

**CHARACTERIZATION OF INDUSTRIAL FLOCCULANTS THROUGH
INTRINSIC VISCOSITY MEASUREMENTS**

by

ESAU ARINAITWE

B.Sc., Makerere University, 2000

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE

in

THE FACULTY OF GRADUATE STUDIES
(Mining Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA
(Vancouver)

August 2008

© Esau Arinaitwe, 2008

ABSTRACT

The effect of pH, temperature, and ionic strength on the molecular conformation of five industrial polyacrylamide-based flocculants was investigated by determining intrinsic viscosities from viscometric measurements performed on dilute flocculant solutions. The Fedors equation was found to be most suitable for all flocculants for evaluating the raw viscosity data and determining the intrinsic viscosity. The results indicated that the flocculants are fully extended in distilled water at natural pH and at 25°C as evidenced by the high intrinsic viscosities. The data pointed to the strong dependence of the intrinsic viscosity on the presence of salts as a result of the shielding of the negatively charged carboxylate groups by the counterions. At a constant ionic strength of 0.01 M NaCl, the flocculants assumed a coiled conformation, and further coiling was observed in the presence of small quantities of CaCl₂ (0.001 mol/L). There was a decrease in intrinsic viscosities at high pH (~8.5 and 10.5) that was merely attributed to an increase in ionic strength with the increase in concentration of Na⁺ at high pH. Intrinsic viscosity measurements at higher temperatures (35°C and 50°C) showed a very small effect of temperature on the conformation of the flocculants. Higher temperature, however, seemed to accelerate the aging of the flocculant solutions.

The degrees of anionicity of the flocculants were found to be in the range 1.5% – 50%, as determined through chemical analysis and Fourier transform infrared spectroscopy (FTIR). It was established that the determination of the total organic carbon content and sodium assays is an accurate way of obtaining the degrees of anionicity of industrial flocculants. The infrared spectroscopy results were comparable to the chemical analysis results only for the most anionic flocculants.

The solution stability of the nonionic flocculant (N100) and the most anionic flocculant (A150) in distilled water and in 0.01M NaCl was also investigated over a period of three days. The reduced viscosities of the anionic flocculant in distilled water steadily decreased. The decrease was more dramatic at high temperature (50°C) than at room temperature, but no viscosity loss was observed in the presence of sodium chloride (0.01M). The viscosity of the nonionic flocculant was stable in both distilled water and in 0.01M NaCl over the time and temperatures investigated. The viscosity loss with time (aging) in the case of the anionic flocculant can be correlated with the hydrolysis of the weakly acidic carboxylate (COO⁻) groups to release OH⁻ ions and simultaneous association into uncharged carboxylic (COOH) groups that promote coiling of polyacrylamide. This effect is therefore very similar to the earlier-mentioned effect of sodium chloride.

Table of Contents

Abstract	ii
List of Tables.....	v
List of Figures	vii
Acknowledgements	ix
1.0 Introduction	1
1.1 Importance of this study	1
1.2 Specific Research Objectives	2
2.0 Literature Review	4
2.1 Polymeric Flocculants: Polyacrylamide.....	4
2.1.1 Properties of Flocculants in Solution	7
2.1.2 Mode of Action of Flocculants	8
2.2 Dilute Solution Viscometry of Flocculants	10
2.2.1 Terminology used in Dilute Solution Viscometry	11
2.2.2 The Intrinsic Viscosity, $[\eta]$	12
2.2.3 Determination of $[\eta]$ from viscosity measurements: Nonionic PAM.....	14
2.2.4 Determination of $[\eta]$ from viscosity measurements: Polyelectrolytes.....	20
2.2.5 Evaluation of Flocculant Molecular Weight from Intrinsic Viscosity.....	23
2.2.6 Aging of Solutions in Viscometry Measurements	24
3.0 Experimental Program	27
3.1 Materials	27
3.1.1 Equipment.....	27
3.1.2 Flocculant samples	27
3.1.3 Reagents.....	29
3.2 Methods.....	29
3.2.1 Viscosity measurements.....	29
3.2.2 Chemical Analysis.....	32
3.2.3 Infrared Spectroscopy.....	33
3.2.4 Aging studies.....	33

4.0	Results and Discussion	35
4.1	Degree of anionicity (D.A)	35
4.2	Aging studies	39
4.3	Molecular Weight Determination.....	42
4.4	Intrinsic Viscosity Measurements	45
4.4.1	Intrinsic Viscosities of Flocculants in Distilled Water: Effect of pH and Temperature	53
4.4.2	Effect of Electrolyte Addition	57
5.0	Conclusions and Recommendations.....	62
6.0	References	64
Appendix I: Example of a Typical Measurement of Kinematic Viscosity.....		70
Appendix II: Viscosity Data of flocculants in distilled water		71
Appendix III: Viscosity Data of Flocculants in 0.01M NaCl.....		86
Appendix IV: Viscosity Data of N100 and A130 in 0.01M NaCl and 0.001M CaCl₂		101
Appendix V: Intrinsic Viscosities of Flocculants at different pH and Temperature.....		105
Appendix VI: FTIR Spectra of Flocculants at Natural pH and pH 3.		107
Appendix VII: Standard Deviation between Intrinsic Viscosity Values for the N100 and A110 flocculants		109

List of Tables

Table 4.1:	Total organic carbon and sodium assays of flocculants	35
Table 4.2:	Degree of anionicity (D.A) of flocculants determined from chemical assays and infrared spectroscopy.....	38
Table 4.3:	Changes in pH with aging of flocculant solutions (The distilled water used to prepare the flocculant solutions had a pH of 5.3)	41
Table 4.4:	Intrinsic viscosities, M-H-S parameters and apparent molecular weights (M) of the flocculants in 0.5 M NaCl at 25°C and natural pH.....	44
Table 4.5:	Intrinsic viscosities of the anionic flocculants obtained by different equations at 25°C and 50°C.....	52
Table I-1:	Kinematic viscosity of a solution of A110, concentration 120ppm, prepared in 0.5M NaCl	70
Table II-1:	Viscosity data of N100 in distilled water at natural pH and 25°C, 35°C, 50°C.....	71
Table II-2:	Viscosity data of N100 in distilled water at pH 8.5– 8.6 and 25°C, 35°C, 50°C	72
Table II-3:	Viscosity data of N100 in distilled water at pH 10.5–10.6 and 25°C, 35°C, 50°C	73
Table II-4:	Viscosity data of A100 in distilled water at natural pH and 25°C, 35°C, 50°C.....	74
Table II-5:	Viscosity data of A100 in distilled water at pH 8.5–8.6 and 25°C, 35°C, 50°C	75
Table II-6:	Viscosity data of A100 in distilled water at pH 10.5–10.6 and 25°C, 35°C, 50°C	76
Table II-7:	Viscosity data of A110 in distilled water at natural pH and 25°C, 35°C, 50°C.....	77
Table II-8:	Viscosity data of A110 in distilled water at pH 8.5–8.6 and 25°C, 35°C, 50°C	78
Table II-9:	Viscosity data of A110 in distilled water at pH 10.5–10.6 and 25°C, 35°C, 50°C	79
Table II-10:	Viscosity data of A130 in distilled water at natural pH and 25°C, 35°C, 50°C.....	80
Table II-11:	Viscosity data of A130 in distilled water at pH 8.5–8.6 and 25°C, 35°C, 50°C.....	81
Table II-12:	Viscosity data of A130 in distilled water at pH 10.5–10.6 and 25°C, 35°C, 50°C	82
Table II-13:	Viscosity data of A150 in distilled water at natural pH and 25°C, 35°C, 50°C.....	83
Table II-14:	Viscosity data of A150 in distilled water at pH 8.5–8.6 and 25°C, 35°C, 50°C	84
Table II-15:	Viscosity data of A150 in distilled water at pH 10.5–10.6 and 25°C, 35°C, 50°C	85
Table III-1:	Viscosity data of N100 in 0.01 M NaCl at natural pH and 25°C, 35°C, 50°C	86
Table III-2:	Viscosity data of N100 in 0.01 M NaCl at pH 8.5–8.6 and 25°C, 35°C, 50°C.....	87
Table III-3:	Viscosity data of N100 in 0.01 M NaCl at pH 10.5–10.6 and 25°C, 35°C, 50°C.....	88
Table III-4:	Viscosity data of A100 in 0.01 M NaCl at natural pH and 25°C, 35°C, 50°C	89
Table III-5:	Viscosity data of A100 in 0.01 M at pH 8.5–8.6 and 25°C, 35°C, 50°C.....	90

Table III-6: Viscosity data of A100 in distilled water at pH 10.5–10.6 and 25°C, 35°C, 50°C	91
Table III-7: Viscosity data of A110 in 0.01 M NaCl at natural pH and 25°C, 35°C, 50°C	92
Table III-8: Viscosity data of A110 in 0.01 M NaCl at pH 8.5–8.6 and 25°C, 35°C, 50°C.....	93
Table III-9: Viscosity data of A110 in 0.01 M NaCl at pH 10.5–10.6 and 25°C, 35°C, 50°C.....	94
Table III-10: Viscosity data of A130 in 0.01 M NaCl at natural pH and 25°C, 35°C, 50°C	95
Table III-11: Viscosity data of A130 in 0.01 M NaCl at pH 8.5–8.6 and 25°C, 35°C, 50°C.....	96
Table III-12: Viscosity data of A130 in 0.01 M NaCl at pH 10.5–10.6 and 25°C, 35°C, 50°C.....	97
Table III-13: Viscosity data of A150 in 0.01 M NaCl at natural pH and 25°C, 35°C, 50°C	98
Table III-14: Viscosity data of A150 in 0.01 M NaCl at pH 8.5–8.6 and 25°C, 35°C, 50°C.....	99
Table III-15: Viscosity data of A150 in 0.01 M NaCl at pH 10.5–10.6 and 25°C, 35°C, 50°C.....	100
Table IV-1: Viscosity data of N100 in 0.01 M NaCl and 0.001 M CaCl ₂ at natural pH at 25°C.....	101
Table IV-2: Viscosity data of N100 in 0.01 M NaCl and 0.001 M CaCl ₂ at pH 10.5 at 25°C.....	102
Table IV-3: Viscosity data of A130 in 0.01 M NaCl and 0.001 M CaCl ₂ at natural pH at 25°C.....	103
Table IV-4: Viscosity data of A130 in 0.01 M NaCl and 0.001 M CaCl ₂ at pH 10.5 at 25°C.....	104
Table V-1: Intrinsic viscosity data of flocculants in distilled water at different pH and temperature.	105
Table V-2: Intrinsic viscosity data of flocculants in 0.01 M NaCl at different pH and temperature.	106
Table VII-1: Intrinsic viscosity values and standard deviations for the N100 and A110 flocculants.....	109

List of Figures

Figure 2.1: A chemical structure of polyacrylamide (left) and acrylamide/acrylic acid copolymer (right).....	5
Figure 2.2: A typical graph showing the concentration dependence of reduced viscosity for polyelectrolytes	20
Figure 3.1: Schematic of the Cannon-Fenske capillary viscometer used in the viscosity measurements.....	30
Figure 4.1: FTIR spectrum of A150 prepared at natural pH.	37
Figure 4.2: FTIR spectrum of A150 prepared at pH 3.....	37
Figure 4.3: FTIR spectra of the nonionic flocculant N100 prepared at natural pH and pH 3.....	38
Figure 4.4: Reduced viscosities of N100 and A150 as a function of time in distilled water and 0.01 M NaCl.	40
Figure 4.5: Dependence of reduced viscosity of the flocculants on concentration in 0.5 M NaCl at 25°C and natural pH.....	43
Figure 4.6: Dependence of reduced viscosity of the A150 on concentration in 0.5 M NaCl at 25°C and natural pH.	43
Figure 4.7: Reduced viscosity vs. polymer concentration for N100 in distilled water (natural pH 4.9–6) and 0.01 M NaCl (natural pH 5.3-5.7) at different temperatures.....	46
Figure 4.8: Reduced viscosity vs. polymer concentration for the anionic flocculants in distilled water at natural pH and 25°C	47
Figure 4.9: Reduced viscosity vs. polymer concentration for the anionic flocculants in 0.01 M NaCl at natural pH and 25°C.....	48
Figure 4.10: Fuoss and Cathers representation of data in Figure 4.8 (Anionic flocculants in distilled water at natural pH and 25°C).	49
Figure 4.11: Fuoss and Cathers representation of data in Figure 4.9 (Anionic flocculants in 0.01 M NaCl at natural pH and 25°C).....	49
Figure 4.12: Fedors representation of data in Figure 4.8 (Anionic flocculants in distilled water at natural pH and 25°C).....	51
Figure 4.13: Fedors representation of data in Figure 4.9 (Anionic flocculants in 0.01 M NaCl at natural pH and 25°C).....	51
Figure 4.14: Effect of pH on the intrinsic viscosities of flocculants in distilled water at 25°C	53
Figure 4.15: Effect of pH on the intrinsic viscosities of flocculants in distilled water at 35°C	53

Figure 4.16: Effect of pH on the intrinsic viscosities of flocculants in distilled water at 50 ⁰ C	54
Figure 4.17: Effect of pH and 0.01 M NaCl on the intrinsic viscosities of flocculants at 25 ⁰ C	57
Figure 4.18: Effect of pH and 0.01 M NaCl on the intrinsic viscosities of flocculants at 35 ⁰ C	57
Figure 4.19: Effect of pH and 0.01 M NaCl on the intrinsic viscosities of flocculants at 50 ⁰ C	58
Figure 4.20: Effect of 0.001 M CaCl ₂ on the intrinsic viscosities of flocculants in 0.01M NaCl at different temperatures.	60
Figure VI-1: FTIR spectra of A100 prepared at natural pH and pH 3.....	107
Figure VI-2: FTIR spectra of A110 prepared at natural pH and pH 3.....	107
Figure VI-3: FTIR spectra of A130 prepared at natural pH.....	108
Figure VI-4: FTIR spectra of A130 prepared at pH 3.	108

ACKNOWLEDGEMENTS

I wish to wholeheartedly express my thanks to Dr. Marek Pawlik for his expert supervision of this study. His enthusiasm and knack for imparting critical research skills to me are sincerely appreciated. Dr. Pawlik's ability to inspire and motivate me to complete this study and his open-door policy made working under his supervision a pleasurable experience. My gratitude also goes to the faculty members and staff at the Norman B. Keevil Institute of Mining Engineering who helped me settle down in Vancouver and have continuously supported me.

I am grateful to Sally Finora for competently providing laboratory assistance and support during the course of this study. Her ability to help out in every wanting situation is amazing.

This study was possible through financial assistance in form of a collaborative research and development grant by the Natural Sciences and Engineering Research Council (NSERC) and Canada Natural Resources Limited (CNRL). I would also like to sincerely thank the Department of Geological Survey and Mines, Uganda under whose auspices I was able to come to Canada for graduate studies. Thanks to all individuals who supported me in one way or another.

My deepest appreciation goes to my family in Kabale, Uganda who offered me tremendous moral support during the course of this research. Most important of all, the love, encouragement and inspiration from my wife, Annette and son, Shawn were sources of strength that I needed to complete this research.

Finally, I am grateful for God's daily provision of joys and challenges. I am thankful to Him for the short time that He allowed me to share with my departed daughter, Audrey Atuhaire who passed on when I had just commenced studies towards the Master's program.

1.0 Introduction

1.1 Importance of this study

Increased generation of fine particles in the tailings of oil sands and mineral processing operations has become a major technological challenge in the recent past. For many processing plants, separation of these fine particles from the tailings pulp is an economic and environmental necessity that ensures recovery and recycling of process water, and eventual disposal of the solid fraction. This has made solid-liquid separation one of the most important unit operations in the industry.

Optimal recovery of fine particles is often a challenge especially more so if the solid particles are only a few microns in diameter. The small particle sizes mean that reliance on the natural settling rate of the particles does not produce a satisfactory supernatant for recycling. An example of this scenario is the oil sands processing industry where particles in the size range from 1 mm to 1 micron appear in the tailings fraction after bitumen extraction. This size range contains a considerable amount of particles below 44 microns which is the upper limit of fines as defined by the oil sands industry (Long et al., 2006). Most of the fine particles are predominantly water-insoluble clay minerals, such as illite and kaolinite, which are known to be problematic materials in clarification operations (Long et al., 2006). The result of having non-settling particles in solid-liquid dispersions leads to accumulation of a rather concentrated and stable suspension referred to as mature fine tailings (MFT). This suspension is estimated to contain about 30% by weight of fine solids. It was estimated that the volume of this aged tailings suspension will reach over one billion cubic meters by the year 2020 (Chalaturnyk et al., 2002).

Flocculation is the most popular method that has been practiced for well over 50 years, and has been applied in the oil sands industry only over the last dozen or so years to reduce the tailings volume by treatment of the fine clays with high molecular weight flocculants (Cymerman et al., 1999). Flocculation is induced by either natural or synthetic high molecular weight polymeric flocculants. The majority of commercial flocculants are anionic in character but some of them are non-ionic and some are cationic (Sastry et al., 1999; Wills, 1997). These flocculants are predominantly based on polyacrylamides. The performance of flocculants could be a result of changes in the pulp solids content or changes in the flocculant's physico-chemical behaviour.

Previous studies devoted much attention to the flocculation process with a focus on the surface properties of the aggregated particles and the mixing conditions, largely neglecting the physical and chemical characteristics/behaviour of the flocculants themselves. Also, there are no clear guidelines as to which flocculant should be used for a given solid-liquid separation process and for a given set of physicochemical conditions (presence of salts, pH, temperature), further strengthening the need to have a detailed study that could enhance our understanding of the behavior and performance of flocculants in a solution environment of interest.

Viscometry is a useful and convenient tool that is widely used to deduce the behavior of polymers in dilute solutions. Through capillary viscometric measurements, interesting data about, for example, the quality of the solvent and the conformation of the flocculants in solution, and hence the ease of their adsorption on particles, can be obtained. Also, an important parameter – the intrinsic viscosity can be determined. The intrinsic viscosity is believed to be a measure of the size, shape and structural conformation of the flocculants in solution and hence the flocculant's flocculating power (Lovell, 1989). It can also be used to study polymer-solvent interactions as well as estimate the viscosity average molecular weights of polymers. In spite of its importance, the influence of solution chemistry on the viscosity of flocculants has not been studied systematically. An example is the important role that temperature and pH play in the extraction of bitumen and subsequent treatment of tailings, yet there is no literature data on the influence of these parameters, especially of temperature, on the viscometric behaviour of aqueous solutions of flocculants.

For this reason, the main goal of this study is to carry out systematic viscometric studies on the behaviour of commercial flocculants in different solution environments (pH, ionic strength, temperature, polymer concentration) and establish the dependence of the flocculant intrinsic viscosities on the changing solution environment. Determining such a dependence should be very useful in predicting the performance of a particular flocculant in a given solid-liquid suspension.

1.2 Specific Research Objectives

As already pointed out, while there is sufficient information on flocculation in terms of the surface properties of the dispersed particles, research on the solution chemistry of the flocculant itself is very limited. Most of the available studies have been carried out in rather concentrated solutions, a situation that is far from real industrial conditions where very low dosages of

flocculants are used thus creating a very dilute system in terms of flocculant concentration in the aqueous phase. Therefore, the primary objective of this study is to perform systematic intrinsic viscosity measurements on various commercial flocculants in dilute solution with the aim of understanding the behaviour of the flocculants under various physico-chemical conditions of pH, flocculant concentration, ionic strength and temperature. Several other characterization tests will be performed with the following objectives:

- To determine the degree of anionicity of the flocculants,
- To determine the approximate molecular weights of the polymers,
- To identify a suitable method of raw data treatment for determining the intrinsic viscosities of the flocculants in the dilute solution range where the polymers exhibit difficult-to-evaluate polyelectrolyte behaviour,
- To investigate the effect of time on the viscosities of flocculant solutions through aging experiments.

2.0 Literature Review

It is well established that flocculation is an important unit operation in the mineral and oil sands industries. It is also widely applied in a number of areas including the pulp and paper, pharmaceutical, cosmetics and paints industries. During flocculation, small particles in a suspension are brought together to form larger aggregates, often highly porous in nature (Krishnamoorthi & Singh, 2006). These aggregates settle more rapidly than individual non-flocculated particles. To facilitate such particle size enlargement (aggregation), chemical additives known as flocculants are utilized. The majority of commercial flocculants are polymeric in nature and can be classified based on properties such as molecular weight, functional groups, charge, chemical structure or origin (Krisnan & Attia, 1988). In the following sections, a detailed review of principles and methods used to characterize polymeric flocculants as well as their behavior in solution is presented.

2.1 Polymeric Flocculants: Polyacrylamide

Commercial flocculants are available as naturally-occurring polymers or synthetic polyelectrolytes (Lewellyn & Avotins, 1988). Naturally occurring polymers include starch, guar gum, high-molecular weight carboxymethyl cellulose (CMC), and gelatin. Although these polymers are important flocculants and have been used widely for many decades, the introduction of more efficient synthetic, high-molecular weight, water-soluble polymers in the 1950's led to a reduction in the use of natural polymers in the water treatment and mining industries (Gregory, 1987; Lewellyn & Avotins; 1988).

There is a wide variety of commercial flocculants available on the market. It is therefore plausible to imagine that different industrial applications utilize specific formulations of flocculants. The minerals and oil sands industries commonly use high molecular weight non-ionic and anionic flocculants, while cationic flocculants of relatively low molecular weight are used as coagulants. When used at high concentrations, high molecular weight flocculants can act as dispersants through steric stabilization. It must also be said that flocculation of pre-coagulated systems can be more effective than straight flocculation and so it is sometimes prudent to use both a coagulant and a flocculant on one suspension. The most commonly used flocculants are based on polyacrylamides (PAM). PAM is a non-ionic polymer with a molecular structure comprising of repeating acrylamide units as shown in Figure 2.1, but because it is obtained by synthesis

(using free radical polymerization) of acrylamide monomers under aqueous conditions, it is always inadvertently hydrolyzed. It is not uncommon to find a nominally non-ionic PAM to actually contain up to 30% carboxylic units making the polymer strongly-anionic. This has practical implications since this type of information is very vaguely provided by flocculant manufacturers. Such anionic units can aid in fully stretching the PAM chain through electrostatic repulsion between the anionic groups which can cause unexpected action in a suspension in which the flocculant is placed.

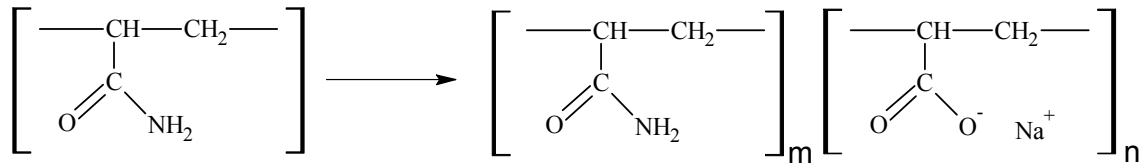


Figure 2. 1: A chemical structure of polyacrylamide (left) and acrylamide/acrylic acid copolymer (right)

The cationic forms of PAM are usually co-polymers of acrylamide and monomers such as N-N-dimethylaminoethylmethacrylate. Anionic forms of PAM are often co-polymers of acrylamide and acrylic acid or partially hydrolyzed PAM (sodium acrylate) (Fig. 2.1). The negatively charged acrylic units are the active functional groups on the polymer chain responsible for fully stretching the chain in solution thereby facilitating the so-called ‘bridging’ action of the flocculant. The number of acrylic acid, or hydrolyzed acrylamide repeating units, defines the degree of anionicity (or the degree of substitution) of the flocculant. The degree of anionicity, *D.A* (sometimes also called the charge density of the flocculant) can therefore be defined by the following equation:

$$D.A = 100 \times \frac{n}{m+n} \quad (2.1)$$

Where: *D.A* = degree of anionicity

n = number of acrylic acid or hydrolyzed acrylamide repeating units

m = number of acrylamide repeating units

There are a number of experimental methods for determination of the degree of anionicity of flocculants. One of them, a relatively fast method, was developed by Rogers and Poling (1978) in which infrared spectroscopy was employed to determine the degree of anionicity of

commercial flocculants. In the method, a volume of 2.2 ml of a 0.10% flocculant stock solution was frozen on an AgCl infra-red window, and then freeze-dried under vacuum. The resultant flocculant film was matted against the window by a few seconds exposure to steam and dried in air to obtain a flat uniform film of the flocculant. Infrared spectra of this film were obtained using an infrared spectrophotometer. After analyzing the spectra, Rogers and Poling found that the ratio of intensity of two adjacent bands within any one spectrum remained constant from one spectrum to the other. They then measured band intensities of pure polyacrylamides samples of known anionic characters and used them to plot a calibration graph of the correlation between band-intensity-ratios and the degree of anionic character. The degree of anionicity of an unknown flocculant could thus be obtained by comparing its infrared spectrum with the data on the correlation chart.

Polyacrylamides are often classified (Dixon, 1986) according to the weight-average molecular weight (MW) as follows: ultra high weight-average molecular weight (above 5×10^6 g/mol), high weight-average molecular weight ($10^6 - 5 \times 10^6$ g/mol), medium molecular weight ($10^5 - 10^6$ g/mol) and low weight-average molecular weight ($10^4 - 10^5$ g/mol). Hogg (1999) also generally classified polymers according to their molecular weight (MW): flocculants with MW ranging from several to ~ 20 million, coagulants with MW between 50,000 and 1,000,000, and dispersants with MW lower than 50,000. Industrial polyacrylamides are typically of high molecular weight usually in the range 1×10^6 to 25×10^6 g/mol. The molecular weight distribution of polymers is very important since the nature of the distribution has an influence on the physicochemical and mechanical properties of the polymer (Onyon, 1959). The values reported by suppliers are only averages. The actual distribution of molecular weights can range from very broad to relatively narrow or even bimodal (Lewellyn & Avotins, 1988). In addition, the distribution of the acrylic acid or hydrolyzed acrylamide units on the flocculant chain can be random or in blocks depending on the synthesis method. For these reasons, it is possible to have two flocculants with the same anionicity and molecular weight but different flocculating performance. It should also be noted that due to the high molecular weights of synthetic flocculants, even dilute solutions of flocculants are very viscous which makes their handling and preparation an industrial problem. For this reason, the majority of the flocculants are sold as dry products or water-in-oil emulsions (Heitner, 2004). Solution preparation from dry flocculant products requires proper mixing with water to ensure complete dissolution. Incomplete dissolution creates lumps or the so-called 'fish eyes' that present downstream problems leading to

ineffective flocculation. As a general rule, to ensure maximum effectiveness, solutions of dry flocculant products should be made up as dilute as possible, because the rate of dissolution decreases as the viscosity of the solution increases. Also, distilled water should be used for solution preparation of anionic flocculants in laboratory experiments as these flocculants may degrade rapidly in the presence of ferrous ions sometimes present in tap water (Heitner, 1989). The rate of agitation is another key variable during solution preparation since PAM molecules are both flexible and long with a relatively small diameter thereby making them susceptible to shear degradation and mechanical breakage.

2.1.1 Properties of Flocculants in Solution

The degree of anionicity and molecular weight of a flocculant are key polymeric characteristics in the flocculation process. Polymeric conformation in solution is of paramount importance as it defines the action of PAM in aqueous solution. PAM's molecular conformation in solution largely depends on ionic strength, temperature, and pH, presence of simple and hydrolyzable metal ions, solid concentration and dilution (Sastry et al., 1999.) Therefore, interaction of PAM with solvent molecules results in modification of the size and shape of the molecules ranging from flexible to rigid molecules, which in turn determines the efficiency of the flocculation process.

