
> x:=.01003;
> eta[5]:=solve(eq_fit);
> x:=.02006;
> eta[6]:=solve(eq_fit);
> x:=.03009;
> eta[7]:=solve(eq_fit);
> x:=.040120;
> eta[8]:=solve(eq_fit);
> variance:=(1/7)*(sum(((eta[i]-Y[i])^2),i=1..8));
```

Output File:

```
                    Y[1] := .004540

                    Y[2] := .01286

                    Y[3] := .02109

                    Y[4] := .04167

                    Y[5] := .0814
```

$Y[6] := .1582$

$Y[7] := .2309$

$Y[8] := .3034$

Xvalues := [.0005015, .001505, .002508, .005015, .01003, .02006,.03009, .04012]

Yvalues :=[.004540, .01286, .02109, .04167, .08140, .1582, .2309, .3034]

$eq\_fit := y = 9.239189505\,x - 4.273814755\,x^{1.29}$

$x := .0005015$

$\eta[1] := .004396771552$

$x := .001505$

$\eta[2] := .01292810795$

$x := .002508$

$\eta[3] := .02128412106$

$x := .005015$

$\eta[4] := .04171960446$

$x := .01003$

$\eta[5] := .08138426993$

$x := .02006$

$\eta[6] := .1577436375$

$x := .03009$

$\eta[7] := .2314507130$

$x := .040120$

$\eta[8] := .3031999788$

$variance := .8815773217\;10^{-7}$

B.8 Input and Output Files Generated by Maple V Using Equation 18 For Non-Ionic Polyacrylamide (Mw = 18*10^6)

Input File:

```
> restart;
> Y[1]:=0.1195;
> Y[2]:=0.2606;
> Y[3]:=0.6064;
> Y[4]:=1.066;
> Y[5]:=2.049;
> Y[6]:=3.513;
> Y[7]:=4.449;
> Y[8]:=5.004;
> with(stats):
> Xvalues:=[.0005015,.001003,.002508,.005015,.01003,.02006,.03009,.04012];
> Yvalues:=[0.1195,0.2606,0.6064,1.066,2.049,3.513,4.449,5.004];
> eq_fit:=fit[leastsquare[[x,y],y=a*x+b*x^1.76,{a,b}]]([Xvalues,Yvalues]);
> x:=.0005015;
> eta[1]:=solve(eq_fit);
> x:=.001003;
> eta[2]:=solve(eq_fit);
> x:=.002508;
> eta[3]:=solve(eq_fit);
> x:=.005015;
> eta[4]:=solve(eq_fit);
> x:=.01003;
> eta[5]:=solve(eq_fit);
> x:=.02006;
> eta[6]:=solve(eq_fit);
> x:=.03009;
> eta[7]:=solve(eq_fit);
> x:=.04012;
> eta[8]:=solve(eq_fit);
> variance:=(1/7)*(sum(((eta[i]-Y[i])^2),i=1..8));
```

Output File:

```
                    Y[1] := .1195

                    Y[2] := .2606

                    Y[3] := .6064

                    Y[4] := 1.066

                    Y[5] := 2.049
```

Y[6] := 3.513

Y[7] := 4.449

Y[8] := 5.004

Xvalues := [.0005015, .001003, .002508, .005015, .01003, .02006,.03009, .04012]

Yvalues := [.1195, .2606, .6064, 1.066, 2.049, 3.513, 4.449, 5.004]

eq_fit := $y = 245.8817141\ x - 1397.199953\ x^{1.76}$

x := .0005015

η[1] := .1211332962

x := .001003

η[2] := .2392479893

x := .002508

η[3] := .5796821321

x := .005015

η[4] := 1.107859001

x := .01003

η[5] := 2.042015529

x := .02006

η[6] := 3.495704039

x := .03009

η[7] := 4.465786415

x := .04012

η[8] := 4.998755495

variance := .0005116883019

B.9 Input and Output Files Generated by Maple V Using Equation 18 For Anionic Polyacrylamide (Mw > 10*10^6)

Input File:

```
> restart;
> Y[1]:=.1086;
> Y[2]:=.2335;
> Y[3]:=.3593;
> Y[4]:=.5354;
> Y[5]:=1.032;
> Y[6]:=1.890;
> Y[7]:=2.401;
> Y[8]:=3.391;
> Y[9]:=4.471;
> with(stats):
>Xvalues:=[.0005015,.001003,.001505,.002508,.005015,.01003,.01254,.020,.03009];
> Yvalues:=[.1086,.2335,.3593,.5354,1.032,1.890,2.401,3.391,4.471];
> eq_fit:=fit[leastsquare[[x,y],y=a*x+b*x^1.76,{a,b}]]([Xvalues,Yvalues]);
> x:=.0005015;
> eta[1]:=solve(eq_fit);
> x:=.001003;
> eta[2]:=solve(eq_fit);
> x=.001505;
> eta[3]:=solve(eq_fit);
> x:=.002508;
> eta[4]:=solve(eq_fit);
> x:=.005015;
> eta[5]:=solve(eq_fit);
> x:=.01003;
> eta[6]:=solve(eq_fit);
> x:=.01254;
> eta[7]:=solve(eq_fit);
> x:=.02006;
> eta[8]:=solve(eq_fit);
> x:=.03009;
> eta[9]:=solve(eq_fit);
> variance:=(1/9)*(sum(((eta[i]-Y[i])^2),i=1..9));
```

Output File:

```
                    Y[1] := .1086

                    Y[2] := .2335

                    Y[3] := .3593

                    Y[4] := .5354
```

Y[5] := 1.032

Y[6] := 1.890

Y[7] := 2.401

Y[8] := 3.391

Y[9] := 4.471

Xvalues := [.0005015, .001003, .001505, .002508, .005015, .01003,.01254, .02006, .03009]

Yvalues :=[.1086, .2335, .3593, .5354, 1.032, 1.890, 2.401, 3.391, 4.471]

eq_fit := $y = 227.7915208\,x - 1135.786970\,x^{1.76}$

x := .0005015

η[1] := .1124682607

x := .001003

η[2] := .2224826923

x := .001505

η[3] := .3305868108

x := .002508

η[4] := .5412325251

x := .005015

η[5] := 1.040568393

x := .01003

η[6] := 1.939933657

x := .01254

η[7] := 2.345647262

$x := .02006$

$\eta[8] := 3.401614961$

$x := .03009$

$\eta[9] := 4.470171758$

$\text{variance} := .0007487651708$

B.10 Input and Output Files Generated by Excel Using equation 19 for the Three Polyacrylamide Samples

Input File :

The experimental data points were fitted to a third order polynomial equation using the « Insert Trendline » option.

Output File :

Non-Ionic Polyacrylamide (Mw = 5-6 × 10^6)

$y = 8.490\ x - 38.43\ x^2 + 380.7\ x^3$

Variance = 4.15×10^{-8}

Non-Ionic Polyacrylamide (Mw = 18 × 10^6)

$y = 236.9\ x - 3412.4\ x^2 + 15359\ x^3$

Variance = 4.91×10^{-4}

Anionic Polyacrylamide (Mw > 10 × 10^6)

$y = 221.2\ x - 2906.5\ x^2 + 16369\ x^3$

Variance = 8.62×10^{-4}

Appendix C

Details of the Calculation Procedures.

C.1 Sample Calculation of the Concentration

C.1.a. Preparation of the Stock Polymer Solution:

T = 22.5 °C

Density of Distilled Water = 0.9977 g/mL. If a 1000 mL beaker is used to prepare the stock polymer solution, then,

$$m_{water} = 1000mL \times 0.9977g / mL = 997.7g$$

The stock polymer solution has a concentration of 0.5 % $\frac{w}{w}$, hence,

$$0.005 = \frac{m_{polymer}}{m_{water} + m_{polymer}} = \frac{m_{polymer}}{997.7g + m_{polymer}}$$

$$m_{polymer} = 5.014g$$

C.1.b. Dilution to of the Stock Polymer Solution:

The sample calculation is based on the non-ionic polyacrylamide sample (Mw = 5-6 × 10^6) having 5 ppm concentration.

$$5ppm = 5 \times 10^{-6} = \frac{m_{polymer}}{m_{stock\ solution} + m_{water}}$$
$$= \frac{m_{stock\ solution} \times 0.005}{m_{stock\ solution} + 997.7}$$

Hence,

$$m_{stock\ solution} = 0.9987g$$

The density of the polymer solution was found to be 0.9970g/mL. So, the volume of stock polymer solution that has to be diluted in a 1L beaker is:

$$v_{stock\ solution} = \frac{0.9987g}{0.9970g\ /\ mL} = 1.002\ mL$$

The concentration in g/dL can be determined as follows,

$$\begin{aligned} 5ppm &= 5 \times 10^{-6}\ \frac{g\ polymer}{g\ water} \\ &= 5 \times 10^{-6}\ \frac{g\ polymer}{0.997\ mL\ water} \\ &= 5.015 \times 10^{-4}\ \frac{g\ polymer}{dL\ water} \end{aligned}$$

C.2 Calculation of the Specific Viscosity

Recalling the relationship defining the specific viscosity, η_{sp},

$$\eta_{sp} = \frac{\eta - \eta_s}{\eta_s} = \frac{t - t_s}{t_s}$$