The presence of charged functional groups on polymer chains is responsible for PAM's behavior in solution. There are two possible interactions that can take place: repulsive interactions between similarly charged groups on the polymer chain, and attractive interactions between charged groups and counterions in solution. The net extent of these interactions depends on the number of charged units and on the type and concentration of the counterions, and results in a wide range of molecular conformations in solution. The two extreme conformations are typically referred to as "fully-expanded" (straight chain), when repulsive interactions between functional groups govern the behavior of the polymer, and "fully-coiled" (sphere-like), when attractive interactions dominate or when the repulsive forces are minimized.

The charged units on anionic polyacrylamides are carboxylic (COOH) groups and because they are weakly acidic, their ionization in solution is a strong function of pH. Richardson and Connelly (1988) discussed the acid-base behaviour of acrylate in solution at neutral pH (7.0) and low pH (3.0). They calculated that the pKa value of acrylic acid (4.25) allows the relative

amounts of acrylate and acrylic acid to be estimated. At pH 7, the acrylate:acrylic acid ratio was approximately 560:1, at pH 5, the ratio decreased to 5.6:1 and at pH 3, essentially all the acrylate ($-\text{COO}^-$) was in the acid form ($-\text{COOH}$). This trend illustrates the influence that pH can have on the structure of the polymers and eventually on their performance. Non-ionic polyacrylamides are expected to show minimal response to changes in solution chemistry although the presence of residual anionic units during their synthesis may in fact lead to conformational changes as pH changes.

In solution, there is an exchange between the polymer's own counterions (anionic polyacrylamides are supplied as sodium salts) and those in the surrounding external solution (Das, 1999). At high polymer concentrations and without additional salts, only a few of the ionic groups on the polymer chain are dissociated and as a result, the osmotic pressure inside the polymer coil is higher than that of the external solution (Das, 1999; Kulicke and Clasen, 2004). The addition of simple electrolytes like sodium chloride or potassium chloride causes a reduction in the osmotic pressure as a result of the increased concentration of counterions in the external solution compared to those inside the polymer chain. This results in a decrease of polymer swelling and leads to the eventual coiling of the polymer chain.

2.1.2 Mode of Action of Flocculants

Different flocculants produce varying results even when they have the same molecular weight. This is because the different functional groups on the flocculant chains have different modes of action depending on the properties of the suspension. Most suspensions contain negatively charged particles but it is normal to find positively charged ions – both univalent and multivalent in process water such as Ca^{2+} , Mg^{2+} , Al^{3+} and Na^+ ions. Whereas dispersants serve to stabilize solid-liquid suspensions due to steric effects, flocculants of high molecular weights destabilize the suspensions and facilitate flocculation. The flocculants adsorb on particle through specific and non specific types of forces depending on the nature and polarity of the polymer and the particle surfaces (Sastry, 1999).

Flocculants with relatively low charge densities and high molecular weights are known to facilitate flocculation by adsorbing on different particles in a mechanism referred to as 'bridging' (Kitchener, 1972; Gregory, 1987). On the other hand, polyelectrolytes with low molecular weights and of opposite charge to the particles induce flocculation by neutralizing the particle

charge thus reducing the electrical repulsion and destabilizing the particles (Gregory, 1987). It must be noted that these two distinct mechanisms sometimes operate simultaneously in the same suspension. A note should also be made on the importance of having the flocculant in an extended conformation in solution for the bridging mechanism to be most effective.

The adsorption of flocculants on suspended particles is thought to take place simultaneously onto many sites on the particles through conformations referred to as trains, loops and tails. Trains are segments of an adsorbed polymer in direct contact with a particle surface, loops are segments bounded by trains that extend into the suspension, and tails are segments bounded by a single train that extend into the suspension. The actual attachment can take place through many different interactions including (Gregory, 1987): ionic (electrostatic) interaction, hydrophobic bonding, hydrogen bonding, ion binding, and dipole-crystal-field effects. Gregory (1989) explained that for non-ionic PAM, hydrogen bonding enables the amide groups to attach to hydroxyl groups on oxide mineral surfaces. He also argued that certain divalent metal ions such as Ca^{2+} and Mg^{2+} are needed to promote adsorption of anionic polymers on negative surfaces. They may bind strongly to carboxylic groups, such as those of hydrolyzed PAM, or they may serve as links between these groups and negative sites on mineral particles.

Several studies have been undertaken to understand the adsorption and conformation of PAM on common mineral particles found in tailings – kaolinite and illite.

Nasser and James (2007) studied the effect of polymer charge type, density and molecular weight on the flocculation and rheological behaviour for negatively charged kaolinite suspensions. Their results indicated that anionic PAM adsorbs via hydrogen bonding between the silanol and aluminol OH groups at the particle surface and polymer's primary amide group. They further concluded that the repulsive forces between PAM and the kaolinite surface allow the polymer molecules to be extended producing loops and tails, which leads to the formation of large open flocs.

Long et al. (2006) have also recently studied the role of illite-illite interactions in oil sands processing using atomic force microscopy. They concluded that at low pH (2.9) and in the presence of Ca^{2+} and Mg^{2+} ions, strong adhesion forces and weak repulsive long-range forces existed between illite particles and caused coagulation of the illite particles. With the addition of partially hydrolyzed PAM at pH 8.3 in a 10%wt illite suspension, strong “bridging” adhesive forces were detected and flocculation of illite particles followed immediately.

The above results indicate that the conformation of a polymer is dependent upon balancing the affinity of the polymer towards the mineral surface and towards the solvent, and is therefore crucial for successful flocculation. It should also be mentioned that the effect of temperature on the flocculation process is largely unknown since the treatment of tailings is typically performed under ambient conditions. However, tailing slurries obtained from oil sands processing can be expected to be rather warm since the bitumen extraction process (the hot water process) is normally carried out at about 70⁰C.

2.2 Dilute Solution Viscometry of Flocculants

It is well established that dilute solution viscometry is one of the simplest and quickest methods for characterizing polymers in solution (Kulicke and Clasen, 2004; Lovell, 1989). The viscosity of a solution is the measure of its resistance to flow when a shearing force is applied. It reflects the frictional forces of all the molecules in the solution. Measurement of solution viscosity allows determination of the intrinsic ability of the polymer to increase the viscosity of a particular solvent at a given temperature. In the previous sections, it was explained that it is of paramount importance to determine the behaviour of flocculants in solution prior to flocculation. It was also mentioned that most of the flocculants used in the mining and oil sands industries are polyacrylamide-based. The next sections will therefore concentrate on a review of literature about the principles and practices of viscometry as well as characterization studies specific to polyacrylamides.

Characterization and application of polyacrylamide has been a subject of a number of studies (Shyluk and Stow Jr, 1969; Conrad and Klein, 1980; Hecker, 1998; Ghannam and Esmail, 1998; Sastry, 1999; Rattanakawin, 2002; Owen et al., 2002). These studies have been carried out using a number of techniques such as size exclusion chromatography (SEC), field-flow fractionation (FFF), light scattering, infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), osmometry, and viscometry. Rattanakawin (2002), Rattanakawin and Hogg (2007) discussed the viscosity behaviour of polymeric flocculants in terms of hydrodynamic and electroviscous effects. Rafi'ee Fanood and George (1987) studied the limiting viscosity numbers (intrinsic viscosities) and Huggins constants of PAM in water and aqueous sodium chloride, as well as single-point determination of intrinsic viscosity of PAM. Sastry (1999) studied the conformation behaviour of PAM in aqueous solutions. Literature provides a great number of

general references on viscometric measurements that are relevant to PAM characterization (Onyon, 1959; Sakai, 1968ab; Lovell, 1989, Kulicke and Clasen, 2004).

The most commonly used devices for viscosity measurements on dilute polymer solutions are capillary viscometers (Kulicke & Clasen, 2004). There are numerous types of capillary viscometers on the market, the most common being the U-tube and suspended level viscometers. The choice of the viscometer depends on the cost, construction and usability, and volume of solution they can handle. Most suspended-level viscometers are based on the design by Übbelohde. Modifications have been made to allow for control of the atmosphere above the liquid, for measurements at high temperatures, and automation of dilution. Examples of U-tube viscometers are Ostwald and Cannon-Fenske.

The Cannon-Fenske viscometers have been used in this study to measure the kinematic viscosities of polymer solutions at ambient as well as elevated temperatures. These types of viscometers were previously used with satisfactory results by Ma and Pawlik (2007) to measure the kinematic viscosities of dilute guar gum solutions at room temperature as well as high temperatures of 45°C, 70°C, and 90°C. This contrasts with the claim by Rushing and Hester (2003) who apparently carried out an extensive search of commercially available viscometers, including several variable temperature viscometers such as the quasi-closed viscometer, but did not find a suitable instrument that could be used for determining the intrinsic viscosities of high molecular weight polymers in aqueous solutions at elevated temperature.

Viscosity measurements, although seemingly easy to execute, need a high level of precise and tidy sample preparation procedures to produce reliable data. In laboratory viscometric studies, the choice of the concentration range of the polymer solutions should be such that the solutions should give a clear Newtonian response. For this reason, measurements in a capillary viscometer are taken under the assumption that the viscosity of the tested solution remains constant over the entire range of shear rates encountered as they pass down capillaries of different diameters.

2.2.1 Terminology used in Dilute Solution Viscometry

The most common method of determining the viscosity of a polymer solution is by simply measuring the time it takes a volume of the solution to flow between two fixed marks in a capillary tube. This time is compared to the time it takes the same volume of solvent to flow between the two marks on the capillary. The flow time, t , for the solution and the solvent is

proportional to the viscosity, η , and inversely proportional to the density, ρ (Kulicke and Clasen, 2004).

$$t_{solution} = Constant \times \frac{\eta_{solution}}{\rho_{solution}} ; \quad t_{solvent} = Constant \times \frac{\eta_{solvent}}{\rho_{solvent}} \quad (2.2)$$

The relative viscosity is defined as the ratio $\eta_{solution}/\eta_{solvent}$. For dilute solutions, it is true that $\rho_{solution}/\rho_{solvent} \approx 1$. Thus to a good approximation, the relative viscosity is a simple time ratio:

$$\eta_{rel} = t_{solution}/t_{solvent} \quad (2.3)$$

The specific viscosity is defined as the fractional change in viscosity upon addition of the polymer:

$$\eta_{sp} = \eta_{rel} - 1 \quad (2.4)$$

The reduced viscosity, $\eta_{red} = \eta_{sp}/c$, is the ratio of the specific viscosity to polymer concentration, c , and is a measure of the specific capacity of the polymer to increase the relative viscosity. The intrinsic viscosity $[\eta]$ is the limit of the reduced viscosity as the polymer concentration approaches zero. It is also the limit of the inherent viscosity ($\ln \eta_{rel}/c$) as the solution polymer concentration tends to zero:

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} \equiv \lim_{c \rightarrow 0} c^{-1} \ln \eta_{rel} \quad (2.5)$$

For purposes of polymer characterization, $[\eta]$ is of great importance. It is evaluated by extrapolation of experimental data to zero concentration (to eliminate polymer intermolecular interactions). It can also be estimated from single-point determinations. The units of $[\eta]$ are inverse concentration, the most commonly used being dL/g.

2.2.2 The Intrinsic Viscosity, $[\eta]$

The intrinsic viscosity, $[\eta]$ (also called the limiting viscosity number according to the International Union of Pure and Applied Chemistry nomenclature) is a useful measure of the

volume demand of the polymer in a dilute solution. It is the most relevant parameter used to describe the viscosity behaviour of a *dilute* polymer solution.

There are a number of factors that influence the flow pattern of a polymer solution. These factors are more pronounced when there are intermolecular interactions between the polymer molecules. The aim of the intrinsic viscosity measurement is to probe the tested solution in a state where interactions between neighboring polymer molecules are minimized and only the polymer–solvent interactions are significant. This is essentially the definition of a dilute solution as given by Huggins (1942) and Kulicke & Clasen (2004). In such dilute solutions, the thermal motion of the molecules predominates over the hydrodynamic and inter-molecular forces, and the intrinsic viscosity of a polymer characterizes in a sense the behavior of a single polymer chain.

As the polymer concentration is increased, individual molecules are brought into contact with one another to form intermolecular entanglements, and this is accompanied by a dramatic change in flow behaviour and, in particular, by a sudden increase in the concentration dependence of viscosity. Robinson, Ross-Murphy, & Morris (1982) showed that the concentration (c^*) at which the formation of entanglements occurs is inversely proportional to the volume occupied by the isolated polymer particles, and for a range of polysaccharides, they showed that $c^* \approx 4/[\eta]$. The value of critical entanglement concentration, c^* , for PAM was related to the intrinsic viscosity by the relationship $c^* = 2.5/[\eta]$ (Kulicke et al., 1982). Kulicke and Clasen (2004) also recommended that in order to evaluate viscosity data with confidence, the polymer stock solution should be diluted to concentrations that give a range of relative viscosities varying from 1.2 – 2.5.

The concept of the critical transition concentration between dilute (Newtonian) and moderately concentrated (non-Newtonian) polymer solutions was also discussed by Bohdanecky & Kovar (1982) who explained that the product $[\eta]^*c$ can be employed as a simple, approximate overlap criterion. For coiling polymers, they showed that the borderlines of the different concentration regimes (dilute, moderately concentrated, and concentrated systems) begin at $[\eta]^*c \cong 1$ (dilute - moderately concentrated), and ends at $[\eta]^*c \cong 10$ (moderately concentrated - concentrated).

When determining the intrinsic viscosity of a polymer from dilute solution viscometry, it is therefore critical to ensure that the highest concentration of the polymer in solution, c_{\max} , is lower than the critical transition concentration as approximately given by $1/[\eta]$. Unfortunately, several published studies on polyacrylamides suffer from this fundamental omission, and the reported intrinsic viscosity values are thus quite questionable.

Another interesting phenomenon that has been the subject of debate (Öhrn, 1955; Bohdanecky & Kovar, 1982; Cheng et al., 1998; Bercea et al., 1999; Pan et al., 2001; Yang et al., 2001) is the adsorption of the polymer on the walls of the capillary viscometer that manifests itself in an anomalous increase in viscosity as the polymer solution becomes extremely dilute. This effect was mostly observed for high molecular weight polymers. Öhrn (1955) suggested that polymer adsorption on the capillary walls causes a reduction in the effective diameter of the capillary tube resulting in longer flow times corresponding to higher viscosities. Bohdanecky & Kovar (1982) explained the phenomenon in terms of a change in the effective concentration of the polymer which can be relatively dramatic considering that these are already very dilute solutions, and so even adsorption of a small amount of polymer on the capillary walls can have a huge influence on the measured and calculated viscosities. However, Bohdanecky and Kovar stated that in practice, adsorption effects can be neglected when viscosity measurements are performed in solutions with concentration above the extremely dilute solution range (10^{-5} – 10^{-6} g/cm³).

2.2.3 Determination of $[\eta]$ from viscosity measurements: Nonionic PAM

The viscosity properties of a polymer solution can generally be represented by a power series in concentration, c , as follows (Lovell, 1989):

$$\eta_{sp}/c = [\eta] + k_1[\eta]^2 c + k_2[\eta]^3 c^2 + \dots \quad (2.6)$$

where $[\eta]$ is the intrinsic viscosity, and $k_1, k_2 \dots$ are dimensionless constants.

In sufficiently dilute solutions, the higher order terms in Equation (2.6) can be neglected. There are some interactions between polymer molecules even in dilute solutions (Kulicke & Clasen, 2004) but these are captured by the second term. However, one of the working assumptions of this thesis is that those higher-order terms cannot be neglected for high molecular weight polymers characterized by high intrinsic viscosities. With the above considerations, recasting Equation (2.6) gives an equation showing a linear dependence of η_{red} on the concentration.

$$\eta_{sp}/c = [\eta] + k_1[\eta]^2 c \quad (2.7)$$

Equation (2.7) is in accordance with the well known Huggins (1942) equation in which the constant k_I is equivalent to the Huggins coefficient k_H .

$$\eta_{sp}/c = [\eta] + k_H [\eta]^2 c \quad (2.8)$$

The Huggins coefficient is a constant for a given polymer-solvent system and it represents the hydrodynamic interactions between the polymer molecules and the solvent. The Huggins equation is strictly applied when $[\eta]*c \ll 1$ because at higher concentrations, experimental data show upward curvature (Lovell, 1989). Simple plots of (η_{sp}/c) versus c according to the Huggins equation should yield a straight line whose intercept and slope are $[\eta]$ and $k_H[\eta]^2$, respectively. $[\eta]$ is usually expressed in dL/g. Sakai (1968a) summarized the physical meaning of the Huggins constant, k_H as follows: (a) a polymer displays a higher value of k_H in a poor solvent than in a good solvent (a good solvent is one in which the polymer – solvent interactions are favorable over polymer - polymer interactions); (b) it has a value of 0.5 in an ideal solvent and a value of 0.5 – 0.7 for polymers in a theta solvent; (c) k_H may be influenced by molecular weight distribution of the polymer; and (d) k_H is very sensitive to formation of molecular aggregates. The slope, $k_H[\eta]^2$ is a measure of the quality of the solvent and is analogous to the exponent α of the $[\eta]$ –molecular weight relationship (See section 2.2.5)

Lovell (1989) stated that the Huggins constant has values which are essentially independent of molecular weight and fall in the range 0.3 for good-polymer solvent pairs to 0.5 for poor polymer–solvent pairs; and that the experimental data for which $k_H > 0.5$ point to the presence of undissolved polymer aggregates, although as noted by Ma and Pawlik (2007) complete dissolution down to molecular level can actually produce Huggins constants on the order of 0.75-0.9 in certain aqueous systems.

Other commonly used *linear* equations for determining the intrinsic viscosity of non-ionic polymers are listed below:

$$\text{Kraemer: } \ln(\eta_{rel})/c = [\eta] + k_K [\eta]^2 c \quad (k_K \text{ is the Kraemer constant}) \quad (2.9)$$

$$\text{Schulz-Blaschke (S-B): } 1/\eta_{red} = 1/[\eta] - k_{SB} c \quad (k_{SB} \text{ is the S-B constant}) \quad (2.10)$$

$$\text{Martin: } \ln(\eta_{sp}/c) = \ln([\eta]) + k_M [\eta] c \quad (k_M \text{ is the Martin constant}) \quad (2.11)$$

Rafi'ee Fanood and George (1987) evaluated alternative equations that were put forward by Nagy, Kelen and Tudos (NKT) (1978) and Chee (1985) to enhance the precision of the determination of $[\eta]$ and k_H by graphical extrapolation. They analyzed samples of polyacrylamide (PAM) by viscometry in distilled water and concentrated NaCl (1M). The equations tested by Rafi'ee Fanood and George were:

Conventional Huggins equation: Equation (2.8)

$$\text{NKT equation: } \frac{t - t_0}{t_0 c} = \frac{[\eta]}{\tau} + \left(k_H [\eta]^2 + \frac{[\eta]}{\tau} \right) \frac{c}{\tau - c}; \quad (2.12)$$

where t is the flow time of the solution, t_0 is the flow time of the solvent, and τ is the sum of the highest and lowest concentrations of any series of results.

$$\text{Quadratic form of Huggins equation: } \eta_{sp} = [\eta] c + k_H [\eta]^2 c^2; \quad (2.13)$$

Chee's method (error in variance method–EVM):

$$r = t - t_0 - t_0 [\eta] c - t_0 k_H [\eta]^2 c^2 \quad (2.14)$$

where r is the difference between the observed and estimated flow times.

Their results showed that the quadratic form of the Huggins equation gives the best estimates of $[\eta]$ and k_H judging from the lowest standard deviation of $[\eta]$, t and k_H . They also disagreed with the conclusions of Chee (that the EVM, equation 2.14, is more accurate) and concluded that the EVM, when applied to PAM, is more accurate only when $[\eta] < 4.0$ (dL/g). Chee used a sample of polyvinyl chloride in tetrahydrofuran to arrive at the conclusion. The polymer had a value of $[\eta]$ equal to 1.0 (dL/g) at 25⁰C.

Rafi'ee Fanood and George (1987) also concluded that k_H may be affected by (a) branching that may take place during polymerization (b) molecular weight distribution (c) intra and inter-molecular hydrogen bonds (d) ionic strength – with different values of k_H in water and NaCl solution, and (e) history of the solution (aging) prepared for viscosity measurements, since it affects the extent of hydrogen bonding.

Sakai (1968b) proposed that $[\eta]$ and k_H are best estimated by taking the arithmetic averages of the values calculated from the Huggins plot and either the Schulz-Blaschke equation (for poor solvents systems) or the Martin equation (for good solvents systems).

Due to the inconvenience of the extrapolation methods in the conventional plots and the time-consuming nature of the experimental procedures, some authors studied single-point (i.e., using one solution of one polymer concentration) methods for evaluation of intrinsic viscosity. Most of the equations used are empirical modifications of equations according to Huggins, Kraemer, Schulz-Blaschke and Martin. The most-widely used equation is the Solomon and Ciuta equation - $[\eta] = [2(\eta_{sp} - \ln \eta_{rel})]^{0.5} / c$. It generally gives good results of $[\eta]$ when the constant $k_I = 1/3$, meaning that the equation is only valid for use with good polymer-solvent pairs. Rafi'ee Fanood and George (1987) showed that the Solomon and Ciuta equation can be used for single point determination of $[\eta]$ for PAM-water and PAM-NaCl systems with good results.

Silberberg et al. (1957) studied the intrinsic viscosity of a low molecular weight PAM (degree of polymerization = 10,000, molecular weight = 710,000g/mol) at different temperatures ($25^\circ C - 60^\circ C$). They observed an increase in intrinsic viscosity as the temperature increased. The η_{sp}/c vs. c plots had negative slopes above $35^\circ C$. Silberberg et al. speculated that such a reduction in reduced viscosity with increase in concentration could be the result of aggregation if the aggregates are more compact or spherical than the individual molecules. Kulicke and Clasen (2004) presented similar data for polyacrylamide in the temperature range $20^\circ C - 80^\circ C$ in which there was only a slight increase in the intrinsic viscosity with increase in temperature. They explained the increase as resulting from rising solvation of the polymer chain at high temperature due to enhanced polymer-solvent interactions.

In his PhD thesis, Rattanakawin (2002) used capillary viscosity measurements to study totally nonionic PAM samples with molecular weights of $\sim 15 \times 10^6$. Concentration ranges were from 0.03 to 0.24 g/dL. Temperature was maintained at $30^\circ C$. The Huggins equation was used to evaluate the experimental results by plotting (η_{sp}/c) versus c . Rattanakawin also tested an acrylic acid/acrylamide co-polymer and a cationic dimethyldiallylammonium chloride. The results showed that relative viscosity increased with polymer concentration, which was attributed to increased polymer crowding as the concentration increased. The reduced viscosity for non-ionic PAM showed a slight linear increase with concentration. This was attributed to increasing intermolecular interactions as the polymer concentration increased. The reduced viscosity increased with increasing ionicity and polymer concentration, which was attributed to the second

order electroviscous effects. For non-ionic PAM polymers, the increase in the viscosity was less than that observed for the ionic polymers, a fact attributed to less repulsive interactions in nonionic polymers compared with those in ionic polymers. The reduced viscosities did not change much with pH at a concentration of 0.03g/dL, except a slight increase in the alkaline region (~pH 8.5–12). This was attributed to the lack of ionized groups on the polymer chain which kept the polymer conformation unchanged, except at high pH values when minor anionic groups in the commercial hydrolyzed PAM could cause a slight rise in the reduced viscosity. The viscosity of the nonionic PAM slightly decreased with sodium chloride addition. This took place at a solution concentration of 0.03g/dL and natural pH, while there was a sharp decrease in viscosity of the ionic polymers. The reduction in viscosity with addition of the electrolyte was attributed to the third order electroviscous effects, the effect being less pronounced in the nonionic PAM polymer than in the ionic polymers due to the absence of charged groups in the nonionic PAM polymer.

However, it is possible that these measurements were carried out in the semi-dilute region since *dilute solution* viscometry is strictly based on the assumption that *intermolecular* interactions do not take place. It is interesting that Rattanakawin (2002) described the viscosity behaviour of the polymers in terms of first order, second order and third order electroviscous effects. Electroviscous effects are electrostatic contributions of particles to the viscosity of a colloidal suspension. The assumption made by Rattanakawin is that electroviscous effects in polymer solutions are analogous to those in colloidal suspensions. It should however be mentioned that polymer molecules are rather more flexible than colloidal particles. This is an incorrect assumption if the tested solutions were indeed dilute.

Studies by other researchers showed varying effects of electrolyte addition on PAM solutions. Munk et al. (1980) showed that the intrinsic viscosities of PAM samples increased moderately with the addition of NaCl. Mabire et al. (1984) showed that the intrinsic viscosity of PAM samples studied in sodium chloride solutions for salt concentrations between 0.02mol/L and 1mol/L was practically independent of the ionic strength and Eliasaf and Silberberg (1959) did not find any effect of NaCl on the specific viscosity of PAM up to 3.66 M NaCl.

Muller et al. (1979) studied the influence of ionization and added salts on the conformation of commercially available PAM (Molecular weight ~ 4,000,000 g/mol). They used a totally non-ionic PAM sample and obtained higher reduced viscosities in the presence of higher salt concentrations. They argued that this confirmed the absence of residual ionic groups in the sample

as their presence would cause a decrease in the viscosity values since typical polyelectrolyte behaviour should become apparent even at a small charge density of the polymer. The viscosity increase was larger in the presence of divalent salts (CaCl_2 and MgCl_2) than in the presence of a monovalent salt (NaCl). They speculated that the observed differences in the behaviour of PAM in water and salts could be due to the existence of entanglements in pure water – a purely physical phenomenon inherent to the high molecular weight of the sample and also to the presence of hydrogen bonding between macromolecules that would be eliminated in the presence of salts. Again, however, such conclusions must be viewed with caution since dilute solution viscometry implies that intermolecular associations do not form.

Sastry et al. (1999) observed a systematic decrease of $[\eta]$ of PAM (MW $\sim 2,000,000$) with increase in ionic strength irrespective of the pH of the media. The ionic strength was adjusted with KCl at two pH values: 3.0 and 9.0. The Huggins constant (k_H) values increased with ionic strength which was attributed to enhanced inter-unit attractive interactions as ionic strength increased. A point of interest in their study was that Sastry et al. noted partial hydrolysis of the amide groups on nonionic PAM into carboxylic groups judging from the shape of η_{sp}/c vs concentration plots. The plots were found to be linear in the acidic and neutral media while curvatures were observed in the lower concentration (\sim up to 0.08 g/dL) regions in the basic pH media. Hydrolysis of PAM was also reported by Caulfield et al. (2003). Caulfield et al. stated that PAM is susceptible to hydrolysis under basic conditions in a reaction involving nucleophilic addition of hydroxide to the amide carbonyl, followed by elimination of the amide ion to afford an acrylic acid residue.

Wu and Shanks (2003) studied the viscosity behaviour of low molecular weight polyacrylamide (10,000 g/mol) in dilute aqueous solutions of NaCl, glucose and sodium dodecylsulfate. These authors used the Huggins equation to determine the intrinsic viscosity, $[\eta]$ and Huggins constant, k_H as a measure of PAM's chain conformation and PAM–solvent interaction. Without any additive (in pure water), they obtained an intrinsic viscosity value of 0.1101 dL/g. With the addition of NaCl (between 3.3 g/l – 99 g/l) the intrinsic viscosity increased from 0.0904 g/dL to a maximum of 0.1204 dL/g in the very concentrated solution of 99 g/L. The k_H value in pure water was 0.99 and this reduced to 0.469 in 99 g/L NaCl. In light of these values, they arrived at the conclusion that water is not a thermodynamically-good solvent for PAM owing to the high value of k_H (0.99). They also concluded that PAM chains became more expanded in higher concentrations of NaCl solution as inferred from the increase in the $[\eta]$ value.

They suggested that the ion-permanent dipole interaction between NaCl and amide groups makes the polymer chains more expanded than in pure water, and that higher ionic strength improves such interactions.

2.2.4 Determination of $[\eta]$ from viscosity measurements: Polyelectrolytes

Polyelectrolytes are polymers with ionic functional groups along their chains. Co-polymers of acrylamide and acrylic acid or partially-hydrolyzed PAM are examples of polyelectrolytes. Their behaviour in dilute solution is different from nonionic polymers due to the dissociation of the ionic groups that causes coil expansion, the extent of which depends on the degree of dissociation of the groups, and on the ionic strength of the solution. When polyelectrolytes are studied in aqueous solutions, they exhibit a typical behaviour showing an increase of reduced viscosity with decreasing concentration in the low concentration region. At higher concentrations, the reduced viscosity decreases with decreasing concentration as expected for a polymer solution. Thus two extremes, a minimum and a maximum are observed at high and low concentrations, respectively as depicted in Figure 2.2. There appears to be no universal concentration range at which the η_{sp}/c vs. c plots for polyelectrolytes change shape. The range is specific for each polymer-solvent system, but it is quite clear that none of the linear equations described in the previous section for non-ionic polymers would fit such a set of experimental results.

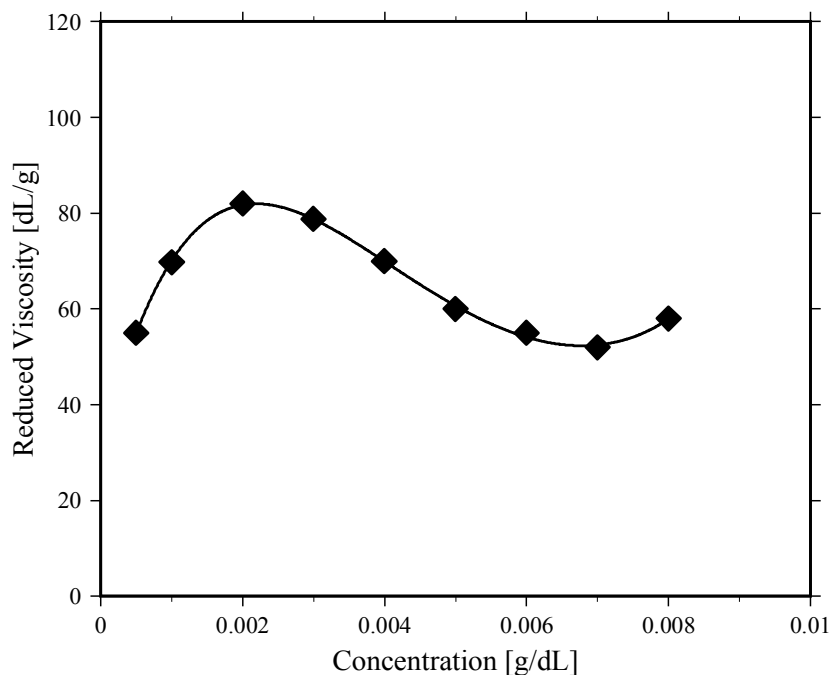


Figure 2.2: A typical graph showing the concentration dependence of reduced viscosity for polyelectrolytes

When simple inert electrolytes such as NaCl or KCl are added to polyelectrolyte solutions, the dissociated ionic groups are shielded by the electrolyte and at high enough concentration of the salt, the η_{sp}/c vs. c plots become linear allowing for the determination of $[\eta]$ by extrapolation of η_{sp}/c to $c \rightarrow 0$. However, Kulicke and Clasen (2004) pointed out that the intrinsic viscosity determined in this way does not reflect the coil expansion in more dilute, or salt-free solutions. A number of empirical relationships have been developed to evaluate viscosity data for polyelectrolyte solutions and to determine their intrinsic viscosities.

Fuoss and co-workers (1948, 1949) proposed an equation (2.15) to describe the extrapolation of the reduced viscosity of polyelectrolytes from a series of experiments.

$$\left(\frac{\eta_{sp}}{c}\right)^{-1} = [\eta]^{-1} + \gamma[\eta]^{-1}c^{\frac{1}{2}} \quad (2.15)$$

Where γ is a polymer–solvent dependent constant. According to this equation, the intrinsic viscosity can be obtained by taking the reciprocal of the y-axis intercept of the $\left(\frac{\eta_{sp}}{c}\right)^{-1}$ vs. $c^{\frac{1}{2}}$

plot. The Fuoss equation was used by Rattanakawin (2002) to determine intrinsic viscosities of anionic PAM with degrees of anionicity up to 30%. Rey and Machado (2000) also used the Fuoss equation to determine intrinsic viscosities of fulvic acid samples in the pH range 3.0 – 8.0 where the samples exhibited strong polyelectrolyte behaviour. However, earlier studies (Cohen et al., 1988; Bohdanecky & Kovar, 1982) showed that the $\left(\frac{\eta_{sp}}{c}\right)^{-1}$ vs. $c^{\frac{1}{2}}$ plot is in fact not linear

due to the maximum and minimum in the η_{sp}/c vs. c plots, and that the Fuoss equation fails in the neighborhood of the maximum at low polymer concentrations. Consequently, the value of $[\eta]$ evaluated according to Equation (2.15) is not quite reliable. Still, the values of $[\eta]$ obtained using the Fuoss equation can be taken as a relative measure of a coil expansion for comparison with other methods (Kulicke & Clasen, 2004).

Fedors (1979) working with latex solutions developed an equation (2.16) to describe the viscosity behaviour of uncharged polymers over a wide range of polymer concentrations.

$$[2(\eta_{rel}^{1/2} - 1)]^{-1} = ([\eta]c)^{-1} - ([\eta]c_m)^{-1} \quad (2.16)$$

where c_m is a polymer concentration parameter. Rao (1993) and Ghimici & Popescu (1998) applied the Fedors equation to polyelectrolytes by plotting $\frac{1}{[2(\eta_{rel}^{1/2} - 1)]}$ vs. $1/c$ and concluded that it can be used to describe the viscosity of some polyelectrolyte solutions over a wide concentration range including the dilute solution range. Ghimici and Popescu (1998) also fitted viscometric data with the Fuoss equation and observed that the Fedors equation gave a better fit than the Fuoss equation over a greater concentration range.

Muller et al. (1979) investigated the effect of ionization and added salts (NaCl, CaCl₂, MgCl₂) on the dimensions of PAM (~4,000,000 g/mol) by viscosity and light scattering measurements. The degrees of hydrolysis of the samples ranged from 4% to 49%. Viscosity measurements were performed with an Übbelohde-type capillary viscometer at 25^oC – 30^oC. The authors first characterized the samples using independent methods (potentiometric titration, ultraviolet absorption, elemental analysis) to ascertain the exact degree of hydrolysis. There was a fair agreement between the values obtained from potentiometry and ultraviolet absorption but the elemental analysis method proved imprecise. The values determined by these methods were somewhat different from those provided by the manufacturers. In distilled water, a high molecular weight hydrolyzed PAM sample neutralized to $\alpha = 0.75$ ($\alpha = 1$ is the fully ionized form) showed an anomalous concentration dependence of reduced viscosity which decreased continuously with dilution in the concentration range 100–700ppm. However, Kulicke and Clasen (2004) presented evidence showing that polyelectrolytes show such behaviour at concentrations above the critical polymer concentration (c^* - described in section 2.2.2) and that the reduced viscosity in fact increases with dilution below the critical polymer concentration. Muller et al. further found out that the viscosities of hydrolyzed PAM samples in ionized states decreased sharply in the presence of divalent cations (Ca²⁺ and Mg²⁺) and that precipitation occurred as more salt was added corresponding to the complexation of the salt ions by carboxylate groups. Overall, their results showed that in flocculation applications where the concentrations of mono- and especially divalent salts are high, unhydrolyzed or low hydrolyzed PAM samples should be used to avoid precipitation of the flocculant. Under salt-free conditions or in the presence of low concentration of salts, the use of highly hydrolyzed samples would be preferred.

Makogon et al. (1986) evaluated the hydrodynamic effectiveness of polyacrylamide by studying the effect of pH on the dimensions and shape of the macromolecules. These authors

used viscometry to obtain reduced viscosities of a 17% hydrolyzed PAM sample in distilled water of varying pH. Through these measurements, they found that at a pH value of 6.1, the molecules were in a fully extended state due to electrostatic repulsive forces arising from the presence of fully ionized carboxylic groups. This was indicated by a maximum in the η_{sp}/c vs. pH plot. They also visualized that the shape of the molecules was asymmetrical at this pH due to the sudden increase in the reduced viscosity when the shear strain was increased from 0 to 2.5 Pa. Above pH 6.1, the reduced viscosity gradually decreased and they ascribed this behaviour to the shielding of the charged carboxylic groups by increased amounts of sodium ions in solution (pH was adjusted using sodium hydroxide).

2.2.5 Evaluation of Flocculant Molecular Weight from Intrinsic Viscosity

The intrinsic viscosity of a polymer can be used to determine the polymer's molecular weight (M) by utilizing equation (2.17). This equation is commonly referred to as the $[\eta]$ -M relationship, or the Mark-Houwink-Sakurada equation.

$$[\eta] = K\bar{M}_v^\alpha \quad (2.17)$$

where \bar{M}_v is the viscosity-average molecular weight, and K and α are constants for a given polymer/solvent/temperature system. The viscosity-average molecular weight is defined by equation (2.18) and lies between the weight-average molecular weight, \bar{M}_w and the number-average molecular weight, \bar{M}_n .

$$\bar{M}_v = \left[\frac{\sum w_i M_i^\alpha}{\sum w_i} \right]^{\frac{1}{\alpha}} \quad (2.18)$$

where w_i is the total weight of molecules of molecular weight M_i . It can be seen that when $\alpha = 1$, $\bar{M}_v = \bar{M}_w$. The exponent α is a measure of the solvent quality and is therefore indicative of the shape of the polymer coil in solution – whether stiff or flexible chains. It is a measure of the interactions of the polymer and the solvent. Kulicke and Clasen (2004) provided a review of the influence of the solvent quality and solution structure on the $[\eta]$ -M relationship. When the polymer chain-solvent interactions are so small that the coil is not contracted or expanded, the

so-called theta conditions are reached and the coil has unperturbed dimensions in solution. In such a solution, the theoretical value of the exponent α should be 0.5. The exponent α increases as the coil expands in good solvents. Generally, $0.5 \leq \alpha \leq 0.8$ for flexible chains in a good solvent, $0.8 \leq \alpha \leq 1.0$ for inherently stiff molecules and $1.0 \leq \alpha \leq 1.7$ for highly extended chains (Lovell, 1989).

The published exponents of K and α for PAM are as follows: $K = 1.05 \times 10^{-4}$ dl/g, $\alpha = 0.73$ for cationic PAM; $K = 1.91 \times 10^{-4}$ dl/g, $\alpha = 0.71$ for non-ionic PAM (Mabire et al., 1984); and $K = 3.20 \times 10^{-4}$ dl/g, $\alpha = 0.66$ for anionic PAM (Clark et al., 1990). Kulicke et al. (1982) also provided values of $K = 1.0 \times 10^{-2}$ ml/g and $\alpha = 0.755$ for non-ionic PAM determined in water at 25°C.

Conrad and Klein (1978, 1980) characterized PAM samples in the molecular weight region of 5×10^5 to 5.5×10^6 by viscometry, osmometry, light scattering, and ultracentrifugation. They established the following relationships: $[\eta] = 4.9 \times 10^{-3} (M_w)^{0.8}$ in water, $[\eta] = 7.19 \times 10^{-3} (M_w)^{0.77}$ in 0.5M solution of NaCl, and $[\eta] = 1.36 \times 10^{-1} (M_w)^{0.54}$ in ethylene glycol. Their results showed that a single molecule of PAM forms a random coil in water and ethylene glycol, and that in aqueous solutions, the coil is appreciably expanded beyond the unperturbed dimension by the influence of the “good” solvent (water) as could be deduced from the M-H-S exponent $\alpha = 0.8$.

Rearrangement of Equation (2.17) allows the evaluation of \bar{M}_v from intrinsic viscosity measurements provided K and α are known. It is important to determine the intrinsic viscosity using the same solution conditions as used for the determination of K and α . The set-back of using the $[\eta] - M$ relationship is that the K and α values found in literature are limited in most polymer cases, including PAM, to the determination of molecular weights lower than 9×10^6 g/mol (Haas and Kulicke, 1984). Theoretically, determination of molecular weights of high molecular weight polymers (up to infinity) can be done by light scattering, but this method is also prone to errors at high molecular weights due to the hyperbolic increase of the molecular weight as the ratio of the polymer concentration to the light scattering intensity decreases (Haas and Kulicke, 1984). Therefore, to determine very high molecular weights, the $[\eta]-M$ relationship has to be extrapolated beyond the documented molecular weight range.

2.2.6 Aging of Solutions in Viscometry Measurements

The performance of flocculants in dewatering operations depends on their solution properties. When there is instability or change in these properties, there is invariably a change in

flocculation performance. For polyacrylamide, such time-dependent alterations manifest themselves in a decrease of the viscosity of polyacrylamide solutions. This peculiar phenomenon is the so-called aging and in the case of PAM, several studies have been performed in an attempt to interpret it (Narkis & Rebhun, 1966; Shyluk and Stow Jr., 1969; Kulicke & Kniewske, 1981; Henderson and Wheatley, 1987; Hecker et al., 1998; Owen et al., 2002).

Narkis and Rebhun (1966) investigated the effects of solution aging on the viscosity of a solution of PAM (molecular weights 2.24×10^5 and 1.95×10^6). Aging times up to 57 days were examined. The intrinsic viscosity $[\eta]$ was found to decrease with time to a constant value. Maintaining a high temperature (55°C) did not shorten the time needed to reach the limiting viscosity values. The aging effect was attributed to disentanglement of the polymer chains with time. It should, however, be recalled that the measurement of the intrinsic viscosity must be performed in dilute polymer solutions in which entanglements *by definition* do not form, so “disentanglement” is highly unlikely. It must also be noted that the aging times studied by these researchers are unrealistic in practice where it is quite common to use flocculant solutions within days or even hours of preparation.

Shyluk and Stow Jr., (1969) observed that aging of PAM of high intrinsic viscosity was paralleled by a decrease in the flocculation activity, attributable to chemical aging as well as to the weakening of the inter-particle bridging. They presented some evidence that chemical aging involved the production of free radicals from traces of persulphate left over from the polymer polymerization reaction.

Kulicke & Kniewske (1981) conducted studies on polyacrylamide-acrylates and established that there was an unusual viscosity decrease with time in the scale of weeks. They did not observe any viscosity loss when the PAM samples were prepared in NaCl solutions of high enough concentration. Contrary to previous interpretation of solution aging, Kulicke and Kniewske attributed the viscosity loss to a conformational change of single molecules involving hydrogen bonding. They explained that with aging, there was a transition from a partly stiffer, higher viscous structure to a more flexible one. They ruled out chain breakdown to smaller units.

Henderson and Wheatley (1987) studied the aging of PAM samples over several months and found out that shear degradation resulted in decrease in intrinsic viscosity. Flocculation activity for tailings from a coal preparation plant was reduced when the intrinsic viscosity decreased. Viscosity-aging of PAM solutions in terms of molecular degradation resulted in small reductions in intrinsic viscosities that were not sufficient to affect the flocculation rate. The

presence of a small amount of 3% ethanol or methanol was apparently sufficient to stop the molecular degradation of PAM.

Owen et al. (2002) summarized four main stages for the dissolution and aging of flocculant solutions as follows: (a) after very short aging periods, the capacity of flocculation is limited due to the small fraction of dispersed polymer chains in solution, (b) after several hours, gel lumps disperse, supra-micron agglomerates appear as well as sub-micron species of entangled chains, (c) after several days, the concentration of free polymer chains may reach an equilibrium level due to the dispersion of most agglomerates. This maximizes the flocculation activity, and (d) longer term aging may lead to loss of flocculant activity due to reduction in dimensions from chain reformation. In their studies, aqueous solutions of PAM were used to flocculate mineral slurries. Aging times from 1 hour to 6 days were examined. Decreasing flocculant dosages were observed with increasing flocculant age, the optimal flocculant performance being observed at 72 hours. However, despite the maximization of discrete polymer concentration at 72 hours, the density of the aggregates formed did not change showing that only the discrete polymer chains influenced the flocculation.

These studies about solution aging show that systematic procedures for preparation of high molecular mass polymers are necessary. Onyon (1959) recommended that in order to ensure that the polymer was completely dissolved; close examination in a powerful beam of light should be done. Cloudy solutions usually indicate the presence of finely divided insoluble matter, or undissolved polymer aggregates. Cloudiness may also be caused by traces of water in the sample if it has not been dried well (Onyon, 1959).

3.0 Experimental Program

3.1 Materials

3.1.1 Equipment

A PVS1 Lauda photo-timing and processing system interfaced with a computer was used in viscosity measurements to measure flow times used for calculation of kinematic viscosities. The viscosities were measured using Cannon–Fenske capillary viscometers (Schott Geräte GmbH, Germany). To control the solution temperature, a Lauda 015T water bath and a Lauda E100 thermostat were used. A Perkin Elmer system 2000 FT-IR spectrophotometer was used to obtain spectra of flocculant films prepared on an AgCl window. The films were freeze-dried in a Baxter vacuum oven. For pH determination, an Accumet model 50 pH-meter was employed. The pH meter was calibrated daily with pH 4, 7, and 10 buffer solutions. All sample weights were made using an Ohaus Explorer analytical balance.

3.1.2 Flocculant samples

The polyacrylamide-based “Superfloc A” type of flocculants were provided by Cytec Industries Inc. (Lakeland, FL). Five PAM samples – N100, A100, A110, A130 and A150 were evaluated. The samples were received as dry white granules and were used without any further treatment or purification. As reported by the manufacturer, these flocculants are of “high molecular weight and varying degree of anionicity”. The degrees of anionicity of these polymers were determined as described in section 4.1.

For viscosity measurements, stock solutions at concentrations of 1 g/L (N100) and 0.5 g/L (rest of the flocculants) were prepared by mixing the appropriate amount of flocculant in distilled water (and sodium chloride) at room temperature. The solution preparation procedure usually followed the sequence: to prepare a 1 g/L solution, 0.5 g of the flocculant was weighed in a small sample bottle. Distilled water (500 mL) was then added into a beaker and a magnetic stirrer was used to create a vortex reaching the top of the stirrer. The flocculant granules were carefully added into the sides of the vortex making sure that the granules did not form a gel but were individually dispersed in water. The exact amount of flocculant added was determined by weighing the amount of flocculant left in the sample bottle and subtracting it from the initial amount weighed. This small correction was used to calculate the exact stock solution concentration. The top of the beaker was then covered with a parafilm and the entire beaker was

covered with an opaque container to prevent any potential degradation due to exposure to light or due to contamination with dust. The flocculant solution was then mixed for 3 hours for the N100 (5 hours in the case of the other flocculants) to achieve complete dissolution of the flocculant. After this time, the stock solution was allowed to stand overnight (~ 8 hours) after which working solutions were prepared prior to the viscosity measurements. Fresh stock solutions were prepared daily to minimize aging effects. The N100 was tested in the concentration range from 50 – 150 mg/L while A100, A110, A130 and A150 were evaluated in the concentration range from 10 – 50 mg/L. These ranges were chosen to satisfy the critical concentration (c^*) criteria (see section 2.2.2) and were below the critical concentration limit - $c^* = 2.5/[\eta]$ proposed for PAM by Kulicke et al. (1982). The lower limit of the concentration range was conveniently chosen to avoid possible adsorption of the flocculant molecules on the sides of the capillary tube during viscosity measurements (Bohdanecky & Kovar, 1982).

The dilution calculation was made as follows: in order to dilute a 1.0036 g/L (C_1) stock solution to a final concentration of 50 mg/L (0.05 g/L - C_2), the volume of stock solution (V_1) needed to make up to 100 mL (V_2) was calculated using equation (3.1)

$$C_1V_1 = C_2V_2 \quad (3.1)$$

$$(1.0036) \times V_1 = (0.05) \times (100)$$

Hence

$$V_1 = 4.9821 \text{ mL}$$

This is the volume of stock solution that would be added into a volumetric flask and made up to the 100-mL mark. The actual amount added was 4.9981 mL. This is the actual volume V_1 that was used to calculate the final flocculant concentration, C_2 , used also in the calculation of the reduced viscosity. From equation (3.1):

$$C_2 = C_1V_1/V_2 = (1.0036 \times 4.9981)/100 = 0.0502 \text{ g/L}$$

Such accurate volumes were actually measured by mass using an analytical balance and assuming that the density of the polymer solution was equal to the density of water. Such precision was deemed necessary since small errors in polymer concentration would produce large errors in the calculation of reduced viscosities. To reduce the possibility of systematic errors associated with the procedures for preparing and diluting the flocculant solutions, the foregoing steps were applied to all the samples and solutions. All the glassware used were thoroughly cleaned by adding 3 ml of concentrated nitric acid to the glassware and adding three drops of concentrated ethanol to produce strong oxidizing fumes capable of removing any organics in the

glassware that could potentially introduce errors in the measurements. The glassware was then rinsed with plenty of distilled water and dried.

3.1.3 Reagents

Sodium chloride (NaCl) from Fisher Scientific (Assay: 100.00%) was used to prepare flocculant solutions to study the effect of electrolyte addition on the solution intrinsic viscosities. The NaCl concentration was kept constant at 0.01M and was prepared by weighing 1.1688 g in a 2-L volumetric flask and adding distilled water to the 2000-mL mark.

Calcium chloride (CaCl₂) also from Fisher Scientific (Assay: 100.98%) was added to the diluted flocculant solutions to investigate the effect of divalent salts on the solution intrinsic viscosities. A concentrated solution of CaCl₂ (1M) was prepared by weighing 14.701 g in a volumetric flask and making up to the 100-mL mark with distilled water. This concentrated calcium chloride solution was then used to prepare a background solution containing 0.01 mol/L NaCl and 0.001 mol/L CaCl₂.

The pH of solutions was adjusted with analytical grade sodium hydroxide (NaOH) or hydrochloric acid (HCl), both from Fisher Scientific.

3.2 Methods

3.2.1 Viscosity measurements

Kinematic viscosity measurements of flocculant solutions in distilled water and NaCl were carried out at various pH values and temperatures. Stock flocculant solutions were prepared and left overnight (8-10h) and then diluted the next day. All viscosity measurements were made within 24 h of the stock solution preparation. The measurements were made using two Cannon - Fenske capillary viscometers (Fig. 3.1) of different calibration constants. The capillary constant, K is a specific factor for a particular capillary and is usually provided by the manufacturer. The constants (0.00866 & 0.00836) that were indicated on the viscometers turned out to be only approximate values. When used to determine the viscosity of distilled water at 25⁰C, kinematic viscosity values of 0.92179 mm²/s and 0.91905 mm²/s were obtained with these two capillaries. These values are ~3% higher than the accepted literature value of 0.89304 mm²/s (Weast, 1970). The constants were therefore re-calculated to 0.008289 and 0.008206 respectively by carrying

out carefully controlled measurements with distilled water at 25⁰C. These new constant values were then used throughout the measurements. These rather small adjustments in calibration parameters were considered important since small differences in kinematic viscosities can have a dramatic impact on the calculated specific viscosities in very dilute polymer solutions, which would then affect the accuracy of the extrapolated intrinsic viscosities.

Before the first use, the viscometers were cleaned with a mixture of 15% hydrogen peroxide (H₂O₂) and 15% HCl as recommended by the manufacturer.

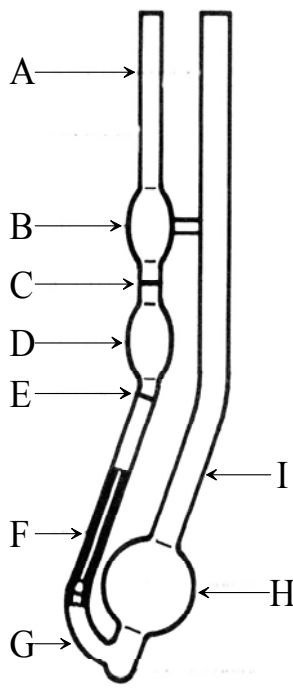


Figure 3.1: Schematic of the Cannon-Fenske capillary viscometer used in the viscosity measurements.

It consists of two tubes – the tube with the capillary (A) and the venting tube (I). Other features are the pre-run bulb (B), the upper timing mark (C), the measuring sphere (D), the lower timing mark (E), the capillary (F) and the reservoir (H). Feature G (tube expanding) makes the viscometer convenient for automatic measurements.

After dilution of the stock solution, 50 ml of the diluted sample was transferred to a beaker and its natural pH was determined with an Accumet 50 pH-meter. Measurements were also carried out at higher pH values (~8.5 and 10.5). After determining/adjusting the pH (about 10 minutes were typically needed to ensure a stable pH reading before the measurements), 7-ml aliquots were transferred to the capillary viscometer reservoir (H in Figure 3.1), the viscometer was then placed in a water bath whose temperature was kept constant at 25 ± 0.1⁰C for an equilibration time of 30 minutes. The kinematic viscosity was then determined by allowing the flocculant solution to flow down the capillary under gravity. A PVS1 Lauda photo-timing and

processing system interfaced with a computer was used to automatically measure three flow times, the average of which was used to calculate the kinematic viscosity, ν (in mm²/s) according to equation (3.2):

$$\nu = K(t - v) \quad (3.2)$$

where K is the capillary constant, t is the average flow time in seconds, and v (seconds) is the Hagenbach correction - a kinetic energy correction. The standard deviation of the flow times was always less than 1 second. The capillary viscometers (diameter 0.54mm) were chosen such that the flow times were between 100 and 200 seconds giving relative viscosities between 1.2 and 2.5.

For high temperature measurements, with the capillary and sample still in the bath, the temperature of the bath was increased to 35⁰C and then to 50⁰C. At each temperature, an equilibration time of 30 minutes was necessary to allow the sample to attain the temperature of the bath. Finally, the temperature of the bath was returned to 25⁰C by circulating cold water through the bath. Kinematic viscosity measurements were repeated at 25⁰C to test the reversibility of the effect of temperature.

In the case of N100 and A130, additional measurements involving addition of CaCl₂ were made to investigate the effect of divalent salts on the intrinsic viscosity. A predetermined amount of a concentrated calcium chloride solution was added to a given volume of the diluted flocculant solution to achieve a final CaCl₂ concentration of 0.001mol/L. A concentration correction was made to take into account a small change in the volume of the flocculant solution after addition of the calcium chloride solution.