where η and η_s are respectively the viscosities of the polymer solution and the solvent, t and t_s are respectively the flow times of the polymer solution and the solvent through the viscometer.

As mentioned earlier in this thesis, t and t_s are determined using a Cannon-Fenske routine viscometer for transparent liquids. For the non-ionic polyacrylamide sample (Mw = 5-6 × 10^6) having a 5 ppm concentration, a size 50 viscometer is used.

t = 250.01 s

t_s = 248.88 s

$$\eta_{sp} = \frac{250.01 - 248.88}{248.88} = 0.004540$$

C.3 Calculation of the Specific Viscosity Using Equation 18 and 19

C.3.a. Calculation of η_{sp} Using Equation 18:

Equation 18 fitted to the experimental data points of the non-ionic polyacrylamide sample (Mw = 5-6 × 10^6) is the following:

$$\eta_{sp} = 9.2392\ c - 4.2738\ c^{1.29}$$

For the 5 ppm concentration,

$$\eta_{sp} = (9.2392 \times 0.0005015) - (4.2738 \times 0.0005015^{1.29}) = 0.004397$$

C.3.b. Calculation of η_{sp} Using Equation 19:

Equation 19 fitted to the experimental data points of the non-ionic polyacrylamide sample (Mw = 5-6 × 10^6) is the following:

$$\eta_{sp} = 8.4904\ c - 38.429\ c^2 + 380.72\ c^3$$

For the 5 ppm concentration,

$$\eta_{sp} = (8.4904 \times 0.0005015) - (38.429 \times 0.0005015^2) + (380.72 \times 0.0005015^3)$$
$$= 0.004248$$

C.4 Calculation of the Error Magnification

C.4.a Calculation of the Error in η_{sp}:

The calculation is based on the non-ionic polyacrylamide sample (Mw = 5-6 × 10^6) having a 5 ppm concentration.

Recalling equation 20,

$$\text{Experimental Error} = \eta_{sp}(\text{true cue}) - \eta_{sp}(\text{experimental})$$

$$= 0.004248 - 0.004540$$

$$= -\,0.000292$$

C.4.b Calculation of the Error in the Quotient η_{sp}/c:

The error magnification factor is c^{-1}, then,

$$\text{Error in quotient } \eta_{sp}/c = \text{Experimental Error} \times (1/c)$$

$$= -\,0.000292 \times (1/0.0005015)$$

$$= -\,0.5823$$

C.4.c Calculation of the Error in η_{sp}/c:

And, in Huggins plot (η_{sp}/c versus c),

$$\text{Error in } \eta_{sp}/c = \eta_{sp}/c\ (\text{true curve}) - \eta_{sp}/c\ (\text{experimental})$$

$$= 8.471 - 9.053$$

$$= -\,0.5820$$

C.5 Calculation of the Average Molecular Weight

The sample calculation is based on the non-ionic polyacrylamide sample having a Mw= 5-6 × 10^6.

The intrinsic viscosity of this sample determined using the alternative method is 849 (cm^3/g).

Using equation 24,

$$[\eta] = 1 \times 10^{-2}\,\overline{M_w}$$

where [η] is in (cm^3/g).

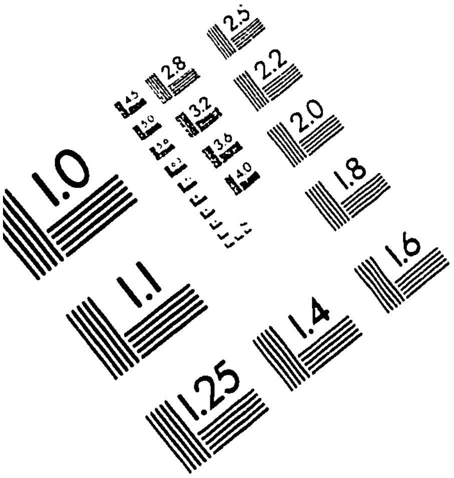
Hence,

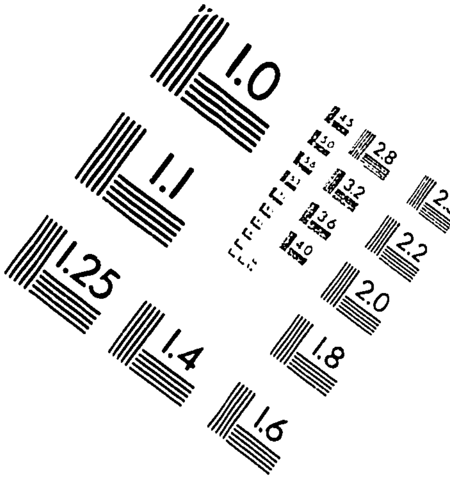
$$\overline{M_w} = \left(\frac{[\eta]}{1 \times 10^{-2}}\right)^{(1/0.755)}$$

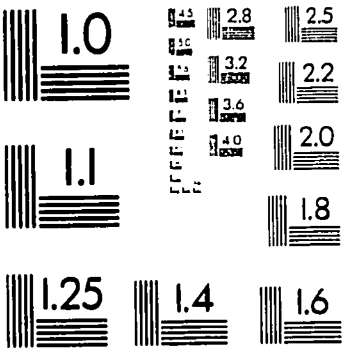
$$= \left(\frac{849}{1 \times 10^{-2}}\right)^{(1/0.755)}$$

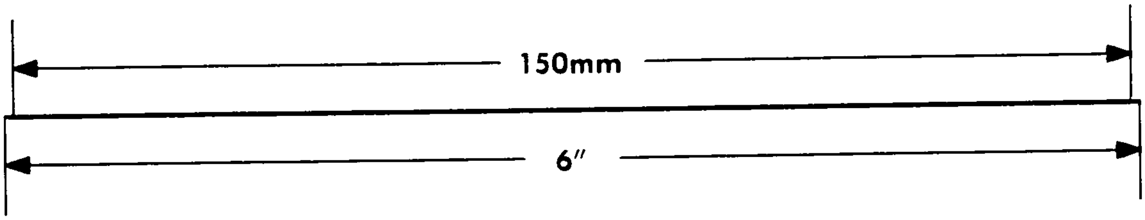
$$= 3.38 \times 10^6$$

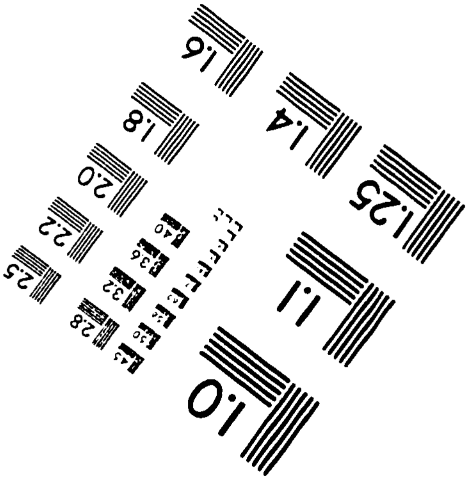
IMAGE EVALUATION TEST TARGET (QA-3)

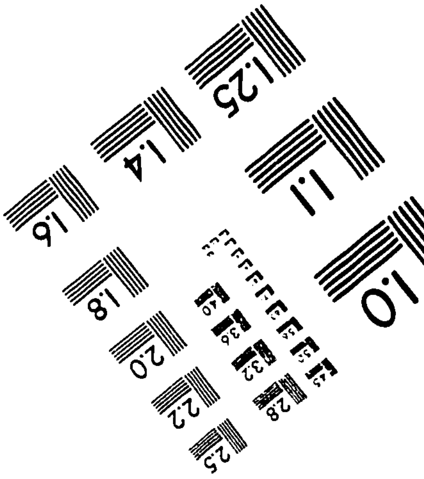












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