From the kinematic viscosities, the relative, specific and reduced viscosities of the flocculants in distilled water and NaCl and with addition of CaCl₂ for N100 and A130 were calculated at each concentration, pH and temperature. The effect of these parameters on the solution viscosities was assessed by determining the intrinsic viscosity of the flocculants in the tested solution environments by graphical extrapolation. The percent errors involved in the determination of the intrinsic viscosities were 3.9% for the A110 flocculant and 5.2% for the N100 flocculant. This is a good indication of the experimental errors involved since it is well established that dilute solutions of PAM are extremely difficult to handle (see Appendix VII).

A general relationship between the intrinsic viscosity and flocculant viscosity is given by Equation (2.6) ($\eta_{sp}/c = [\eta] + k_1[\eta]^2 c + k_2[\eta]^3 c^2 + \dots$). A linear approximation is often truncated from this relationship when viscosity measurements are made in sufficiently dilute solutions. The resulting equation - the Huggins equation (2.8) ($\eta_{sp}/c = [\eta] + k_H[\eta]^2 c$) is a very convenient means of assessing the solution behaviour of nonionic polymers. In this equation, η_{sp}/c is the reduced viscosity, η_{red} , which should yield a straight line when plotted against the flocculant concentration, c . The intercept is equal to $[\eta]$ - the intrinsic viscosity while the slope is equal to $k_H[\eta]^2$. Thus the intrinsic viscosity and the Huggins constant, k_H can graphically be calculated. The intrinsic viscosities of the nonionic flocculant N100 were obtained using the Huggins equation.

For the anionic flocculants (A100, A110, A130, A150), plots of η_{sp}/c vs. c cannot be described by the Huggins equation. As a result, several equations were tested with the aim of choosing one that would best fit the raw viscosity data. Equation 2.6 is the general equation on which all other empirical equations are based. As already discussed, it is usually convenient to ignore higher terms in very dilute solutions of polymers. However, a working assumption of this thesis was that, for solutions of polymers of high intrinsic viscosities such as the tested flocculants, it was no longer valid to ignore the higher order terms because even though the polymer concentrations (c) were very small, the high intrinsic viscosities made substantial contributions to those higher order terms.

Therefore, polynomial equations were used to fit the data, and the intrinsic viscosities so obtained were used as reference against which values from the other equations (Fuoss and Cathers – Equation 2.15; and Fedors - Equation 2.16) were compared. The Fedors equation turned out to be the best one as it consistently gave very good linear fits to intrinsic viscosities close to those obtained from the polynomial fits under various conditions for all the polymers tested.

3.2.2 Chemical Analysis

Total organic carbon (TOC) and Na assays for 0.01% solutions of the polymers were determined and the molar ratios of these two elements were compared to directly determine the percentage of the anionic acrylate units in the polymer solution. It should be recalled that anionic polyacrylamides are actually sodium salts. Three sets of TOC assays were obtained from two

different laboratories - Environmental Engineering Laboratory (Department of Civil Engineering), and Department of Chemical and Biological Engineering, both at University of British Columbia while the Na assays were performed by International Plasma Labs Ltd. (Richmond, BC). The TOC assays were performed by the combustion-infrared method on an IL-550 TOC/TN analyzer using a platinum catalyst at a temperature of 750°C.

3.2.3 Infrared Spectroscopy

To complement the chemical assay method for determination of the degree of anionicity, Fourier Transform Infrared (FTIR) Spectroscopy was employed in which FTIR spectra of the polyacrylamide films were recorded using a Perkin Elmer system 2000 FT-IR spectrophotometer. A resolution of 8 cm⁻¹, plotting interval of 1 cm⁻¹ were used and 100 scans were collected. From the resulting spectra, peaks corresponding to the carboxylate (-COO⁻) and carbonyl (-C=O) groups at wave numbers around 1568 cm⁻¹ and 1667 cm⁻¹ respectively were identified and their absorbances were recorded. An empirical equation (3.3) suggested by Kulicke and Hörl (1985) was used to determine the degree of anionicity:

$$D.A = 100 - \left[96.78 * e^{-0.5836 * E_{COO^-} / E_{CO}} \right] \quad (3.3)$$

where *D.A* is the degree of anionicity, *E_{COO-}* is the absorbance of the carboxylate group and *E_{CO}* is the absorbance of the carbonyl group.

The equation was empirically obtained by Kulicke and Hörl after infrared analysis of 14 samples of polyacrylamide co-sodium acrylate with a wide range of degrees of anionicity (8% - 85.5%). The authors established that the method had an accuracy of ±5% and that it worked best for polymers with degrees of anionicity between 10% and 90%.

The method used for film preparation was that of Rogers and Poling (1978) in which an amount of flocculant solution (0.600 ± 0.05g, 0.5 g/L) previously adjusted to the required pH was frozen on a 25 × 25 mm AgCl window, then the solvent was evaporated under vacuum and the resulting film was matted on the AgCl window for a few seconds using hot water steam.

3.2.4 Aging studies

Flocculant solutions for the aging studies were prepared and diluted in exactly the same manner as in the viscosity measurements except that the stock solutions did not stay overnight. Only the nonionic flocculant (N100) and the most anionic flocculant (A150) were investigated.

Tests were done both in distilled water and in 0.01M NaCl. The diluted solutions (150 mg/L for N100 and 50 mg/L for A150) were transferred to a capillary viscometer and their flow times were determined at 1 hour intervals over a period of 72 hours. The measurements were started immediately after preparing the stock solutions. In distilled water, two temperatures - 25⁰C and 50⁰C were investigated while in NaCl, measurements were only taken at 25⁰C. Reduced viscosities were calculated and plotted as a function time.

In another experiment, the pH values of the flocculant solutions were measured before and after storing them for 3 days to investigate the effect of aging on the chemistry of the solutions.

4.0 Results and Discussion

4.1 Degree of anionicity (D.A)

The total organic carbon (TOC) and sodium (Na) assays obtained from chemical assays were converted to moles by dividing by the respective molar weights of carbon and sodium. The degree of anionicity was then determined from equation (3.4):

$$\text{Degree of anionicity} = \frac{3 \times (\text{Moles of Na})}{\text{Moles of C}} \times 100\% \quad (3.4)$$

The above equation assumes that one mole of sodium is equivalent to one mole of carboxylic groups in the polymer. Three sets of TOC assays were obtained from two different laboratories. It was observed from the results in Table 4.1 that it was increasingly difficult to achieve the same TOC assay for all the flocculants (about 50ppm from a solution of concentration 100ppm), as would be expected since all flocculants, whether nonionic or anionic, should contain three carbon atoms (moles) in an acrylamide or acrylic unit (mole).

Table 4.1: Total organic carbon and sodium assays of flocculants

Flocculant	TOC-1 (mg/L)	TOC-2 (mg/L)	TOC-3 (mg/L)	Average (mg/L)	Na Assays (mg/L)
N100	46.60	43.70	44.81	45.0	0.42
A100	41.50	39.20	40.72	40.5	2.12
A110	41.20	39.60	40.11	40.3	3.63
A130	35.00	34.70	37.63	35.8	6.45
A150	34.50	33.00	37.29	34.9	10.03

TOC-1 and TOC-2 assays were determined by the Environmental Engineering Laboratory, Department of Civil Engineering, University of British Columbia

TOC-3 assays were determined by the Department of Chemical and Biological Engineering, University of British Columbia

An average value of the three sets of TOC data was subsequently used to determine the degree of anionicity. Initially, it was anticipated that reasonable results would be obtained by comparing the molar ratios of C:N but the nitrogen assays did not seem to yield meaningful results which prompted the use of Na assays.

Similarly for infrared spectroscopy, it was initially assumed that carboxylic (-COOH) and amide (NH₂) groups would be compared but it was increasingly difficult to obtain a peak

corresponding to the carboxylic groups as the anionicity of the polymers decreased (see Table 4.2. for degree of anionicity values of the flocculants). The carboxylate ($-\text{COO}^-$) peak should change its relative position or intensity when the pH is lowered to 3.0, which results in the protonation of the dissociated carboxylate groups ($-\text{COO}^-$) to COOH . A small peak was only obtained in the case of the most anionic polymer, A150 as shown in Figure 4.2. It can be seen in Figure 4.1 that at natural pH, there is a very sharp peak at a wavenumber of 1568 cm^{-1} which is usually assigned to the dissociated carboxylic groups. Note that for clarity, the two spectra for the A150 flocculant are presented in different figures. When the pH is lowered to 3.0, a new peak appears near a wavenumber of 1710 cm^{-1} which is where the protonated carboxylic groups in polyacrylamides are expected to produce a peak. The infrared spectra of the nonionic flocculant N100 shown in Figure 4.3, at natural pH and pH 3, indicate that due to the presence of very small amounts, if any, of $-\text{COOH}$ (at pH 3.0) and $-\text{COO}^-$ (natural pH) groups, no peaks can easily be assigned to the protonated $-\text{COOH}$ group.

The main objective of this part of the thesis was to determine the degree of anionicity using a method *not requiring* any prior calibration. Therefore, it was found that FTIR could provide only a qualitative assessment of the degree of anionicity since the broad peak around 1667 cm^{-1} completely masked the presence of the 1710-cm^{-1} peak characteristic of the protonated $-\text{COOH}$ group, especially for the weakly- and moderately-anionic flocculants.

The infrared spectra of all the flocculants can be found in Appendix VI. The spectra exhibit peaks and bands characteristic of polyacrylamides. The $3200\text{--}3400\text{ cm}^{-1}$ range is associated with the symmetrical and asymmetrical stretching modes of the N-H bonds in amide (NH_2) groups, the strong peak at $\sim 1665\text{ cm}^{-1}$ is the characteristic band of the C=O stretching (Lu and Mi, 2005). The peak at 1568 cm^{-1} is assigned to the dissociated carboxylate group, while the peaks at 1452 cm^{-1} and 1416 cm^{-1} are associated with the C-H bending of CH_2 and C-N stretching/amide III band respectively (Lu and Mi, 2005). The peaks at 1452 cm^{-1} and 1416 cm^{-1} were used by Rogers and Poling (1978) to determine the degree of anionicity of polyacrylamide flocculants by comparing with spectra and band intensities of standard polymers of known (i.e., assumed) anionicity.

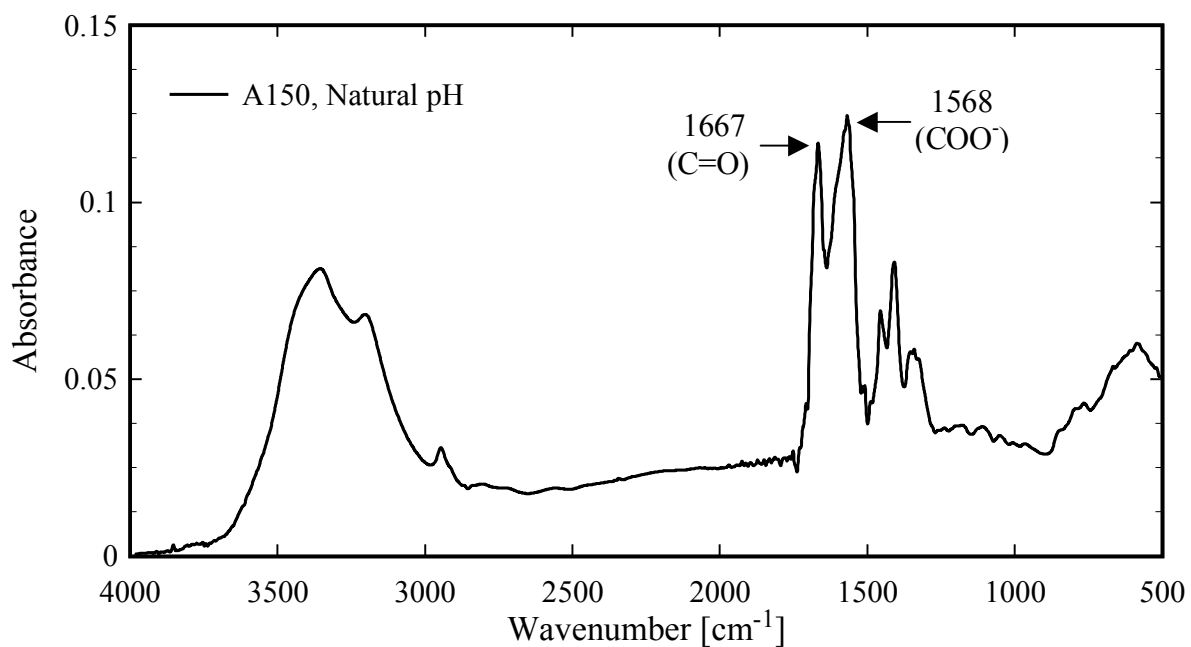


Figure 4.1: FTIR spectrum of A150 prepared at natural pH.

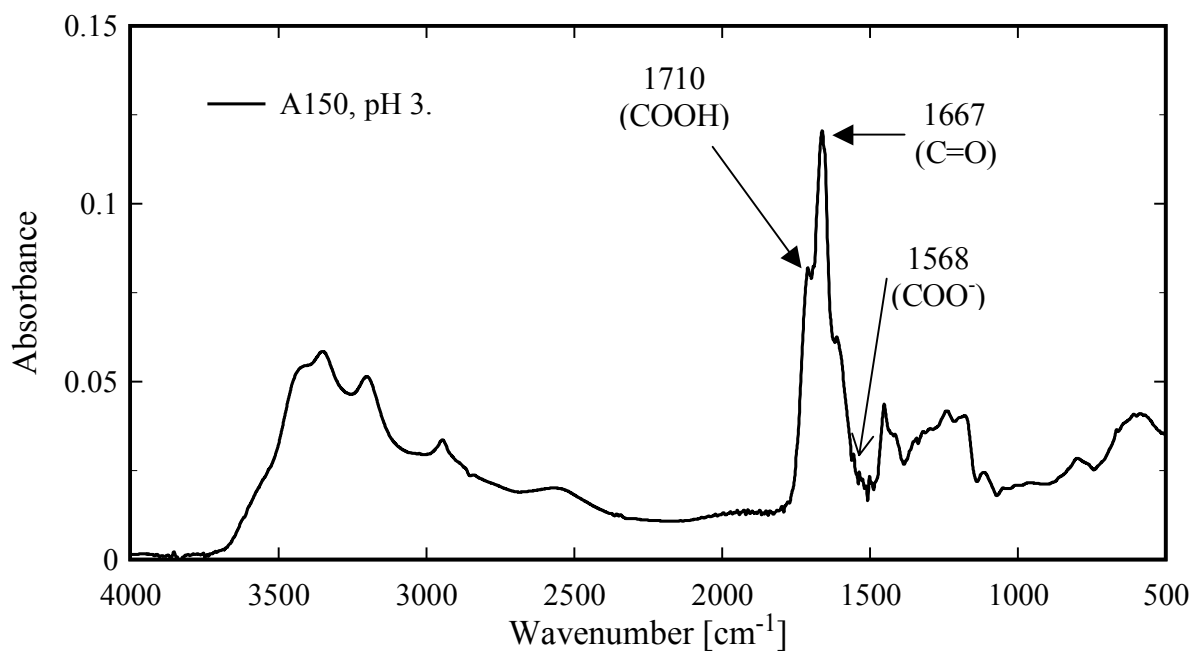


Figure 4.2: FTIR spectrum of A150 prepared at pH 3.

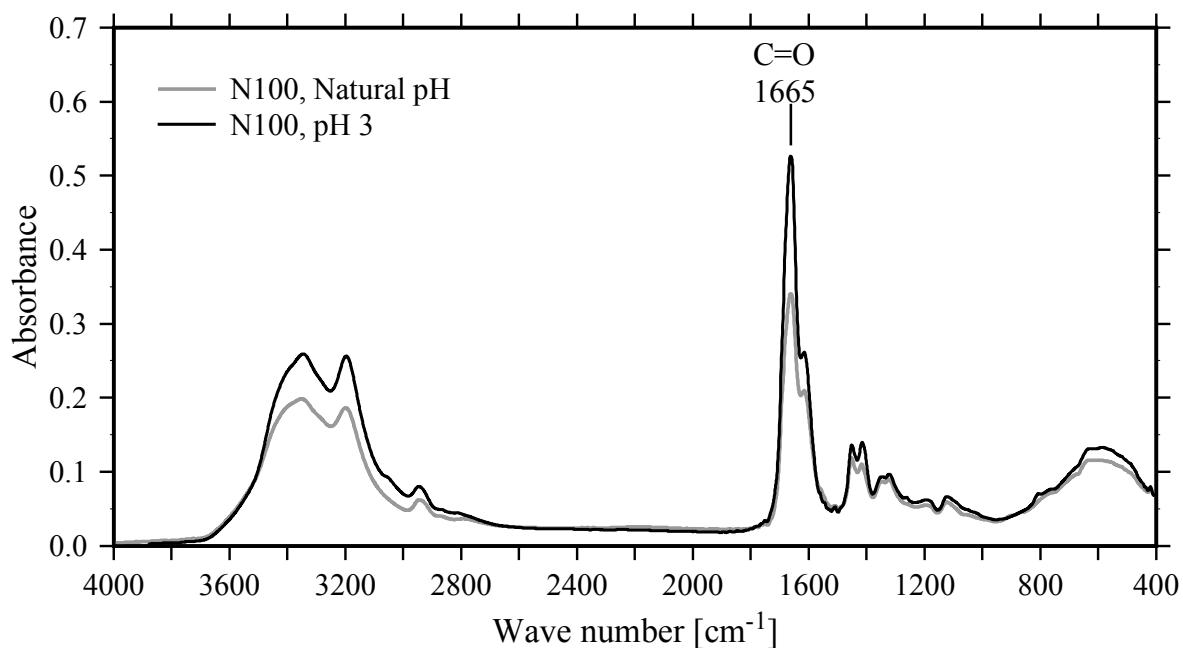


Figure 4.3: FTIR spectra of the nonionic flocculant N100 prepared at natural pH and pH 3.

Having applied equation 3.3 (page 33) it was found that comparing the carboxylate ($-\text{COO}^-$) and carbonyl ($-\text{C}=\text{O}$) groups at the natural pH of the flocculant solutions gave meaningful results that could be correlated with the chemical assays (TOC and Na contents). The results from the chemical assays and infrared spectroscopy are summarized in Table 4.2.

Table 4.2: Degree of anionicity (D.A) of flocculants determined from chemical assays and infrared spectroscopy.

Flocculant	D.A from Chemical assays (%)	D.A from Infrared spectroscopy (%)	D.A taken from Ding (2007)
N100	1.5	15.2	<2
A100	8.2	20.5	7.0
A110	14.1	23.8	16.0
A130	28.2	34.8	33.0
A150	45.0	48.1	50.0

As can be seen from Table 4.2, when the values from the two methods are compared, there is not much quantitative agreement especially for the least anionic polymers but there is a clear qualitative trend with the degree of anionicity increasing in the order $\text{N100} < \text{A100} < \text{A110} < \text{A130} < \text{A150}$. The fourth column in Table 4.2 indicates the degrees of anionicity provided by Cytec, and used by Ding (2007) for flocculation and flotation studies in his PhD thesis. Cytec did not disclose the method that was used to calculate the degrees of anionicity but it is believed that

the values were estimated from the relative quantities of acrylamide and acrylic acid used in the synthesis of the copolymers. Nonetheless, the results are qualitatively in agreement with the data obtained from infrared spectroscopy and chemical assays, and in fact quantitatively, it can be seen that chemical assays based on sodium content in the samples are accurate to within 5% of the values provided by Cytec. The infrared spectroscopy data for A110, A130 and A150 are also within ~7% of the values reported by Cytec. The large difference of the values obtained for polymers with a degree of anionicity below 10% (N100 and A100) is due to the fact that two potentially significant peaks ($-\text{COO}^-$ and $-\text{C}=\text{O}$) with very low and very high absorbances are being compared to each other (Kulicke and Hörl, 1985). The same effect is expected if the method is used to evaluate a polymer with degree of anionicity above 90%.

It is important to note that the small residual fraction of charged units along the polymer chain of N100 appears to be sufficient to impart a detectable polyelectrolyte behaviour to the theoretically non-ionic N100, as seen from its viscosity behaviour in distilled water and 0.01M NaCl (see sections 4.4.1 and 4.4.2). The decrease of intrinsic viscosity from 42.9 dL/g to 9.9 dL/g (at natural pH, 25⁰C) in distilled water and 0.01M NaCl respectively indicates coiling of the polymer chain at higher ionic strength which clearly shows the effect of the presence of residual charged units. The intrinsic viscosity of a purely non-ionic polymer should practically be unaffected by the presence of salts.

4.2 Aging studies

Fig. 4.4 shows the aging effects in polymer solutions of N100 and A150. The aging effects were monitored by measuring the kinematic viscosities of the polymer solutions through capillary viscometric experiments. The measurements were made at hourly intervals over a period of 72 hours, both in distilled water and NaCl. The kinematic viscosity data were converted to relative and reduced viscosities, which were then plotted as a function of time to investigate possible changes in polymer behavior over time. It can be seen from Figure 4.4 that in distilled water, the viscosity of the nonionic polymer N100 at both temperatures is very stable over the entire time investigated, but the most anionic polymer - A150 shows a steady decrease in reduced viscosity with time. The decrease is more dramatic at 50⁰C than at room temperature especially at longer aging times.

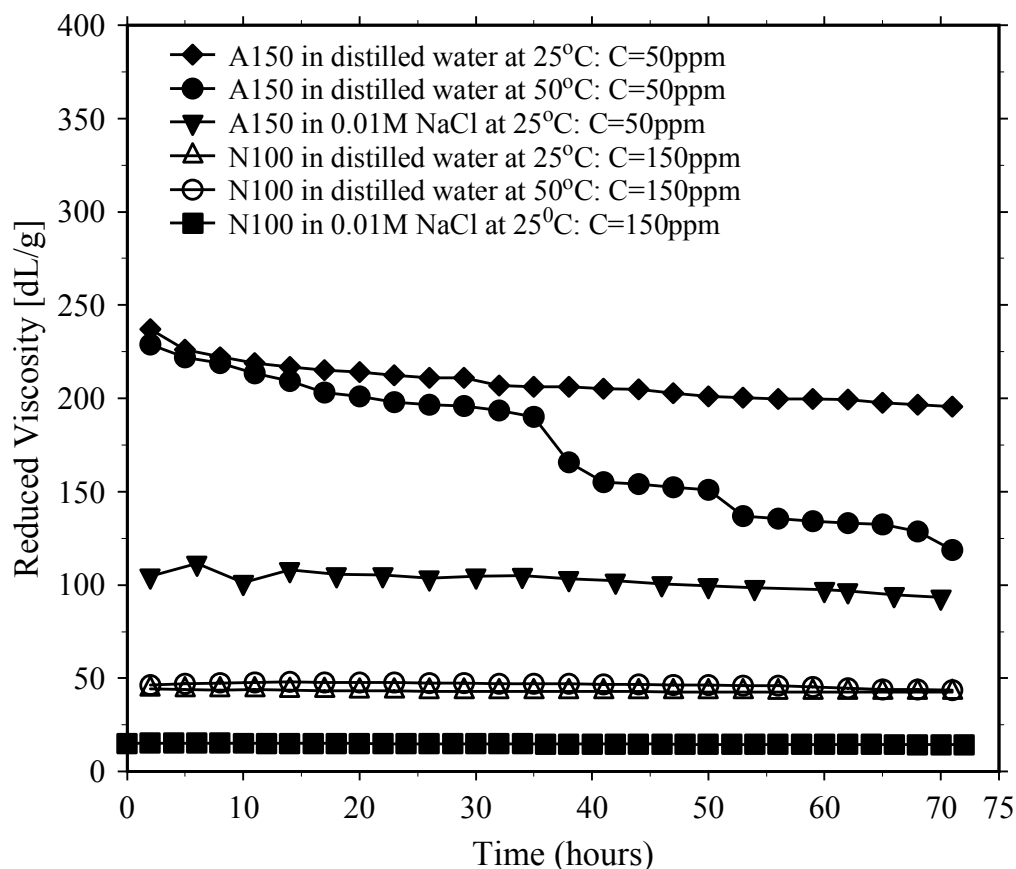
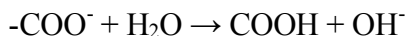


Figure 4.4: Reduced viscosities of N100 and A150 as a function of time in distilled water and 0.01M NaCl.

It is likely that changes in the conformation of the polymer single molecules are responsible for the viscosity loss as the polymer chain changes from a more extended structure to a more compact or coiled one. The decreasing solvation of the polymer chain at higher temperature results in the contraction of the polymer chain characterized by a decrease in the reduced viscosity. Kulicke and Kniewske (1981) attributed the viscosity loss of aqueous polyacrylamide co-sodium acrylates to a conformational change of single molecules involving intra-molecular hydrogen bonds. These authors interpreted the pronounced time dependence of the viscosity by a cooperative effect of loosening and combining of hydrogen bonds. As could be expected, the nonionic polymer (N100), which is naturally coiled in aqueous solutions should be unaffected by such conformation transitions.

In 0.01M NaCl, the reduced viscosity of both N100 and A150 are remarkably stable over the entire time investigated. In the case of A150, the presence of counterions in solution from NaCl compensates the repulsive forces along the polymer chain by shielding the dissociated carboxylate functional groups resulting in a coiled conformation that is not further affected by

aging effects. The data show that aging of PAM results in a change of polymer conformation rather than in polymer degradation. Since carboxylate groups are weakly acidic, they can be expected to hydrolyze over time. The reaction would possibly proceed as:



yielding increasing amounts of associated uncharged carboxylic groups. The presence of these uncharged groups along the polymer chain should reduce electrostatic repulsion between carboxylic groups and promote the coiling of PAM. This chemical change would have a similar effect on the overall conformation of PAM to the screening role of sodium ions mentioned earlier. Simultaneously, OH^- ions should be released into solution and this was confirmed by measuring the pH of the flocculant solutions after the aging process. It can be seen from Table 4.3 that the steady increase in the pH from N100 to A150 is consistent with increasing content of carboxylate groups. Due to the presence of residual anionic charges in the nonionic flocculant (N100), its pH increased only slightly compared to that of distilled water (pH 5.3) that was used to prepare the solutions. A larger increase in pH can be observed for the more anionic flocculants as more carboxylate groups hydrolyze to release higher amounts of OH^- .

Table 4.3: Changes in pH with aging of flocculant solutions (distilled water used to prepare the flocculant solutions had a pH value of 5.3)

Flocculant	pH after aging (3 days)
N100	5.86
A100	6.17
A110	6.41
A130	6.92
A150	7.44

From the experimental point of view, it was important that further viscosity investigations be carried out with these results in mind, and consequently all polymer solutions were prepared daily, left to stand overnight (for 8-10 hours) and used within 24 hours of preparation.

4.3 Molecular Weight Determination

The molecular weights of the flocculants were determined using the $[\eta]$ - M relationship described in section 2.2.5. It should be clearly stated that the value obtained using this relationship is the viscosity-average molecular weight, \bar{M}_v , and not the weight-average molecular weight (M_w), as usually reported by polymer suppliers. The Mark-Houwink-Sakurada (M-H-S) parameters for nonionic and anionic polyacrylamides utilized in the calculation of the viscosity-average molecular weights were presented by Conrad and Klein (1978). It should be noted that there are numerous studies in literature that present M-H-S parameters (see section 2.2.5). Most of these studies have shortcomings in that they seldom state the precise conditions under which the experiments were performed. For example, it is very rare to find studies that mention the pH under which the parameters were obtained.

The intrinsic viscosities of the flocculants for the calculation of molecular weights were determined under exactly the same conditions as those used by Conrad and Klein, i.e., 0.5M NaCl and 25°C. The experiments were performed at natural pH since Conrad and Klein did not provide the pH value at which they determined the M-H-S parameters. It was possible to obtain the intrinsic viscosities of the anionic flocculants from the Huggins plots since polyelectrolyte effects are basically suppressed in 0.5M NaCl. Figure 4.5 shows the reduced viscosity vs. concentration plots from which the intrinsic viscosities were obtained. For clarity, the plot for the A150 flocculant is shown on a separate figure (4.6).

A set of results for a totally nonionic polyacrylamide (from Polysciences Inc.) of known weight-average molecular weight (5-6 million) is shown in Figure 4.5 as reference.

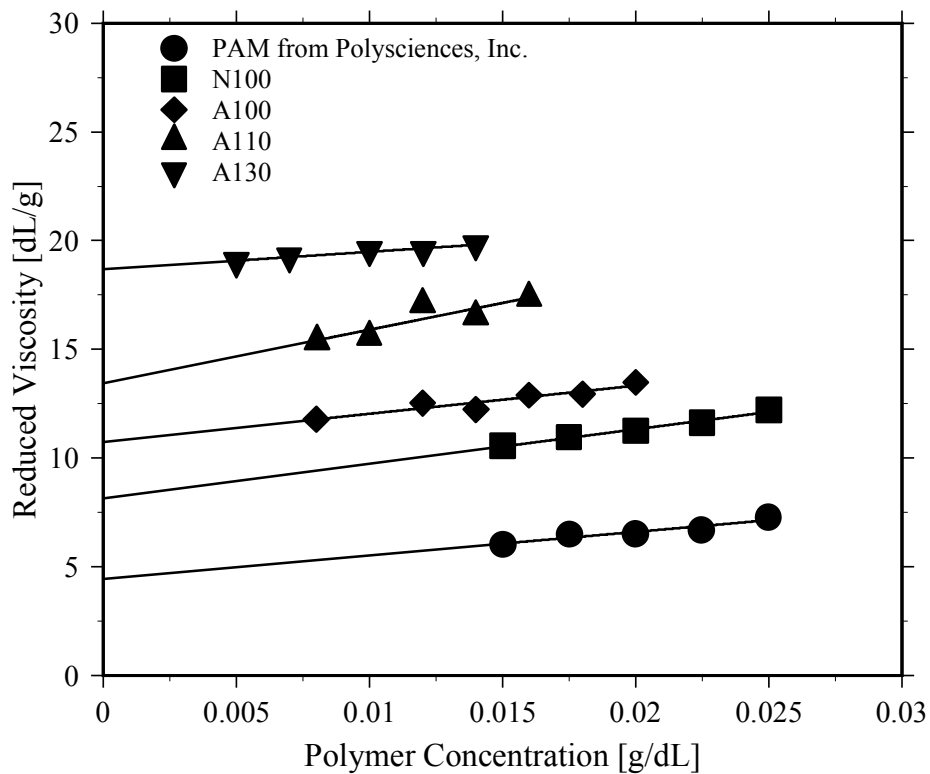


Figure 4.5: Dependence of reduced viscosity of the flocculants on concentration in 0.5 M NaCl at 25°C and natural pH.

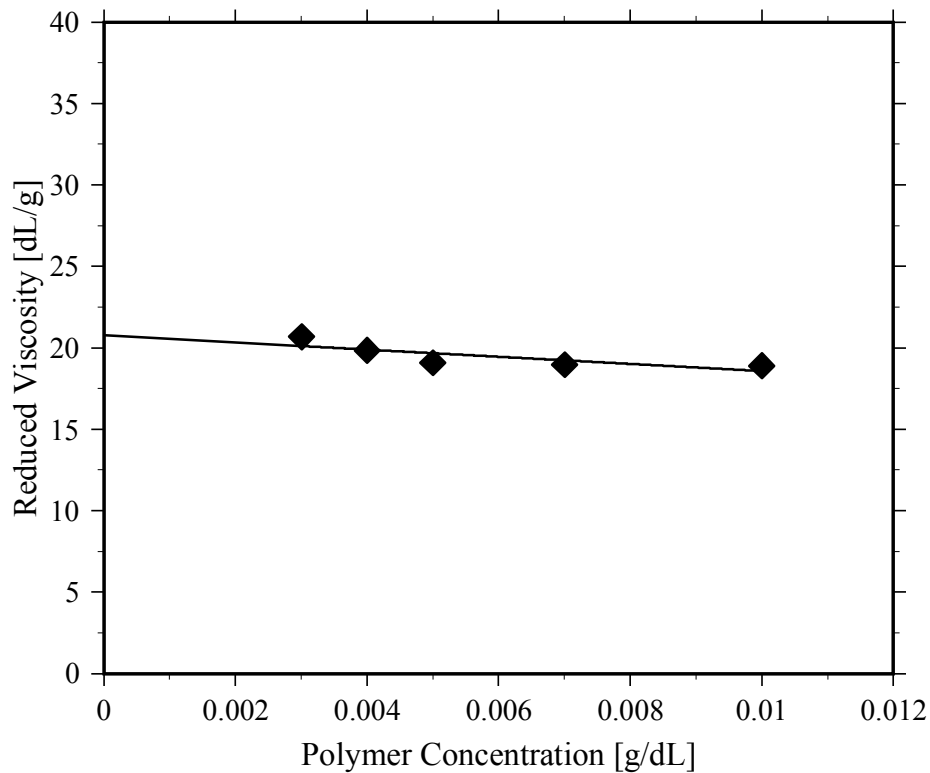


Figure 4.6: Dependence of reduced viscosity of the A150 on concentration in 0.5 M NaCl at 25°C and natural pH.

It should be noted that different concentration ranges were used for the flocculants in order to satisfy the conditions described in sections 2.2.2 and 3.1.2. Table 4.4 displays the intrinsic viscosity values and viscosity-average molecular weights of the flocculants.

Table 4.4: Intrinsic viscosities, M-H-S parameters (K and α) and viscosity-average molecular weights (M_v) of the flocculants in 0.5 M NaCl at 25°C and natural pH.

Flocculant	Intrinsic viscosity [dL/g]	K	α	M_v [g/mol]
PAM (5-6 million)*	4.5	7.2×10^{-3}	0.77	1.7×10^6
N100	8.1	7.2×10^{-3}	0.77	3.6×10^6
A100	10.7	6.6×10^{-3}	0.79	3.9×10^6
A110	13.4	6.2×10^{-3}	0.81	3.9×10^6
A130	18.7	6.3×10^{-3}	0.82	4.7×10^6
A150	20.8	7.2×10^{-3}	0.82	4.6×10^6

* Reference polyacrylamide sample from Polysciences, Inc.

To establish the validity of this method, a nonionic PAM sample obtained from Polysciences, Inc. (Warrington, PA) was tested under the same conditions. As can be seen in Table 4.4, this PAM sample gave an intrinsic viscosity of 4.5 dL/g and a viscosity-average molecular weight of 1.7 million. This is about 3-4 times lower than the weight-average molecular weight value provided by Polysciences, Inc. Thus it seems likely that the viscosity-average molecular weights presented in Table 4.4 are lower than the actual weight-average molecular weights of the flocculants by a factor of 3-4.

One of the limitations of M-H-S parameters found in literature is that they are not valid over the whole range of molecular weights. The parameters provided by Conrad and Klein are valid over the molecular weight range from $M_w = 5 \times 10^5$ to 5.5×10^6 and the acrylate composition range from 0% to 70%.

It must also be said that the M-H-S parameters may be specific to the type of viscometer used. Conrad and Klein used a Zimm-Crother viscometer and Contraves Low-shear-100 viscometer whereas a #75 Cannon-Fenske capillary viscometer was used in this study. Other authors have reported significantly lower molecular weights when different viscometers were used to determine viscosity-average molecular weights. For example, Taylor (2002) used an Übbelohde viscometer to determine viscosity average molecular weights for a nonionic and anionic flocculant and found that the average values obtained using M-H-S parameters by

Conrad and Klein (1978) and McCarthy et al. (1987) were significantly lower than those determined by light scattering. McCarthy and co-workers used a #75 Cannon-Fenske capillary viscometer.

The above discussion shows that the M-H-S parameters found in literature need to be carefully scrutinized before using them. It is also important to observe that different K and α values are assigned to flocculants of different degrees of anionicity, as discussed by Conrad and Klein (1978) and McCarthy et al. (1987). However, despite these shortcomings, $[\eta]$ - M relationships provide a relatively quick method for estimating the molecular weights of flocculants. In this case, the viscosity-average molecular weight values presented in Table 4.4 suggest that there are no significant differences in the molecular weights of the flocculants, and therefore the relative changes of the intrinsic viscosity for the different flocculants are primarily a result of their conformational changes and not so much due to differences in the absolute molecular weights.

4.4 Intrinsic Viscosity Measurements

The principal part of this study involved determination of intrinsic viscosities of the polymer solutions to infer their molecular configuration in solution. For the nonionic polymer (N100), the kinematic viscosity data obtained from capillary viscometry were converted to relative viscosities and reduced viscosities, which were then plotted as a function of polymer concentration according to the Huggins equation ($\eta_{red} = [\eta] + k_H [\eta]^2 c$ - where η_{red} is the reduced viscosity, $[\eta]$ is the intrinsic viscosity, k_H is the Huggins coefficient and c is the polymer concentration). Plots of the reduced viscosity vs. polymer concentration gave straight lines with intercept equal to $[\eta]$. Figure 4.7 shows an example of plots of reduced viscosity against concentration for N100 in distilled water and 0.01 M NaCl at 25°C, 35°C and 50°C. The intrinsic viscosities were obtained from the y-intercepts of the plots.

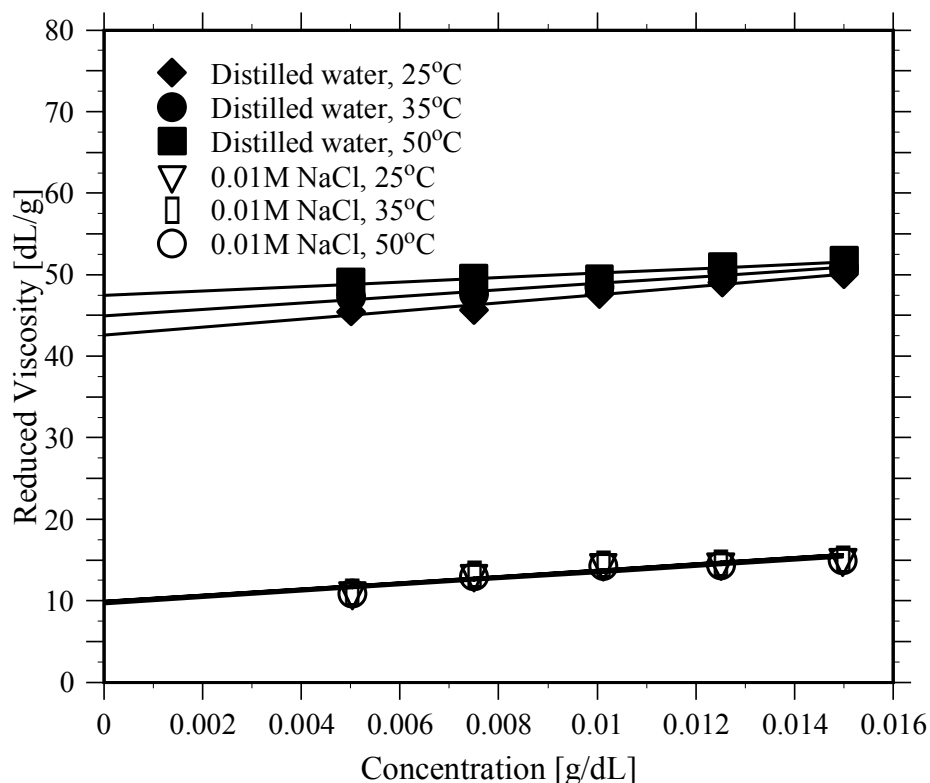


Figure 4.7: Reduced viscosity vs. polymer concentration for N100 in distilled water (natural pH 4.9–6) and 0.01 M NaCl (natural pH 5.3-5.7) at different temperatures.

When Fedors equation (Equation 2.16, section 2.2.4) was fitted to the data in Figure 4.7, the intrinsic viscosity values obtained were virtually the same as those obtained using the Huggins equation. For example, in distilled water at natural pH and 25°C, the $[\eta]$ obtained from the Huggins equation was 42.6 dL/g while that obtained by fitting the Fedors equation to the data was 42.9 dL/g. Similarly, in 0.01M NaCl, the values of $[\eta]$ obtained from the Huggins equation and Fedors equation were 9.9 dL/g and 9.7 dL/g respectively.

Due to the polyelectrolyte effect, the Huggins equation could not be used to obtain intrinsic viscosities of the anionic flocculants. After determining the kinematic viscosities, they were converted to relative viscosities and reduced viscosities. Then, second order polynomial equations (Equation 2.6 up to the c^2 term) were fitted to the data to obtain intrinsic viscosities which were used as reference values. The empirical Fuoss & Cathers and Fedors equations (Equations 2.15 and 2.16 respectively) were then tested on the data and compared to the polynomial fits. Figures 4.8 and 4.9 show the polynomial fits for the anionic flocculants in distilled water and 0.01 M NaCl at natural pH and 25°C.

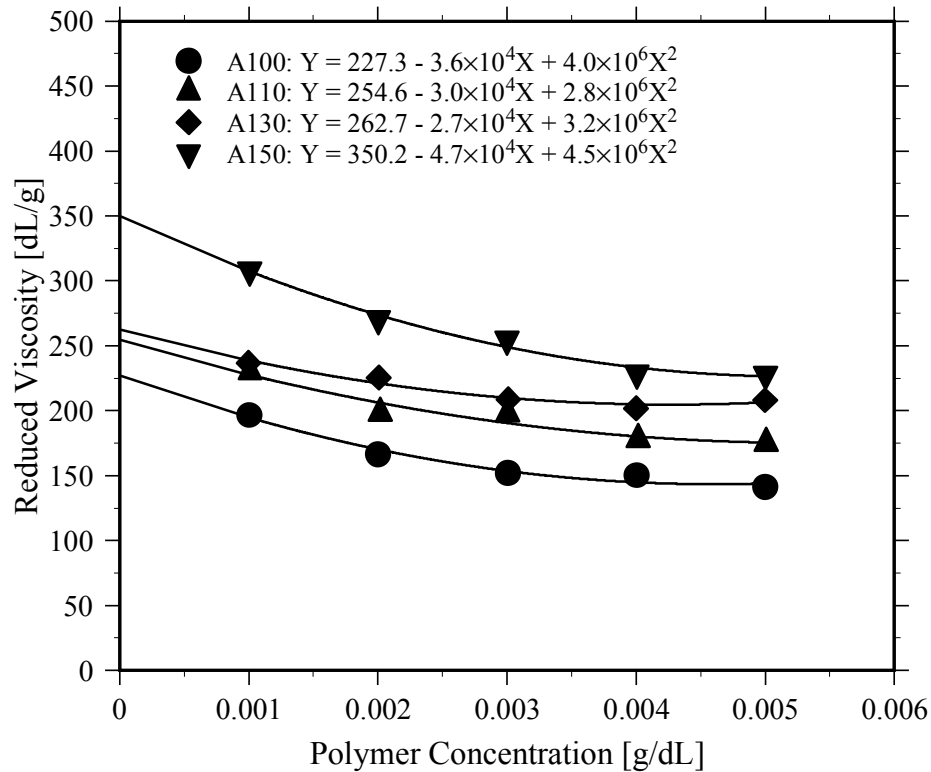


Figure 4.8: Reduced viscosity vs. polymer concentration for the anionic flocculants in distilled water at natural pH and 25°C

As Figure 4.8 shows, the reduced viscosities of the anionic flocculants decrease with increasing polymer concentration. At low polymer concentration, the dissociation of the ionic groups of the flocculant chains increases. This is accompanied by increasing repulsive forces between neighboring carboxylate groups which results in expansion of the chain and hence an increase of the reduced viscosity at low polymer concentration. The intrinsic viscosities of the flocculants are the first constants of the second-order polynomial equations fitted to the data.

Figure 4.9 shows that in the presence of 0.01 M NaCl, there is a decrease in the reduced viscosities and intrinsic viscosities for all the flocculants. However, the NaCl concentration is not enough to completely suppress the polyelectrolyte (non-linear) behaviour. Similarly, second-order polynomial fits allowed the intrinsic viscosities to be determined.

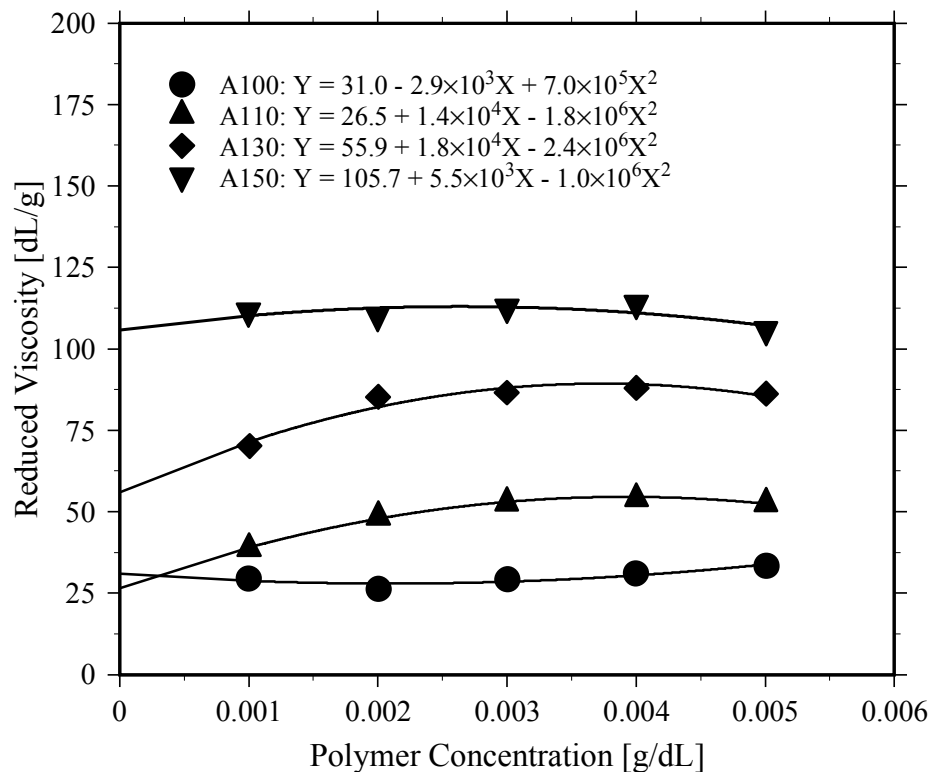


Figure 4.9: Reduced viscosity vs. polymer concentration for the anionic flocculants in 0.01 M NaCl at natural pH and 25°C

Figures 4.10 and 4.11 show the Fuoss and Cathers representation of the data from Figures 4.8 and 4.9, respectively. The inverse of the reduced viscosity (c/η_{sp}) was plotted against $c^{0.5}$ according to Equation 2.15 and the intrinsic viscosities were obtained from the reciprocal of the y-intercepts.

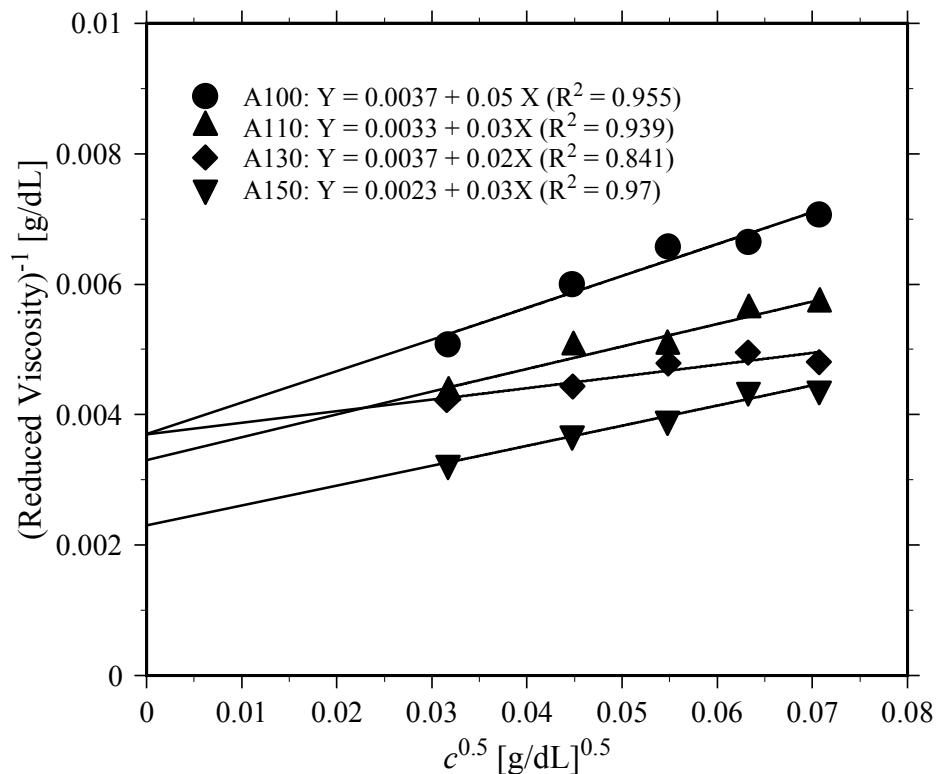


Figure 4.10: Fuoss and Cathers representation of data from Figure 4.8 (Anionic flocculants in distilled water at natural pH and 25°C).

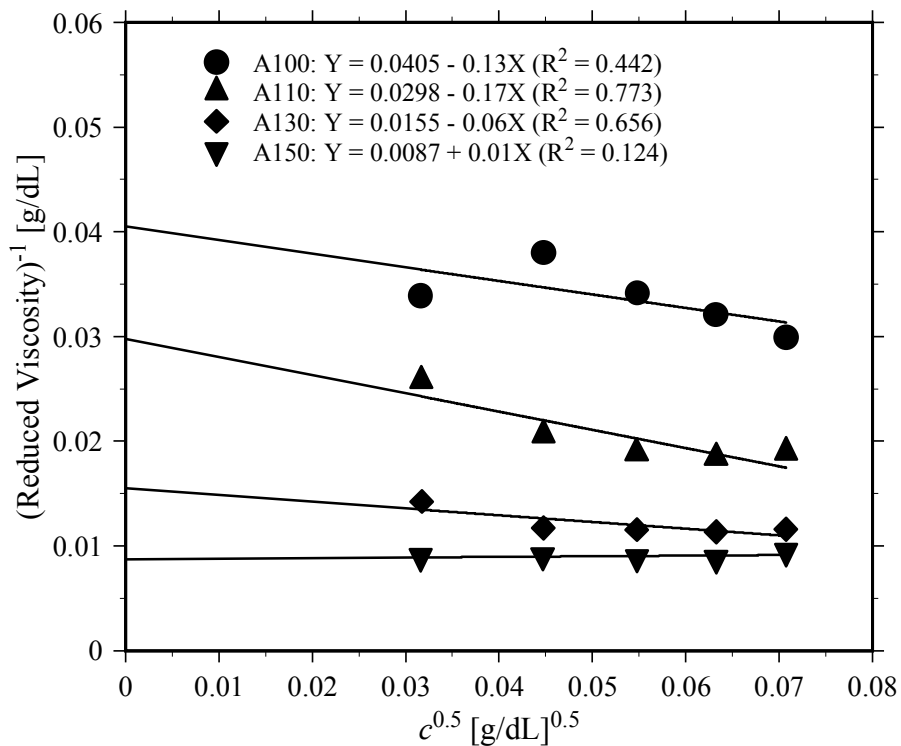


Figure 4.11: Fuoss and Cathers representation of data from Figure 4.9 (Anionic flocculants in 0.01 M NaCl at natural pH and 25°C). Note that due to the left ordinate scale, the low R^2 values and the relative large scatter of the data for the bottom two flocculants (A130 and A150) are not immediately obvious.

It can be seen in Figures 4.10 and 4.11 that the Fuoss and Cathers equation provides fairly good fits in distilled water but the fits obtained in NaCl are not very good as seen from the coefficient of determination (R^2) values, and from the general non-linear trends in the data.

It is well documented in literature that although the empirical Fuoss and Cathers equation can be used as a relative measure of the polymer coil expansion in solution, it does not produce good enough fits to obtain reliable intrinsic viscosities (Cohen et al., 1988; Bohdanecky & Kovar, 1982). Some authors (Ma et al., 2003; Pavlov et al., 2006) used the Fuoss and Cathers equation to obtain intrinsic viscosities of polyelectrolytes and although they obtained fairly good linear fits, they found that not all the data were always well described by the equation. Rattanakawin (2002) reported that he successfully used the Fuoss and Cathers equation to obtain intrinsic viscosities of anionic polyacrylamides (Anionicity of 0% – 30%). However, it should be noted that the solution viscosities of Rattanakawin (2002) were obtained in rather concentrated solutions with polymer concentrations higher than the overlap concentration, c^* (discussed in section 2.2.2). This basic omission makes it difficult to ascertain how applicable the Fuoss and Cathers equation really was.

Pavlov et al. (2006) noted that for some data, $[\eta]$ obtained from the Fuoss extrapolation was on average twice that obtained by the iso-ionic dilution method, suggesting that the Fuoss extrapolation method provides an overestimated volume occupied by the polyelectrolyte molecules at infinite dilution. The iso-ionic dilution method was described by Pavlov et al. (2006).

Figures 4.12 and 4.13 show plots of $\frac{1}{[2(\eta_{rel}^{1/2} - 1)]}$ vs. $1/c$ (η_{rel} - relative viscosity; c - polymer concentration) of the data taken from Figures 4.8 and 4.9 according to the Fedors equation. The intrinsic viscosities were obtained from the reciprocal of the slopes. It should be pointed out that Fedors equation was initially developed using nonionic latex suspensions but was later found to apply to dilute solutions of nonionic and ionic hydrophobically-associating polyacrylamides (Ma et al., 2003).

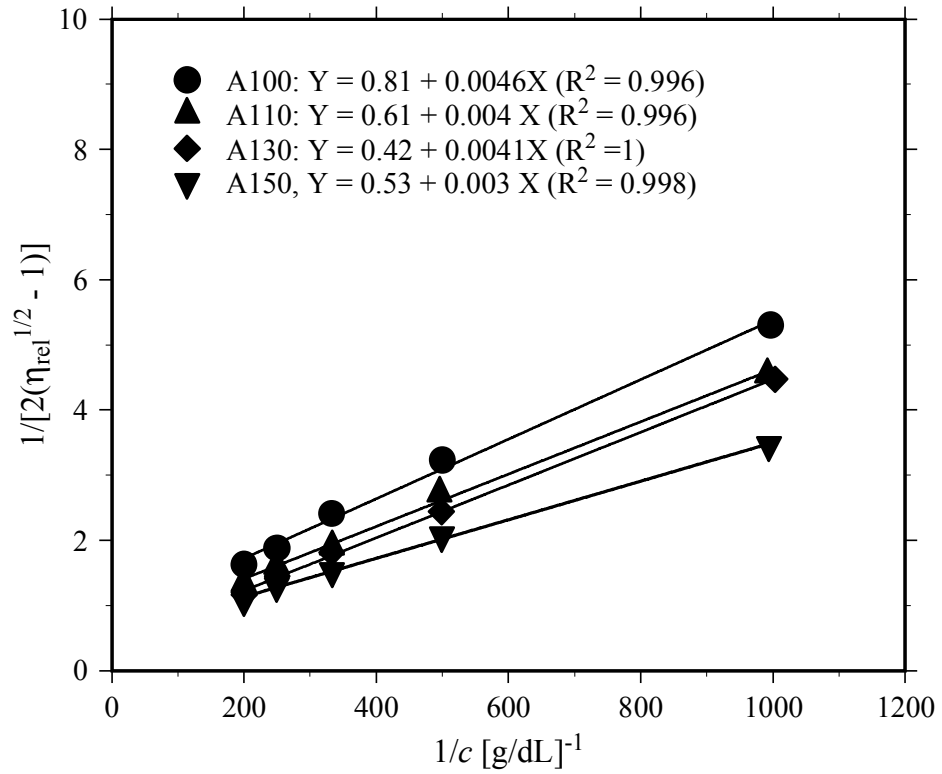


Figure 4.12: Fedors representation of data in Figure 4.8 (Anionic flocculants in distilled water at natural pH and 25°C).

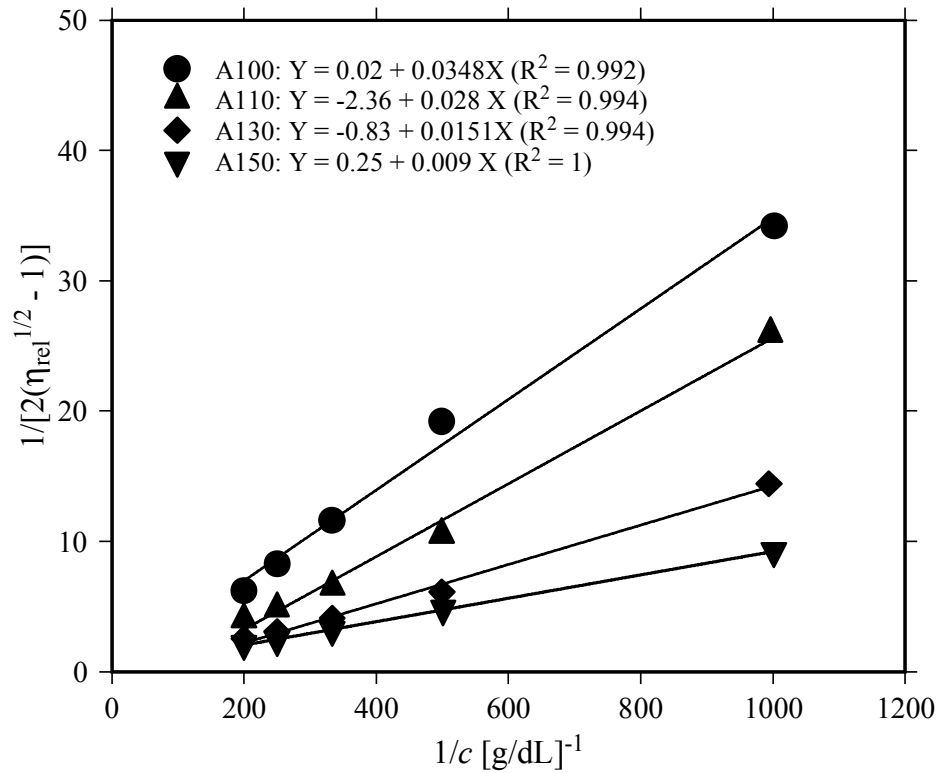


Figure 4.13: Fedors representation of data in Figure 4.9 (Anionic flocculants in 0.01 M NaCl at natural pH and 25°C).

Significantly, the Fedors equation provides excellent fits to the data. The intrinsic viscosities obtained from the polynomial fits (Figures 4.8 and 4.9), Fuoss and Cathers plots (Figures 4.10 and 4.11) and Fedors equation (Figures 4.12 and 4.13) in distilled water and 0.01 M NaCl at 25°C and 50°C are summarized in Table 4.5.

Table 4.5: Intrinsic viscosities of the anionic flocculants obtained by different equations at 25°C and 50°C

Natural pH, 25°C ([η] in dL/g)						
Flocculant	Second-order Polynomial		Fedors		Fuoss & Cathers	
	Distilled water	0.01M NaCl	Distilled water	0.01M NaCl	Distilled water	0.01M NaCl
A100	227.3	31	217.4	28.7	270.3	24.7
A110	254.6	26.5	250	35.7	303	33.6
A130	262.1	55.9	243.9	66.2	263.2	64.5
A150	350.2	123.7	333.3	111.1	400	114.9
Natural pH, 50°C ([η] in dL/g)						
A100	250.8	31.1	243.9	28	322.6	23.6
A110	266.9	23.3	256.4	31.3	312.5	28.7
A130	267.4	42.1	256.4	43.5	303	38.8
A150	341.4	80.2	322.6	82.6	400	80.6

From the comparisons presented in Figures 4.8 through 4.13 and Table 4.5 between Fedors and Fuoss & Cathers equations using the second order polynomial fits as the reference equations, the Fedors equation turned out to be the best equation since it consistently yielded excellent fits to all the raw viscosity data. Consequently, the Fedors equation was used to evaluate all the raw viscosity data and to determine the intrinsic viscosities of the flocculants. The complete results for all the flocculants under all the conditions investigated can be found in Appendices II, III, IV and V.

4.4.1 Intrinsic Viscosities of Flocculants in Distilled Water: Effect of pH and Temperature

Figures 4.14 to 4.16 show the effect of pH on the intrinsic viscosities of the flocculants in distilled water at different temperatures.

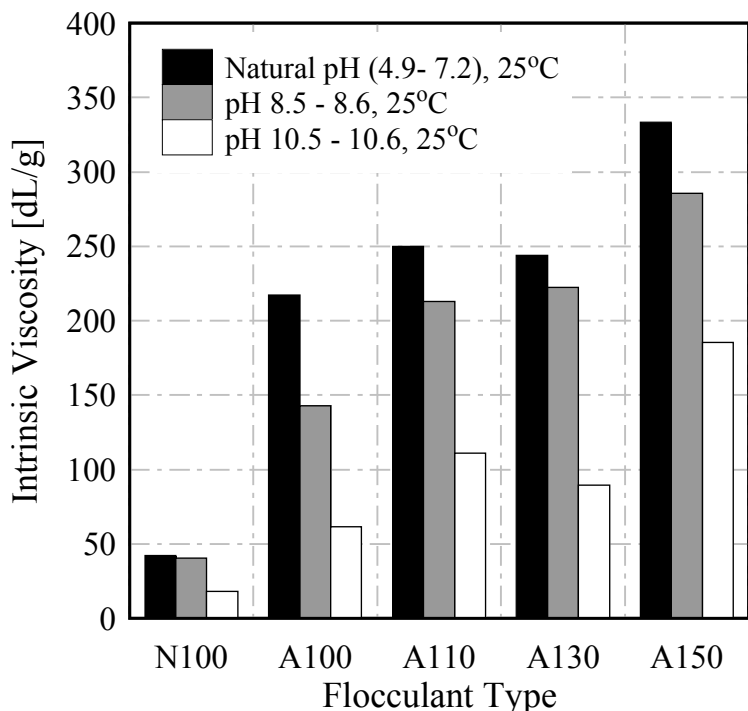


Figure 4.14 Effect of pH on the intrinsic viscosities of flocculants in distilled water at 25⁰C

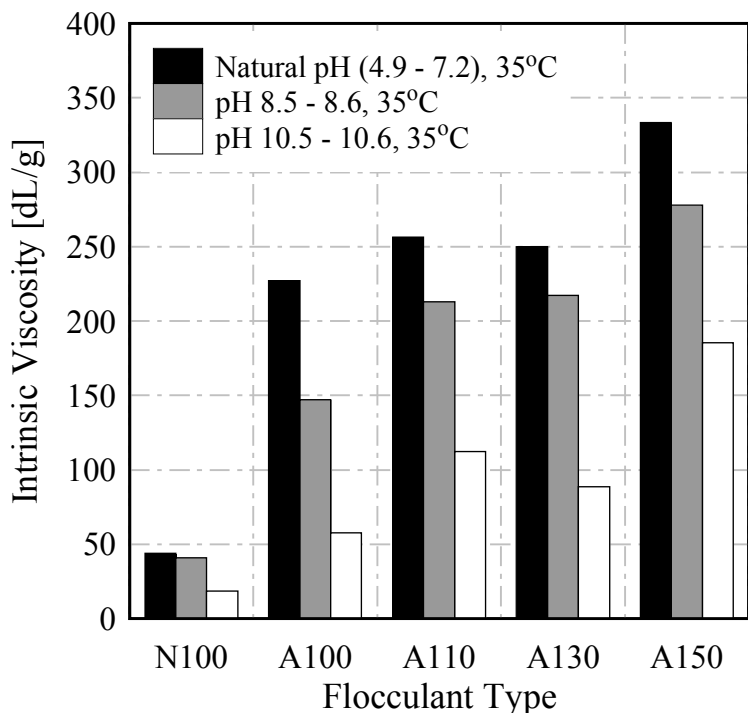


Figure 4.15: Effect of pH on the intrinsic viscosities of flocculants in distilled water at 35⁰C

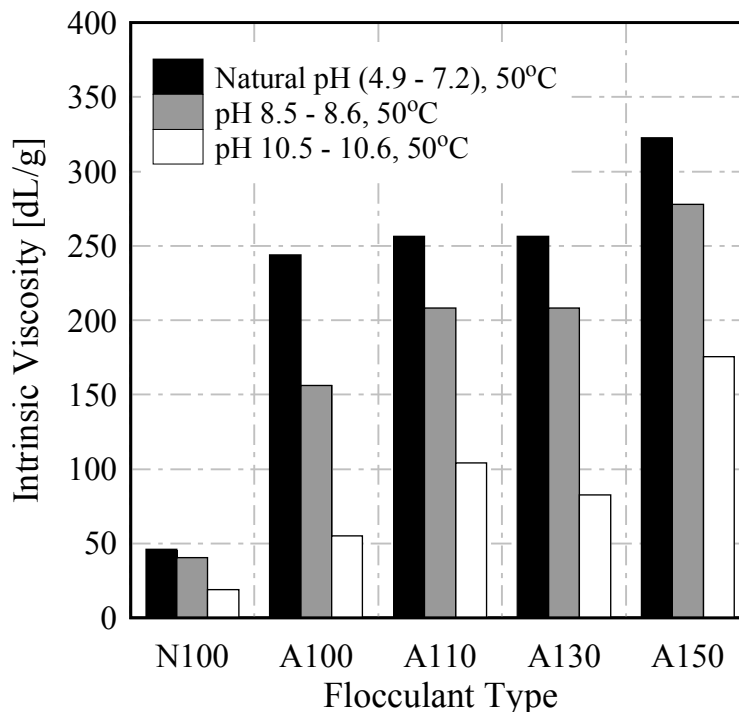


Figure 4.16: Effect of pH on the intrinsic viscosities of flocculants in distilled water at 50°C

As can be seen from Figures 4.14 to 4.16, the intrinsic viscosities generally increase from N100 (lowest degree of anionicity) to A150 (highest degree of anionicity) clearly indicating the effect of the coulomb repulsive forces as the content of the negatively charged carboxylate groups increases from N100 to A150. The repulsion between neighboring charged groups results in a stretched polymer conformation in the case of A150 which produces the highest intrinsic viscosity. The nonionic polymer (N100) is always in a coiled state which explains the relatively low intrinsic viscosity.

The intrinsic viscosities for each flocculant are highest at natural pH in distilled water. The carboxylic acid units on the polymer chains are weakly acidic and so their dissociation is a strong function of pH. It was expected that the dissociation would proceed steadily up to highly alkaline solutions resulting in further extension of the macromolecules and in increasing intrinsic viscosities. However, as the data from Figures 4.14–4.16 indicate, the carboxylic groups seem to be sufficiently dissociated at natural pH, as shown by the highest intrinsic viscosities. This observation is corroborated by studies carried out on polyacrylic acid (PAA) by Gebhardt and Fuerstenau (1983). These authors determined that PAA is already 50% ionized at pH 4.5.

Richardson and Connelly (1988) also reported that, using the pK_a value of acrylic acid (4.25), the acrylate/acrylic acid ratio is approximately 560:1 at pH 7 while at pH 3, all the acrylate is in the acid form meaning that at pH \sim 7, polyacrylate would be extended in solution while the polymer will be much more coiled at pH 3.

The results also indicate excellent solvation of the polymer chains by water. This facilitates chain extension which results in high intrinsic viscosities. It is therefore expected that the macromolecules have the largest effective dimensions at natural pH which should be beneficial for the 'bridging mechanism' of flocculation.

When the pH is increased to approximately 8.5, there is a slight decrease in the intrinsic viscosity. There is a further decrease at higher pH (\sim 10.5) that is more pronounced for the anionic flocculants than for the nonionic flocculant (N100). The pH adjustment with NaOH was effected by the addition of a few drops of concentrated NaOH to minimize dilution of the already dilute polymer solutions. Therefore, the most plausible explanation for this decrease is that an increase in ionic strength at high pH due to NaOH addition results in increased shielding of the repulsive carboxylate groups as more counterions (Na^+ ions) are introduced into solution.

It is interesting to note that the difference between intrinsic viscosities of A110, A130, and A100 (at natural pH and pH 10.5) is not so significant, despite the A130 having a much higher degree of anionicity (Table 4.2).

The intrinsic viscosity is not significantly affected by temperature in the investigated range (25°C to 50°C) as seen from Figures 4.14 through 4.16. The effect of temperature on the conformation of polymers should largely depend on the nature of the solvent (Bit et al., 2006). In a poor solvent, the dissolution of the polymer is an endothermic process. In such a system, there is a tendency of the polymer molecules to attract each other even in dilute solutions and so an increase in temperature results in an increase in $[\eta]$. However, in a good (favorable) solvent, the polymer chains are well solvated resulting in a stretched conformation. The polymer-solvent interactions prevail and an increase in temperature should result in a decrease in $[\eta]$.

Vangani and Rakshit (1996) described two effects that an increase in temperature can have on a polymer system: firstly, increase in temperature can enhance the solubility of the polymer resulting in increased solvation and higher intrinsic viscosity. Secondly, increase in temperature may enhance the flexibility (degree of rotation) of the bonds making up the polymer structure by lowering the rotational barrier. This results in a more coiled conformation leading to a decrease in intrinsic viscosity. Generally, for all the flocculants evaluated, there is little change in the

intrinsic viscosity with temperature without any clear trend at a given pH. This observation suggests that neither of the effects of increasing temperature dominates which leads to a conclusion that distilled water acts as an athermal solvent for these flocculants.

To monitor possible depolymerisation of the flocculants at higher temperature, control measurements were performed by cooling the sample solutions from 50°C to 25°C and determining the intrinsic viscosity again at 25°C. As stressed above, the effect of temperature on the flocculants' intrinsic viscosity is not very significant though measurable changes are noted especially in case of the A130 and A150 flocculants. However, when the values of intrinsic viscosities at 25°C before and after heating are compared (Appendix V), it is seen that whereas the effect of temperature is nearly reversible in the case of flocculants N100, A100 and A110, the reduced viscosity and intrinsic viscosity values for A130 and A150 (the most anionic) do not necessarily recover back to 25°C. The values either do not change after cooling from 50°C to 25°C or they approach the values obtained at 35°C. This could be a result of partial 'depolymerization' of the flocculants although it must be stressed that this breakdown is practically insignificant since the intrinsic viscosity values at 25°C, 35°C and 50°C do not vary significantly. The more likely reason is the earlier observed effect of temperature on the aging, hydrolysis and conformation of the N100 and A150 flocculants. The A150 is affected by temperature more than the N100 is, and this conformational change for the A150 seems to be irreversible.

4.4.2 Effect of Electrolyte Addition

Figures 4.17 to 4.19 show the intrinsic viscosities of the flocculants in sodium chloride solution of constant ionic strength (0.01 M) at different pH and temperature.

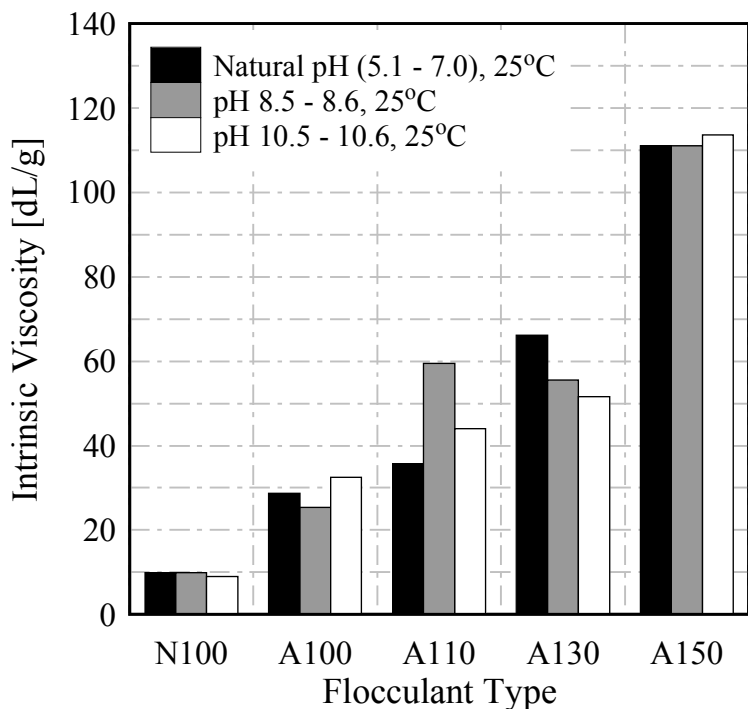


Figure 4.17: Effect of pH and 0.01 M NaCl on the intrinsic viscosities of flocculants at 25°C

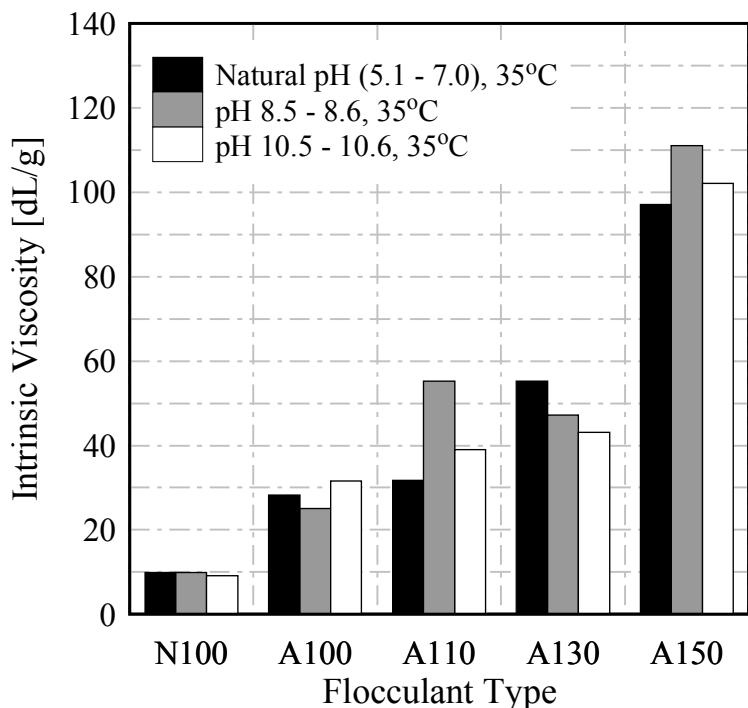


Figure 4.18: Effect of pH and 0.01 M NaCl on the intrinsic viscosities of flocculants at 35°C

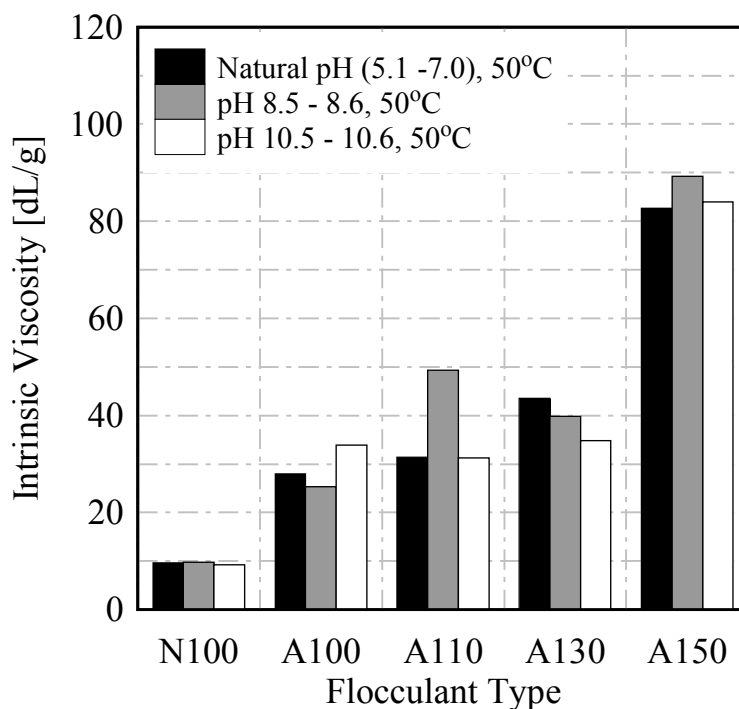


Figure 4.19: Effect of pH and 0.01 M NaCl on the intrinsic viscosities of flocculants at 50°C

When the flocculants are prepared and tested in NaCl solution (0.01mol/L) there is a dramatic contraction of the macromolecules which is reflected in a marked decrease in intrinsic viscosity values. This is clearly seen by comparing Figures 4.14–4.16 and Figures 4.17–4.19. In the case of the anionic flocculants, the intrinsic viscosity values in NaCl decrease as much as 8 times compared to those obtained in distilled water. A decrease of ~75% for the nonionic flocculant (N100) was unexpected since ideally uncharged polymers should be stable in salt solutions but it seems that the residual anionic charge (Table 4.2) is enough to induce a slight polyelectrolyte effect in solutions of N100. A very important observation is the large *relative* decrease (~ 8 times) of the intrinsic viscosities of the moderately anionic flocculants (A100 and A110) compared to the nonionic (N100) and more anionic flocculants (A130 and 150) which show a decrease of 3-4 times when tested in NaCl. This trend seems to suggest that the moderately anionic flocculants are much more flexible than the nonionic and most anionic flocculants, and thus collapse (coil) much more easily in the presence of Na⁺ counterions. This also possibly explains why different Mark-Houwink-Sakurada parameters are used in the calculation of molecular weights of flocculants with different degrees of anionicity (see section 4.3).

Contradictory results on the effect of added electrolyte have been presented in literature. While Conrad and Klein (1978) and Klimchuk (1997) reported that $[\eta]$ of nonionic PAM decreased with increasing NaCl concentration, Muller et al. (1979) determined that the reduced viscosity of nonionic PAM increased with increasing NaCl concentration. Also, Eliassaf and Silberberg (1959) found that the specific viscosity of nonionic PAM was not altered by the addition of up to 3.66 N NaCl. In the case of anionic PAM, similar results as seen in this study were obtained by Muller et al. (1979) and Klimchuk (1997).

The effect of an electrolyte such as NaCl on the polymer solution can be explained in terms of the osmotic potential around the polymer chain. With addition of NaCl, there is an increase in the concentration of counterions outside the polymer coil than inside and this suppresses the diffusion of the counterions. The counterions then shield the dissociated carboxylate groups and this leads to contraction of the polymer chain, and a decrease in the intrinsic viscosity.

As also observed in distilled water, the intrinsic viscosities of the flocculants in NaCl are independent of temperature but there is a measurable decrease as temperature increases in the case of A130 and A150. The effect of pH on the intrinsic viscosities at constant ionic strength is also not dramatic apart from the A110 which shows a marked increase at pH 8.5. At this point, it is not clear why this polymer behaves so. It can, however, be concluded that once the polymer molecules are coiled by the addition of NaCl, electrostatic repulsion between dissociated carboxylate groups at higher pH is insufficient to expand the coils to a more extended conformation. The presence of background ions rather than pH seems to be the dominant factor in determining the conformation of PAM.

The addition of small quantities of CaCl_2 (0.001 mol/L) to N100 and A130 previously prepared in 0.01M NaCl resulted in a further decrease in intrinsic viscosity in the case of A130 while there was practically no effect on N100 as shown in Figure 4.20.

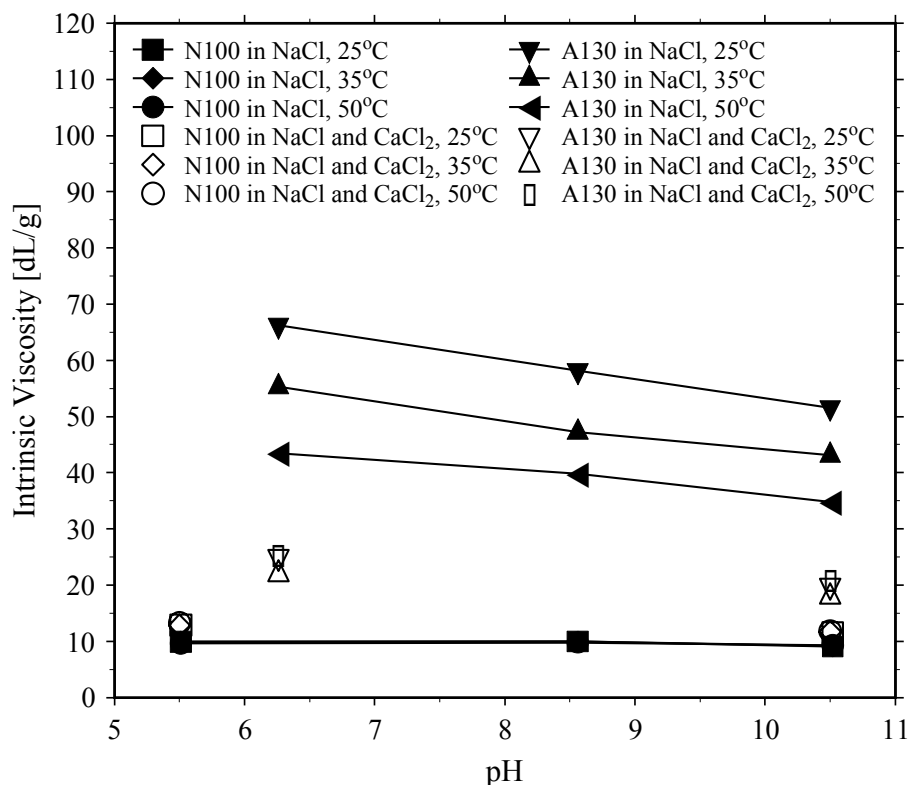


Figure 4.20: Effect of 0.001M CaCl_2 on the intrinsic viscosities of flocculants in 0.01M NaCl at different temperatures.

The results illustrate well the high affinity of calcium ions towards the carboxylic groups of anionic PAM, as similar results were obtained by Muller et al. (1979) working with a highly hydrolyzed PAM sample. The decrease was sharper in calcium chloride solutions than in solutions of monovalent salts (NaCl). At high salt concentrations (1 mol/L NaCl and 0.4 mol/L CaCl_2), Muller et al. found that precipitation took place due to the complexation of Ca^{2+} ions by the negatively charged carboxylate groups.

From Figure 4.20, it is remarkable to observe that in the presence of monovalent and divalent salts (0.001 mol/L CaCl_2 and 0.01 mol/L NaCl), the A130 assumes a similar coiled conformation to the nonionic N100. The already small effect of temperature entirely disappears in the presence of a small amount of calcium ions, and the anionic polymer behaves just like the nonionic one. This observation correlates well with the aging data for the A150 polymer obtained at a higher temperature (50°C). The results suggest that, from a practical point of view, there is

no relative advantage of using highly anionic flocculants over nonionic flocculants in suspensions that contain appreciable amounts of cations, more so if the cations are polyvalent (e.g., Ca^{2+} , Mg^{2+}). In such systems, the overall flocculation result would be determined by the surface properties of the solid rather than by the solution properties of the flocculant.

It is also interesting to note from Figures 4.5 and 4.6 (section 4.3) that there is a further dramatic decrease in the intrinsic viscosities of the anionic flocculants in 0.5 M NaCl compared to the values obtained in 0.01 M NaCl. Also, in case of the A130, the effect of very small amounts of CaCl_2 (0.001 M) is almost the same as that of 0.5 M NaCl as seen from the intrinsic viscosity values (25 dL/g in 0.001 M CaCl_2 and 0.01 M NaCl—Figure 4.20, section 4.4.2; and 18.7 dL/g in 0.5M NaCl—Table 4.4, section 4.3).

5.0 Conclusions and Recommendations

For the first time, a systematic study of the effect of temperature, pH and ionic strength on the intrinsic viscosity of typical industrial flocculants of varying degrees of anionicity was carried out. It was found that the Fedors equation could quite universally be used for obtaining intrinsic viscosities of both weakly- and strongly-anionic flocculants from the raw viscosity data over a wide range of physicochemical conditions.

A simple method of using chemical assays of total organic carbon and sodium was found to be useful in determining the degree of anionicity of industrial flocculants investigated (N100, A100, A110, A130 and A150). The infrared spectroscopy results were not as useful as anticipated especially for the flocculants with low degrees of substitution. The highly anionic flocculants (A130 and A150) produced results comparable to those from chemical assays.

It was established from aging studies that anionic flocculants show a time dependent alteration of the solution viscosity. The reduced viscosities of the most anionic flocculant (A150) decreased over the time investigated with the largest decrease occurring in distilled water at 50°C. No significant aging was observed in 0.01M NaCl and no changes with time were observed in the case of the nonionic flocculant (N100). This observation suggests that the anionic polymer gradually changes its conformation with time from a stretched one to coiled.

The conformation of the nonionic flocculant (N100) was unexpectedly found to be slightly sensitive to pH changes in the range 4.9 to 10.6 and to the presence of NaCl. The intrinsic viscosity of a solution of N100 in 0.01M NaCl was practically unaffected when small quantities of CaCl₂ were added. It seems that the coiling of N100 at high pH (10.5) and in the presence of 0.01M NaCl is due to the residual content of ionic groups that impart a weak polyelectrolyte behavior to the flocculant.

It was established that the anionic polyacrylamide-based flocculants are fully dissociated in distilled water at natural pH. Under these conditions, the flocculants assume fully stretched conformations as can be deduced from the high intrinsic viscosities. It was also found that the conformational properties of the anionic polymers were strongly dependent on the presence of NaCl and CaCl₂. The intrinsic viscosities decreased in the presence of these salts due to shielding of the negatively charged carboxylic groups by the counterions. From a practical point view, the results indicate that highly anionic flocculants should be well suited to suspensions with minimal quantities of salts while nonionic flocculant could be advantageous in suspensions with high concentrations of mixed salts.

The effect of temperature on the conformations of the flocculants was not very significant but was most pronounced for the more anionic flocculants. The intrinsic viscosity data indicated that, within experimental error, the molecular conformations of the flocculants do not appreciably change when temperature is raised from 25°C to 35°C and finally to 50°C. Therefore, it was also established that distilled water is an athermal solvent for these flocculants.

The results show that the behavior of PAM-based industrial flocculants is not affected by temperature or pH, provided that a background electrolyte is present which should be the case with the vast majority of practical systems, and that the overall flocculation result will largely be governed by the interfacial phenomena taking place at the solid-solution interface.

The moderately anionic flocculants, A100 and A110 seem to be much more flexible than the nonionic and most anionic flocculants in terms of their ability to coil or stretch as shown by the large *relative* decrease of their intrinsic viscosities when tested in 0.01M NaCl. This ability to change the effective size in solution should have a profound effect on the ability of the polymers to flocculate fine particles and to conform to the irregular shape and size of the resulting flocs. Therefore, it would appear that the A100 and A110 should be more efficient flocculants than the other PAM-based but more rigid polymers.

There is a need for much more accurate Mark-Houwink-Sakurada parameters for use in the determination of the molecular weight of flocculants. The available constants give good qualitative results but they need to be verified possibly by testing well-prepared molecular weight standards available from flocculant manufacturers.

All the stock flocculant solutions used in this study had concentrations of 1 g/L (the N100) and 0.5 g/L (the anionic flocculants). It would be advisable to perform similar measurements using more concentrated stock solutions, in which shear degradation or mechanical breakage of the PAM molecules may be expected due to the intense mixing required for the preparation of such concentrated polymer solutions.

All the flocculants tested in this study were sodium salts and it turned out that sodium assays together with total organic carbon assays gave most reasonable estimates of the degree of anionicity of the flocculants. There is still a need to develop more standardized direct analytical procedures for determination of degree of anionicity of polyacrylamides.

6.0 References

- Bercea, M., Morariu, S., Ioan, C., Ioan, S., and Simionescu, B.C., 1999, "Viscometric study of extremely dilute polyacrylonitrile solutions," *European Polymer Journal*, 35[11], 2019-2024.
- Bit. G., Debnath, B., Saha, S.K., 2006, "Dilute solution behaviour of progressively hydrolyzed polyacrylamide in water -N, N dimethylformamide mixtures", *European Polymer Journal*, 42, 544-552.
- Bohdanecký, M., and Kovar' R, J., 1982, "Viscosity of polymer solutions", Polymer Science Library 2. Amsterdam: Elsevier.
- Caulfield, M.J., Hao, X., Qiao, G.G., Solomon, D.H., 2007, "Degradation on polyacrylamides. Part I. Linear polyacrylamide", *Polymer*, 44[5], 1331-1337.
- Chalaturnyk R.J., Scott J.D., Özüm B., 2002, "Management of oil sands tailings," *Petroleum Science and Technology*, 20, 1025-1046.
- Chee, K.K., 1985, "Novel methods for efficient estimate of intrinsic viscosity", *Journal of Applied Polymer Science*, 30[6], 2607-2614.
- Cheng, R., Shao, Y., Liu, M., and Qian, R., 1998, "Effect of adsorption on the viscosity of dilute polymer solution," *European Polymer Journal*, 34[11], 1613-1619.
- Clark, A.Q., Herrington T.M., and Petzold J.C., 1990, "The flocculation of kaolin suspensions with anionic polyacrylamide of varying molar mass and anionicity", *Colloids and Surfaces*, 44, 247-261.
- Cohen, J., Priel, Z., Rabin Y., 1988, "Viscosity of dilute polyelectrolyte solutions", *Journal of Chemical Physics*, 88, 7111.
- Conrad, K.D., and Klein, J., 1978, "Molecular weight determination of polyacrylamide and polyacrylamide-co-sodium acrylate," *Makromol. Chem.*, 179, 1635-1638.
- Conrad, K.D., and Klein, J., 1980, "Characterization of polyacrylamide in solution," *Makromol. Chem.*, 181, 227-240.
- Cymerman, G., Kwong, T., Lord, E., Hamza, H. and Xu, Y., 1999, "Thickening and disposal of fine tails from oil sand processing", In: Polymers in Mineral Processing, J.S. Laskowski (Ed.), Metallurgical Society of CIM, Quebec City, p. 605.
- Das, K.K., 1999, "Investigations on the polyelectrolyte induced flocculation/dispersion of colloidal alumina suspensions", PhD. Thesis, Columbia University (USA).
- Ding, K., 2007, "Zero-conditioning time concept in flotation", PhD. Thesis, The University of British Columbia (Canada).

Dixon, J.K., 1986, "Flocculation", In: Encyclopedia of Polymer Science and Engineering, 2nd Ed. Vol 7, H.F. Mark, N.M. Bikales, C.G. Overberger, G. Menges (eds.), Wiley, New York, 211–233.

Eliassaf, J., and Silberberg, A., 1959, "The effect of hydrogen bonding addends on the dilute solution of poly(acrylamide), unionized poly(acrylic acid) and poly(methacrylic acid)", *Journal of Polymer Science*, 41[138], 33-51.

Fedors, R.F., 1979, "An equation for describing the viscosity of dilute to moderately concentrated polymer solutions", *Polymer*, 20[2], 225-228.

Fuoss, R.M., and Cathers, G.I., 1949, "Polyelectrolytes III: Viscosities of butyl bromide addition compounds of 4-vinyl pyridine –styrene copolymers in nitromethane-dioxane mixtures," *Journal of Polymer Science*, 3, 97-120.

Fuoss, R.M., and Strauss, U.P., 1948a, "Polyelectrolytes II: Poly-4-vinyl pyridonium chloride and poly-4-vinyl-N-n butyl-pyridonium bromide," *Journal of Polymer Science*, 3, 246-263.

Gebhardt, J.E., and Fuerstenau, D. W., 1983, "Adsorption of polyacrylic acid at oxide/water interfaces", *Colloids and Surfaces* 7[3], 221–231.

Ghannam, M.T., and Esmail, N.M., 1998, "Rheological properties of aqueous polyacrylamide solutions," *Journal of Applied Polymer Science*, 69, 1587-1597.

Ghimici, L., and Popescu, F., 1998, "Determination of intrinsic viscosity for some cationic polyelectrolytes using Fedors equation", *European Polymer Journal*, 34[1], 13–16.

Gregory, G.J., 1987, "Flocculation by polymers and polyelectrolytes", In: Solid/Liquid Dispersions, Th. F. Tadros (Ed.), Academic Press Inc. Ltd., London, p163.

Gregory, G.J., 1989, "Fundamentals of Flocculation", *Critical Reviews in Environmental Control*, 19[3], 223-226.

Haas, R., and Kulicke, W.-M., 1984, "Flow behavior of dilute polyacrylamide solutions through porous media. 2. Indirect determination of extremely high molecular weights and some aspects of viscosity decrease over long time intervals", *Industrial and Engineering Chemistry Fundamentals*, 23, 316–319.

Hecker, R., 1998, "The characterization of polyacrylamide flocculants," PhD. Thesis, Curtin University of Technology (Australia).

Hecker, R., Fawell, P.D., Jefferson A., 1998, "The agglomeration of high molecular mass polyacrylamide in aqueous solutions," *Journal of Applied Polymer Science*, 70, 2241-2250.

Heitner, H.I., 1989, In B.M. Moudgil and B. J. Scheiner (Eds), "Flocculation and Dewatering", Engineering Foundation, New York, 215-220.

Heitner, H.I., 2004, "Flocculating agents", In: Kirk-Othmer Encyclopedia of Chemical Technology", Kirk-Othmer (ed.), John Wiley and sons, Toronto.

Henderson, J.M., Wheatley, A.D., 1987, "Factors effecting a loss of flocculation activity of polyacrylamide solutions: Shear degradation, cation complexation, and solution aging," *Journal of Applied Polymer Science*, 33[2], 669-684.

Hogg, R., 1999, "Polymer adsorption and flocculation", In: Polymers in Mineral Processing, J.S. Laskowski (Ed.), Metallurgical Society of CIM, Quebec City, p 3.

Huggins, M.L., 1942, "The viscosity of dilute solutions of long-chain molecules. IV. Dependence on concentration, *Journal of the American Chemical Society*, 64, 2716-2718.

Kitchener J.A., 1972, "Principles of action of polymeric flocculants", *British Polymer Journal*, vol. 4, p 217.

Klimchuk, K. A., 1997, "Synthesis, characterization and testing of acrylamide-based polymers", M Sc. Thesis, University of Victoria (Canada).

Krishnamoorthi, S., and Singh, R.P., 2006, "Synthesis, characterization, flocculation, and rheological characteristics of hydrolyzed and unhydrolyzed polyacrylamide-grafted poly(vinyl alcohol)," *Journal of Applied Polymer Science*, 101, 2109-2122.

Krishnan, S.V., and Attia, Y.A., 1988, "Polymeric flocculants", In: Reagents in Mineral Technology, P. Somasundaran and B.M. Moudgil (Eds), Merceel Dekker, Inc. New York, p 485.

Kulicke W.-M., and Clasen C., 2004, "Viscosimetry of Polymers and Polyelectrolytes", Springer Laboratory.

Kulicke, W.-M., and Hörl, H.H., 1985, "Preparation and characterization of a series of poly(acrylamide-co-sodium acrylates), with a polymer composition between 0-96.3 mol-% acrylate units with the same degree and distribution of polymerization", *Colloid and Polymer Science*, 263, 530-540.

Kulicke, W.-M., and Kniewske, R., 1981, "Long-term conformation of macromolecules in solution, Poly(acrylamide-co-sodium acrylate)s", *Makromol. Chem.*, 182, 2277-2287.

Kulicke, W.-M., Kniewske, R., Klein, J., 1982, "Preparation, characterization, solution properties, and rheological behaviour of polyacrylamides", *Progress in Polymer Science*, Vol. 8, 373-468.

Lewellyn, M.E., and Avotins P.V., 1988, "Dewatering/filtering aids", In: Reagents in Mineral Technology, P. Somasundaran and B.M. Moudgil (Eds), Merceel Dekker, Inc. New York, p485.

- Long, J., Xu, Z., and Masliyah, J.H., 2006, "Role of illite-illite interactions in oil sands processing," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 281, 202-214.
- Lovell, P.A., 1989, "Dilute solution viscometry", In: Comprehensive Polymer Science: Polymer Characterization, vol. 1, C. Price & C. Booth (Eds.), Oxford: Pergamon Press. 173-197.
- Lu, X., and Mi, Y., 2005, "Characterization of the interfacial interaction between polyacrylamide and silicon substrate by fourier transform infrared spectroscopy", *Macromolecules*, 38, 839-843.
- Ma, J., Liang, B., Cui, P., Dai, H., and Huang R., 2003, "Dilute solution properties of hydrophobically associating polyacrylamide: fitted by different equations", *Polymer*, 44, 1281-1286.
- Ma, X., and Pawlik, M., 2007, "Intrinsic viscosities and Huggins constants of guar gum in alkali metal chloride solution", *Carbohydrate Polymers*, 70[10], 15-24.
- Mabire, F., Audebert, R., and Quivoron, C., 1984, "Synthesis and solution properties of water soluble copolymers based on acrylamide and quaternary ammonium acrylic comonomer," *Polymer*, 25[9], 1317-1322.
- Makogon, B.P., Pavelko, M. M., Bondarenko, T. A., Klenin, S. I., Povkh, I. L., Toryanik, A. I., Kurlyankina, V. I., Molotkov, V. A., and Ivanyuta F. Y., 1986, "The effect of conformation of macromolecules on the hydrodynamic effectiveness of polyacrylamide", *Journal of Engineering Physics and Thermophysics*, 51[1], 47-52.
- McCarthy, K.J., Burkhardt, C.W., and Parazak, D.P., 1987, "Mark-Houwink-Sakurada constants and dilute solution behavior of heterodisperse poly(acrylamide-co-sodium acrylate) in 0.5M and 1M NaCl", *Journal of Applied Polymer Science*, 33, 1699-1714.
- Muller, G., Laine, J.P., and Fenyo, J.C., 1979, "High-molecular weight hydrolyzed polyacrylamides. I. Characterization. Effect of salts on the conformational properties", *Journal of Polymer Science*, 17, 659-672.
- Munk, P., Aminabhavi, T.M., Williams, P., Hoffman, D.E., Chmelir, M., 1980, "Some Solution Properties of Polyacrylamide," *Macromolecules*, 13(4), 871-876.
- Nagy, T.T., Kelen, T., and Tüdös, F., 1978, "An improved graphical method of molecular weight measurements on polymers", *Polymer*, 19[11], 1360-1361.
- Narkis, N., and Rebhun, M., 1966, "Ageing effects in measurements of polyacrylamide solution viscosities", *Polymer*, 1, 507-512.
- Nasser, M.S., and James, A.E., 2007, "Effect of polyacrylamide polymers on floc size and rheological behaviour of kaolinite suspensions," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 301, 311-322.

- Öhrn, O. E., 1955, "Preliminary report on the influence of adsorption on capillary dimensions of viscometers", *Journal of Polymer Science*, 17, 137 – 140.
- Onyon, P.F., 1959, "Viscometry," In Techniques of Polymer Characterization," P.W. Allen (ed.), Butterworth, London, 171-206.
- Owen, A.T., Fawell, P. D., Swift, J.D. and Farrow, J.B., 2002, "The impact of polyacrylamide flocculant solution age on flocculation performance," *International Journal of Mineral Processing*, 67[1-4], 123-144.
- Pan, Y., Fu, W., Xue, F., Luo, Y., Gu, J., and Cheng, R., 2002, "The viscosity anomaly of polymer mixture solution in extremely dilute concentration region, *European Polymer Journal*, 38[2], 359-364.
- Pavlov, G. M., Gubarev, A. S., Zaitseva, I. I., and Sibileva, M. A., 2006, "Determination of intrinsic viscosity of polyelectrolytes in salt-free solutions", *Russian Journal of Applied Chemistry*, 79[9], 1407–1412.
- Rafi'ee Fanood, M.H., and George, M.H., 1987, "Estimation of the limiting viscosity number and Huggins constant of polyacrylamides in water and 1 M aqueous sodium chloride", *Polymer*, 28[13], 2241-2243.
- Rafi'ee Fanood, M.H., and George, M.H., 1987, "Single-point determination of limiting viscosity numbers of polyacrylamide in water and 1M sodium chloride solution," *Polymer*, 28[13], 2244-2247.
- Rao, M.V.S., 1988, "Viscosity of dilute to moderately concentrated polymer solutions", *Polymer*, 34[3], 592-596.
- Rattanakawin, C., 2002, *Polymeric Flocculation: Effects of Chemical and Physical Variables on Flocculation Formation and Growth*, PhD. Thesis, The Pennsylvania State University (USA).
- Rattanakawin, C., and Hogg, R., 2007, "Viscosity behavior of polymeric flocculant solutions", *Minerals Engineering*, 20[10], 1033–1038.
- Rey, F., and Machado, A., 2000 "Influence of the temperature on the viscosity measurements of solutions of a soil fulvic acid", *Canadian Journal of Chemical Engineering*, 78, 1013–1018.
- Richardson, P.F., and Connelly L. J., 1988, "Industrial coagulants and flocculants", In: Reagents in Mineral Technology, P. Somasundaran and B.M. Moudgil (Eds.), Marcel Dekker, Inc. New York, p 485.
- Robinson, G., Ross-Murphy, S.B., & Morris, E.R. (1982). Viscosity-molecular weight relationships, intrinsic chain flexibility, and dynamic solution properties of guar galactomannan, *Carbohydrate Research*, 107, 17-32.

- Rogers, D. and Poling, G., 1978; "Compositions and performance characteristics of some commercial polyacrylamide flocculants", *CIM Bulletin*, vol. 71 (May), p. 152.
- Rushing, T.S., Hester, R.D., 2003, "Low-shear-rate capillary viscometer for polymer solution intrinsic viscosity determination at varying temperatures", *Review of Scientific Instruments*, 74[1], 176-181.
- Sakai, T., (1968a), "Huggins constant k' for flexible chain polymers", *Journal of Polymer Science A-2*, 6, 1535-1549.
- Sakai, T., (1968b), "Extrapolation procedures for intrinsic viscosity and for Huggins constant k'' ", *Journal of Polymer Science A-2*, 6, 1659-1672.
- Sastry, N.V., Dave, P.N. and Valand, M.K., 1999, "Dilute solution behaviour of polyacrylamides in aqueous media," *European Polymer Journal*, 35[3], 517-525.
- Shyluk, W.P., Stow Jr. F.S., 1969, "Aging and loss of flocculation activity of aqueous polyacrylamide solutions," *Journal of Applied Polymer Science*, 13[5], 1023- 1036.
- Silberberg, A., Eliassaf, J., and Katchalsky, A., 1957, "Temperature dependence of light scattering and intrinsic viscosity of hydrogen bonding polymers", *Journal of Polymer Science*, 23, 259-284.
- Taylor, M.L., 2002, "Mechanisms of flocculant action on kaolinite clay", PhD. Thesis, University of South Australia (Australia).
- Vangani, V and Rakshit, A.K., 1996, "Synthesis and characterization of homopolymer of 2-ethylhexyl acrylate and its copolymers with acrylamide, acrylonitrile, and methyl methacrylate" *Journal of Applied Polymer Science*, 60, 1005-1013.
- Weast, R., 1970, "CRC Handbook of Chemistry and Physics", 50th Ed., CRC Press, Cleveland.
- Wills, B.A., 1997, "Mineral Processing Technology: An Introduction to the Practical Aspects of Ore Treatment and Mineral Recovery", 6th Ed, Butterworth-Heinemann.
- Wu, S., and Shanks, R. A., 2003, "Conformation of polyacrylamide in aqueous solution with interactive additives and cosolvents", *Journal of Applied Polymer Science*, 89, 3122–3129.
- Yang, H., Zhu, P., Peng, C., Ma, S., Zhu, Q., and Fan, C., 2001, "Viscometric study of polyvinyl alcohol in NaCl/water solutions ranging from dilute to extremely dilute concentration," *European Polymer Journal*, 37, 1939-1942.

Appendix I: Example of a Typical Measurement of Kinematic Viscosity

Table I-1: Kinematic viscosity of a solution of A110, concentration 120ppm, prepared in 0.5M NaCl

Sample	A110, concentration 120ppm, prepared in 0.5M NaCl		
Operator	Esau		
Sample No.	PAM 10	Temp.	25°C
Capillary No.	2		
Capillary Constant	0.008289mm ² /s ²		
Capillary size	75		
Type of evaluation	Kinematic Viscosity	Flow times	
Mean	136.777s	136.78	
Standard deviation	0.006s	136.78	
Kinetic energy correction	0.388s	136.77	
Kinematic viscosity	1.1305 mm ² /s		

Appendix II: Viscosity Data of flocculants in distilled water

Tables II-1 to II-15 show the kinematic viscosities determined at different polymer concentrations. The relative viscosities were obtained from the ratio of the kinematic viscosities of the polymer solutions to the kinematic viscosity of the solvent. The relative viscosities were then converted to specific and reduced viscosities.

N100, Natural pH (4.9 – 7.2)

Table II-1: Viscosity data of N100 in distilled water at natural pH and 25°C, 35°C, 50°C

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	1.0964	1.23	0.23	45.46
0.0075	1.1988	1.34	0.34	45.66
0.0100	1.3201	1.48	0.48	47.62
0.0125	1.4421	1.61	0.61	49.04
0.0150	1.5631	1.75	0.75	50.02
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	0.8976	1.24	0.24	47.24
0.0075	0.9850	1.36	0.36	47.62
0.0100	1.0792	1.49	0.49	48.47
0.0125	1.1848	1.63	0.63	50.43
0.0150	1.2793	1.76	0.76	50.83
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	0.6949	1.25	0.25	49.08
0.0075	0.7650	1.37	0.37	49.56
0.0100	0.8348	1.50	0.50	49.46
0.0125	0.9139	1.64	0.64	50.94
0.0150	0.9911	1.78	0.78	51.79
Temperature: Cooled from 50°C to 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	1.1092	1.24	0.24	48.32
0.0075	1.2035	1.35	0.35	46.37
0.0100	1.3307	1.49	0.49	48.79
0.0125	1.4509	1.62	0.62	49.83
0.0150	1.5707	1.76	0.76	50.58

N100, pH 8.5 – 8.6**Table II-2: Viscosity data of N100 in distilled water at pH 8.5 – 8.6 and 25°C, 35°C, 50°C**

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	1.0712	1.20	0.20	40.86
0.0075	1.1553	1.30	0.30	39.90
0.0100	1.2393	1.39	0.39	39.45
0.0125	1.3368	1.50	0.50	40.29
0.0150	1.4268	1.60	0.60	40.27
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	0.8739	1.21	0.21	41.02
0.0075	0.9407	1.30	0.30	39.68
0.0100	1.0125	1.40	0.40	39.75
0.0125	1.0798	1.49	0.49	39.20
0.0150	1.1607	1.60	0.60	40.04
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	0.6724	1.20	0.20	40.47
0.0075	0.7274	1.30	0.30	40.14
0.0100	0.7860	1.41	0.41	40.67
0.0125	0.8347	1.49	0.49	39.48
0.0150	0.8980	1.61	0.61	40.39
Temperature: Cooled from 50°C to 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	1.0686	1.20	0.20	40.27
0.0075	1.1469	1.29	0.29	38.63
0.0100	1.2370	1.39	0.39	39.18
0.0125	1.3177	1.48	0.48	38.58
0.0150	1.4151	1.59	0.59	39.43

N100, pH 10.5 – 10.6**Table II-3: Viscosity data of N100 in distilled water at pH 10.5 – 10.6 and 25°C, 35°C, 50°C**

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	0.9825	1.10	0.10	18.97
0.0075	1.0363	1.16	0.16	20.69
0.0100	1.0933	1.22	0.22	21.92
0.0125	1.1378	1.27	0.27	21.48
0.0150	1.1948	1.33	0.33	22.15
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	0.8022	1.10	0.10	19.08
0.0075	0.8496	1.16	0.16	21.40
0.0100	0.8969	1.23	0.23	22.57
0.0125	0.9338	1.28	0.28	22.06
0.0150	0.9792	1.34	0.34	22.54
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	0.6234	1.10	0.10	20.48
0.0075	0.6614	1.17	0.17	22.65
0.0100	0.7009	1.24	0.24	24.04
0.0125	0.7318	1.29	0.29	23.58
0.0150	0.7686	1.36	0.36	24.00
Temperature: Cooled from 50°C to 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	0.9956	1.11	0.11	21.86
0.0075	1.0567	1.18	0.18	23.71
0.0100	1.1179	1.25	0.25	24.67
0.0125	1.1721	1.31	0.31	24.54
0.0150	1.2340	1.38	0.38	25.06

A100, Natural pH (4.6 – 7.2)**Table II-4: Viscosity data of A100 in distilled water at natural pH and 25°C, 35°C, 50°C**

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	1.0696	1.20	0.20	196.76
0.0020	1.1910	1.33	0.33	166.62
0.0030	1.3029	1.46	0.46	152.09
0.0040	1.4311	1.60	0.60	150.41
0.0050	1.5266	1.71	0.71	141.49
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.8756	1.20	0.20	202.19
0.0020	0.9755	1.34	0.34	170.07
0.0030	1.0660	1.46	0.46	154.19
0.0040	1.1722	1.61	0.61	152.47
0.0050	1.2531	1.72	0.72	144.10
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.6816	1.21	0.21	212.21
0.0020	0.7589	1.35	0.35	175.24
0.0030	0.8298	1.48	0.48	158.19
0.0040	0.9059	1.61	0.61	152.88
0.0050	0.9704	1.72	0.72	144.86
Temperature: Cooled from 50°C to 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	1.0770	1.21	0.21	204.96
0.0020	1.2050	1.35	0.35	174.43
0.0030	1.3235	1.48	0.48	159.73
0.0040	1.4503	1.62	0.62	155.76
0.0050	1.5507	1.73	0.73	146.88

A100, pH 8.5 – 8.6**Table II-5: Viscosity data of A100 in distilled water at pH 8.5 – 8.6 and 25°C, 35°C, 50°C**

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	1.0373	1.14	0.14	141.89
0.0020	1.1472	1.26	0.26	131.64
0.0030	1.2448	1.40	0.40	133.14
0.0040	1.3937	1.53	0.53	133.43
0.0050	1.5069	1.70	0.70	138.76
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.8476	1.14	0.14	144.87
0.0020	0.9323	1.26	0.26	129.85
0.0030	1.0138	1.40	0.40	132.69
0.0040	1.1318	1.53	0.53	132.05
0.0050	1.2213	1.69	0.69	136.78
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.6581	1.15	0.15	151.60
0.0020	0.7219	1.26	0.26	131.78
0.0030	0.7843	1.40	0.40	134.12
0.0040	0.8717	1.53	0.53	131.18
0.0050	0.9414	1.68	0.68	136.62
Temperature: Cooled from 50°C to 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	1.0364	1.14	0.14	140.86
0.0020	1.1454	1.26	0.26	130.64
0.0030	1.2418	1.40	0.40	132.01
0.0040	1.3878	1.53	0.53	131.81
0.0050	1.4956	1.68	0.68	136.23

A100, pH 10.5 – 10.6**Table II-6: Viscosity data of A100 in distilled water at pH 10.5 – 10.6 and 25°C, 35°C, 50°C**

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.9511	1.06	0.06	64.76
0.0020	1.0693	1.17	0.17	86.78
0.0030	1.0987	1.23	0.23	76.78
0.0040	1.2338	1.35	0.35	88.61
0.0050	1.2428	1.39	0.39	78.32
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.7727	1.06	0.06	61.61
0.0020	0.8734	1.18	0.18	88.09
0.0030	0.8975	1.23	0.23	77.75
0.0040	0.9960	1.34	0.34	85.40
0.0050	1.0055	1.38	0.38	76.30
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.5944	1.06	0.06	58.88
0.0020	0.6712	1.17	0.17	85.37
0.0030	0.6873	1.22	0.22	74.88
0.0040	0.7699	1.34	0.34	85.83
0.0050	0.7766	1.38	0.38	76.72
Temperature: Cooled from 50°C to 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.9471	1.06	0.06	60.29
0.0020	1.0616	1.17	0.17	82.52
0.0030	1.0915	1.22	0.22	74.07
0.0040	1.2089	1.33	0.33	81.76
0.0050	1.2230	1.37	0.37	73.89

A110, Natural pH (4.6– 7.2)**Table II-7: Viscosity data of A110 in distilled water at natural pH and 25°C, 35°C, 50°C**

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	1.1006	1.23	0.23	230.08
0.0020	1.2520	1.40	0.40	198.37
0.0030	1.4237	1.59	0.59	197.70
0.0040	1.5336	1.72	0.72	178.18
0.0050	1.6788	1.88	0.88	175.29
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.9003	1.24	0.24	234.85
0.0020	1.0275	1.41	0.41	203.58
0.0030	1.1594	1.60	0.60	198.85
0.0040	1.2518	1.72	0.72	179.04
0.0050	1.3732	1.89	0.89	176.81
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.6964	1.24	0.24	237.27
0.0020	0.7937	1.41	0.41	203.88
0.0030	0.8949	1.59	0.59	197.27
0.0040	0.9752	1.73	0.73	182.90
0.0050	1.0644	1.89	0.89	178.27
Temperature: Cooled from 50°C to 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	1.1024	1.23	0.23	232.08
0.0020	1.2615	1.41	0.41	203.68
0.0030	1.4227	1.59	0.59	197.32
0.0040	1.5478	1.73	0.73	182.15
0.0050	1.6949	1.90	0.90	178.87

A110, pH 8.50 – 8.59**Table II-8: Viscosity data of A110 in distilled water at pH 8.5 – 8.6 and 25°C, 35°C, 50°C**

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	1.1013	1.21	0.21	206.78
0.0020	1.2741	1.40	0.40	200.65
0.0030	1.3886	1.56	0.56	187.34
0.0040	1.5741	1.73	0.73	183.17
0.0050	1.6879	1.90	0.90	179.05
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.8942	1.21	0.21	202.34
0.0020	1.0307	1.39	0.39	195.49
0.0030	1.1234	1.55	0.55	183.37
0.0040	1.2682	1.71	0.71	178.20
0.0050	1.3578	1.87	0.87	174.06
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.6884	1.20	0.20	199.21
0.0020	0.7907	1.38	0.38	191.13
0.0030	0.8656	1.55	0.55	182.92
0.0040	0.9682	1.69	0.69	173.47
0.0050	1.0422	1.86	0.86	172.28
Temperature: Cooled from 50°C to 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	1.0947	1.21	0.21	199.64
0.0020	1.2516	1.38	0.38	188.26
0.0030	1.3706	1.54	0.54	180.60
0.0040	1.5414	1.70	0.70	174.17
0.0050	1.6592	1.87	0.87	172.62

A110, pH 10.5 – 10.6**Table II-9: Viscosity data of A110 in distilled water at pH 10.5 – 10.6 and 25°C, 35°C, 50°C**

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	1.0142	1.11	0.11	112.18
0.0020	1.1194	1.25	0.25	126.43
0.0030	1.2021	1.35	0.35	115.16
0.0040	1.3250	1.45	0.45	113.12
0.0050	1.4108	1.58	0.58	115.71
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.8266	1.11	0.11	112.23
0.0020	0.9080	1.25	0.25	123.50
0.0030	0.9847	1.35	0.35	117.48
0.0040	1.0619	1.43	0.43	107.10
0.0050	1.1391	1.57	0.57	112.81
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.6336	1.11	0.11	104.35
0.0020	0.6958	1.24	0.24	119.56
0.0030	0.7496	1.34	0.34	111.66
0.0040	0.8054	1.40	0.40	100.86
0.0050	0.8772	1.56	0.56	112.35
Temperature: Cooled from 50°C to 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	1.0031	1.10	0.10	100.08
0.0020	1.1001	1.23	0.23	115.61
0.0030	1.1871	1.33	0.33	109.56
0.0040	1.2742	1.40	0.40	99.23
0.0050	1.3815	1.55	0.55	109.15

A130, Natural pH (4.6 – 7.2)**Table II-10: Viscosity data of A130 in distilled water at natural pH and 25°C, 35°C, 50°C**

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	1.1013	1.23	0.23	232.40
0.0020	1.3073	1.46	0.46	231.08
0.0030	1.4314	1.60	0.60	199.67
0.0040	1.6160	1.81	0.81	201.84
0.0050	1.8224	2.04	1.04	208.10
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.8999	1.24	0.24	236.24
0.0020	1.0691	1.47	0.47	233.75
0.0030	1.1683	1.60	0.60	200.72
0.0040	1.3063	1.79	0.79	198.38
0.0050	1.4681	2.02	1.02	203.46
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.6973	1.24	0.24	240.53
0.0020	0.8251	1.47	0.47	233.48
0.0030	0.9055	1.61	0.61	202.72
0.0040	1.0142	1.80	0.80	200.85
0.0050	1.1114	1.98	0.98	195.63
Temperature: Cooled from 50°C to 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	1.1074	1.24	0.24	240.74
0.0020	1.3113	1.47	0.47	233.50
0.0030	1.4371	1.61	0.61	202.44
0.0040	1.6080	1.80	0.80	200.14
0.0050	1.7658	1.98	0.98	195.53

A130, pH 8.5 – 8.6**Table II-11: Viscosity data of A130 in distilled water at pH 8.5 – 8.6 and 25°C, 35°C, 50°C.**

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	1.0851	1.22	0.22	220.88
0.0020	1.2948	1.43	0.43	212.70
0.0030	1.4417	1.62	0.62	206.66
0.0040	1.6486	1.81	0.81	203.83
0.0050	1.8527	2.04	1.04	207.63
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.8781	1.21	0.21	211.96
0.0020	1.0401	1.40	0.40	202.50
0.0030	1.1567	1.60	0.60	198.14
0.0040	1.3147	1.78	0.78	194.09
0.0050	1.4744	1.99	0.99	198.04
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.6729	1.20	0.20	204.24
0.0020	0.7926	1.39	0.39	193.47
0.0030	0.8861	1.59	0.59	194.61
0.0040	1.0022	1.75	0.75	188.55
0.0050	1.1127	1.95	0.95	189.13
Temperature: Cooled from 50°C to 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	1.0647	1.20	0.20	197.89
0.0020	1.2581	1.39	0.39	192.51
0.0030	1.3998	1.57	0.57	190.99
0.0040	1.5911	1.75	0.75	188.01
0.0050	1.7973	1.98	0.98	195.44

A130, pH 10.5 – 10.6**Table II-12: Viscosity data of A130 in distilled water at pH 10.5 – 10.6 and 25°C, 35°C, 50°C**

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.9790	1.10	0.10	96.33
0.0020	1.1144	1.22	0.22	111.42
0.0030	1.2481	1.37	0.37	123.33
0.0041	1.4102	1.55	0.55	133.19
0.0050	1.4745	1.62	0.62	123.67
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.7965	1.09	0.09	94.50
0.0020	0.9005	1.21	0.21	106.28
0.0030	1.0029	1.35	0.35	116.91
0.0041	1.1277	1.52	0.52	126.11
0.0050	1.1731	1.58	0.58	115.95
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.6110	1.09	0.09	88.67
0.0020	0.6867	1.20	0.20	98.83
0.0030	0.7677	1.34	0.34	113.13
0.0041	0.8578	1.50	0.50	120.68
0.0050	0.8909	1.55	0.55	110.81
Temperature: Cooled from 50°C to 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.9719	1.09	0.09	88.28
0.0020	1.0840	1.19	0.19	94.78
0.0030	1.2053	1.32	0.32	107.68
0.0041	1.3582	1.49	0.49	119.31
0.0050	1.4077	1.54	0.54	108.99

A150, Natural pH (4.9 – 7.2)**Table II-13: Viscosity data of A150 in distilled water at natural pH and 25°C, 35°C, 50°C**

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	1.1700	1.31	0.31	307.92
0.0020	1.3785	1.50	0.50	270.55
0.0030	1.5762	1.76	0.76	254.80
0.0040	1.7134	1.92	0.92	228.76
0.0050	1.9135	2.14	1.14	227.86
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.9476	1.30	0.30	300.04
0.0020	1.0856	1.49	0.49	244.93
0.0030	1.2712	1.75	0.75	248.77
0.0040	1.3791	1.89	0.89	223.06
0.0050	1.5333	2.11	1.11	220.87
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.7285	1.30	0.30	294.74
0.0020	0.8345	1.48	0.48	241.64
0.0030	0.9602	1.71	0.71	236.17
0.0040	1.0476	1.86	0.86	215.40
0.0050	1.1658	2.07	1.07	214.44
Temperature: Cooled from 50°C to 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	1.1565	1.29	0.29	292.93
0.0020	1.3251	1.48	0.48	240.69
0.0030	1.5309	1.71	0.71	237.89
0.0040	1.6656	1.86	0.86	215.41
0.0050	1.8478	2.07	1.07	213.18

A150, pH 8.5 – 8.6**Table II-14: Viscosity data of A150 in distilled water at pH 8.5 – 8.6 and 25°C, 35°C, 50°C**

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	1.1609	1.28	0.28	276.47
0.0020	1.3452	1.51	0.51	253.21
0.0030	1.6545	1.82	0.82	273.75
0.0040	1.7825	2.00	1.00	251.30
0.0050	1.9092	2.15	1.15	229.80
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.9407	1.27	0.27	269.25
0.0020	1.0838	1.50	0.50	244.44
0.0030	1.3118	1.77	0.77	257.26
0.0040	1.4290	1.97	0.97	242.97
0.0050	1.5148	2.09	1.09	218.31
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.7234	1.27	0.27	264.40
0.0020	0.8311	1.49	0.49	240.27
0.0030	0.9883	1.73	0.73	243.08
0.0040	1.0821	1.94	0.94	234.05
0.0050	1.1438	2.05	1.05	209.55
Temperature: Cooled from 50°C to 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	1.1463	1.26	0.26	260.46
0.0020	1.3120	1.48	0.48	234.76
0.0030	1.5712	1.73	0.73	243.19
0.0040	1.7082	1.92	0.92	230.40
0.0050	1.8104	2.04	1.04	207.56

A150, pH 10.5 – 10.6**Table II-15: Viscosity data of A150 in distilled water at pH 10.5 – 10.6 and 25°C, 35°C, 50°C**

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	1.0715	1.18	0.18	174.64
0.0020	1.1957	1.34	0.34	168.51
0.0030	1.3265	1.46	0.46	152.09
0.0040	1.4107	1.58	0.58	144.94
0.0050	1.5674	1.75	0.75	151.11
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.8717	1.17	0.17	172.63
0.0020	0.9673	1.33	0.33	163.67
0.0030	1.0616	1.43	0.43	143.35
0.0040	1.1295	1.55	0.55	138.00
0.0050	1.2644	1.74	0.74	147.54
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.6673	1.16	0.16	162.86
0.0020	0.7447	1.33	0.33	162.54
0.0030	0.8083	1.41	0.41	136.77
0.0040	0.8568	1.53	0.53	131.64
0.0050	0.9532	1.70	0.70	139.73
Temperature: Cooled from 50°C to 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	1.0530	1.16	0.16	154.50
0.0020	1.1712	1.31	0.31	154.91
0.0030	1.2681	1.39	0.39	130.69
0.0040	1.3403	1.50	0.50	125.21
0.0050	1.5178	1.70	0.70	139.99

Appendix III: Viscosity Data of Flocculants in 0.01M NaCl

N100, Natural pH (5.1 – 7.0)

Table III-1: Viscosity data of N100 in 0.01M NaCl at natural pH and 25°C, 35°C, 50°C

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	0.9424	1.06	0.06	11.12
0.0075	0.9951	1.10	0.10	13.26
0.0101	1.0389	1.15	0.15	14.61
0.0125	1.0715	1.18	0.18	14.70
0.0150	1.1109	1.23	0.23	15.18
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	0.7678	1.06	0.06	11.12
0.0075	0.8109	1.10	0.10	13.26
0.0101	0.8464	1.15	0.15	14.58
0.0125	0.8728	1.18	0.18	14.67
0.0150	0.9049	1.23	0.23	15.15
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	0.5920	1.05	0.05	10.85
0.0075	0.6247	1.10	0.10	12.96
0.0101	0.6516	1.14	0.14	14.27
0.0125	0.6716	1.18	0.18	14.36
0.0150	0.6966	1.22	0.22	14.92
Temperature: Cooled from 50°C to 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	0.9417	1.06	0.06	10.97
0.0075	0.9939	1.10	0.10	13.08
0.0101	1.0382	1.15	0.15	14.53
0.0125	1.0703	1.18	0.18	14.60
0.0150	1.1104	1.23	0.23	15.14

N100, pH (8.5 –8.6)**Table III-2: Viscosity data of N100 in 0.01M NaCl at pH 8.5 – 8.6 and 25°C, 35°C, 50°C**

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	0.9595	1.06	0.06	11.57
0.0075	0.9917	1.09	0.09	12.43
0.0100	1.0408	1.15	0.15	14.74
0.0125	1.0594	1.18	0.18	14.48
0.0151	1.1154	1.23	0.23	15.23
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	0.7822	1.06	0.06	11.59
0.0075	0.8078	1.09	0.09	12.33
0.0100	0.8476	1.15	0.15	14.64
0.0125	0.8632	1.18	0.18	14.43
0.0151	0.9089	1.23	0.23	15.21
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	0.6035	1.06	0.06	11.48
0.0075	0.6224	1.09	0.09	12.04
0.0100	0.6520	1.14	0.14	14.22
0.0125	0.6639	1.18	0.18	14.12
0.0151	0.6992	1.22	0.22	14.92
Temperature: Cooled from 50°C to 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	0.9590	1.06	0.06	11.45
0.0075	0.9891	1.09	0.09	12.05
0.0100	1.0380	1.14	0.14	14.43
0.0125	1.0560	1.18	0.18	14.17
0.0151	1.1120	1.23	0.23	14.99

N100, pH (10.5 –10.6)**Table III-3: Viscosity data of N100 in 0.01M NaCl at pH 10.5 – 10.6 and 25°C, 35°C, 50°C**

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	0.9588	1.05	0.05	10.59
0.0075	0.9918	1.09	0.09	11.84
0.0100	1.0122	1.13	0.13	13.20
0.0125	1.0655	1.17	0.17	13.61
0.0150	1.1058	1.21	0.21	14.26
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	0.7819	1.05	0.05	10.74
0.0075	0.8089	1.09	0.09	11.95
0.0100	0.8269	1.13	0.13	13.45
0.0125	0.8698	1.17	0.17	13.76
0.0150	0.9032	1.22	0.22	14.44
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	0.6039	1.05	0.05	10.84
0.0075	0.6242	1.09	0.09	11.89
0.0100	0.6379	1.14	0.14	13.54
0.0125	0.6712	1.17	0.17	13.73
0.0150	0.6971	1.22	0.22	14.42
Temperature: Cooled from 50°C to 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	0.9604	1.05	0.05	10.96
0.0075	0.9944	1.09	0.09	12.23
0.0100	1.0162	1.14	0.14	13.64
0.0125	1.0706	1.18	0.18	14.06
0.0150	1.1118	1.22	0.22	14.70

A100, Natural pH (5.1 – 7.0)**Table III-4: Viscosity data of A100 in 0.01M NaCl at natural pH and 25°C, 35°C, 50°C**

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.9317	1.03	0.03	29.49
0.0020	0.9528	1.05	0.05	26.30
0.0030	0.9709	1.09	0.09	29.26
0.0040	1.0177	1.12	0.12	31.14
0.0050	1.0418	1.17	0.17	33.40
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.7589	1.03	0.03	29.05
0.0020	0.7756	1.05	0.05	25.73
0.0030	0.7900	1.09	0.09	28.80
0.0040	0.8282	1.12	0.12	30.75
0.0050	0.8478	1.17	0.17	33.14
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.5856	1.03	0.03	28.58
0.0020	0.5976	1.05	0.05	24.71
0.0030	0.6074	1.08	0.08	27.33
0.0040	0.6367	1.12	0.12	29.62
0.0050	0.6518	1.16	0.16	32.17
Temperature: Cooled from 50°C to 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.9306	1.03	0.03	28.27
0.0020	0.9516	1.05	0.05	25.63
0.0030	0.9697	1.09	0.09	28.81
0.0040	1.0167	1.12	0.12	30.85
0.0050	1.0410	1.17	0.17	33.22

A100, pH 8.5 – 8.6**Table III-5: Viscosity data of A100 in 0.01M at pH 8.5 – 8.6 and 25°C, 35°C, 50°C**

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.9213	1.03	0.03	27.05
0.0020	0.9587	1.06	0.06	28.29
0.0030	0.9837	1.10	0.10	32.17
0.0040	1.0336	1.14	0.14	34.83
0.0050	1.0548	1.18	0.18	35.14
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.7509	1.03	0.03	26.70
0.0020	0.7802	1.06	0.06	27.50
0.0030	0.8006	1.09	0.09	31.52
0.0040	0.8407	1.14	0.14	34.23
0.0050	0.8578	1.17	0.17	34.56
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.5795	1.03	0.03	26.84
0.0020	0.6003	1.05	0.05	25.72
0.0030	0.6154	1.09	0.09	30.13
0.0040	0.6466	1.13	0.13	33.16
0.0050	0.6592	1.17	0.17	33.59
Temperature: Cooled from 50°C to 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.9213	1.03	0.03	27.07
0.0020	0.9564	1.05	0.05	27.06
0.0030	0.9816	1.09	0.09	31.39
0.0040	1.0316	1.14	0.14	34.26
0.0050	1.0524	1.17	0.17	34.62

A100, pH 10.5 – 10.6**Table III-6: Viscosity data of A100 in distilled water at pH 10.5 – 10.6 and 25°C, 35°C, 50°C**

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.9235	1.03	0.03	32.69
0.0020	0.9640	1.06	0.06	29.22
0.0030	0.9811	1.10	0.10	32.39
0.0040	1.0266	1.13	0.13	31.83
0.0050	1.0454	1.17	0.17	33.82
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.7521	1.03	0.03	31.85
0.0020	0.7852	1.06	0.06	28.97
0.0030	0.7975	1.09	0.09	31.37
0.0040	0.8343	1.12	0.12	31.02
0.0050	0.8494	1.17	0.17	33.07
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.5804	1.03	0.03	33.06
0.0020	0.6047	1.06	0.06	27.73
0.0030	0.6132	1.09	0.09	30.48
0.0040	0.6388	1.11	0.11	28.74
0.0050	0.6500	1.16	0.16	31.39
Temperature: Cooled from 50°C to 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.9232	1.03	0.03	32.39
0.0020	0.9618	1.06	0.06	28.02
0.0030	0.9773	1.09	0.09	30.98
0.0040	1.0188	1.12	0.12	29.70
0.0050	1.0372	1.16	0.16	31.99

A110, Natural pH (5.1 – 7.0)**Table III-7: Viscosity data of A110 in 0.01M NaCl at natural pH and 25°C, 35°C, 50°C**

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.9403	1.04	0.04	38.75
0.0020	0.9791	1.10	0.10	48.47
0.0030	1.0485	1.16	0.16	52.87
0.0040	1.0858	1.22	0.22	54.12
0.0050	1.1277	1.26	0.26	52.67
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.7632	1.03	0.03	34.69
0.0020	0.7944	1.09	0.09	46.16
0.0030	0.8499	1.15	0.15	50.84
0.0040	0.8794	1.21	0.21	52.33
0.0050	0.9138	1.24	0.24	47.75
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.5889	1.03	0.03	34.18
0.0020	0.6086	1.08	0.08	42.00
0.0030	0.6500	1.14	0.14	47.25
0.0040	0.6715	1.20	0.20	49.03
0.0050	0.6972	1.24	0.24	48.36
Temperature: Cooled from 50°C to 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.9345	1.03	0.03	32.38
0.0020	0.9723	1.09	0.09	44.67
0.0030	1.0411	1.15	0.15	50.13
0.0040	1.0754	1.21	0.21	51.22
0.0050	1.1172	1.25	0.25	50.32

A110, pH 8.5 – 8.6**Table III-8: Viscosity data of A110 in 0.01M NaCl at pH 8.5 – 8.6 and 25°C, 35°C, 50°C**

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.9611	1.06	0.06	59.55
0.0020	1.0150	1.13	0.13	65.49
0.0030	1.0693	1.18	0.18	59.59
0.0040	1.1306	1.25	0.25	61.60
0.0050	1.1653	1.30	0.30	59.83
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.7805	1.06	0.06	55.59
0.0020	0.8238	1.13	0.13	62.95
0.0030	0.8655	1.17	0.17	56.86
0.0040	0.9116	1.23	0.23	58.25
0.0050	0.9394	1.28	0.28	56.90
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.5994	1.05	0.05	50.14
0.0020	0.6312	1.12	0.12	59.05
0.0030	0.6618	1.16	0.16	53.12
0.0040	0.6970	1.22	0.22	55.28
0.0050	0.7180	1.27	0.27	54.47
Temperature: Cooled from 50°C to 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.9572	1.06	0.06	55.26
0.0020	1.0104	1.13	0.13	62.91
0.0030	1.0613	1.17	0.17	56.65
0.0040	1.1212	1.24	0.24	59.01
0.0050	1.1531	1.29	0.29	57.10

A110, pH 10.5 – 10.6**Table III-9: Viscosity data of A110 in 0.01M NaCl at pH 10.5 – 10.6 and 25°C, 35°C, 50°C**

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.9531	1.05	0.05	46.37
0.0020	0.9866	1.10	0.10	51.52
0.0030	1.0692	1.17	0.17	57.91
0.0040	1.0925	1.22	0.22	55.43
0.0050	1.1405	1.28	0.28	55.06
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.7733	1.04	0.04	41.76
0.0020	0.7999	1.10	0.10	48.58
0.0030	0.8633	1.16	0.16	54.28
0.0040	0.8851	1.21	0.21	53.55
0.0050	0.9220	1.26	0.26	52.98
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.5927	1.03	0.03	34.32
0.0020	0.6112	1.09	0.09	43.83
0.0030	0.6566	1.15	0.15	48.59
0.0040	0.6758	1.20	0.20	50.69
0.0050	0.7031	1.25	0.25	50.27
Temperature: Cooled from 50°C to 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.9439	1.04	0.04	36.37
0.0020	0.9754	1.09	0.09	45.29
0.0030	1.0511	1.15	0.15	51.31
0.0040	1.0803	1.21	0.21	52.01
0.0050	1.1263	1.26	0.26	51.89

A130, Natural pH (5.1 – 7.0)**Table III-10: Viscosity data of A130 in 0.01M NaCl at natural pH and 25°C, 35°C, 50°C**

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.9690	1.07	0.07	70.17
0.0020	1.0596	1.17	0.17	85.23
0.0030	1.1399	1.26	0.26	86.56
0.0040	1.2239	1.35	0.35	88.02
0.0050	1.2958	1.43	0.43	86.26
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.7820	1.06	0.06	59.92
0.0020	0.8550	1.16	0.16	79.54
0.0030	0.9266	1.26	0.26	85.50
0.0040	0.9843	1.33	0.33	83.60
0.0050	1.0442	1.42	0.42	83.08
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.5973	1.05	0.05	48.77
0.0020	0.6442	1.13	0.13	65.66
0.0030	0.7026	1.23	0.23	78.07
0.0040	0.7549	1.33	0.33	81.47
0.0050	0.8013	1.41	0.41	81.39
Temperature: Cooled from 50°C to 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.9567	1.06	0.06	56.70
0.0020	1.0419	1.15	0.15	75.51
0.0030	1.1259	1.24	0.24	81.39
0.0040	1.1856	1.31	0.31	77.44
0.0050	1.2575	1.39	0.39	77.81

A130, pH 8.5 – 8.6**Table III-11: Viscosity data of A130 in 0.01M NaCl at pH 8.5 – 8.6 and 25°C, 35°C, 50°C**

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.9622	1.06	0.06	60.08
0.0020	1.0388	1.16	0.16	79.15
0.0030	1.1283	1.24	0.25	81.22
0.0040	1.1827	1.32	0.32	79.57
0.0050	1.2839	1.43	0.43	85.50
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.7784	1.05	0.05	52.12
0.0020	0.8426	1.15	0.15	76.20
0.0030	0.9164	1.24	0.24	79.77
0.0040	0.9541	1.30	0.30	76.11
0.0050	1.0368	1.42	0.42	82.83
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.5966	1.05	0.05	44.66
0.0020	0.6396	1.13	0.13	66.83
0.0030	0.6984	1.22	0.22	74.48
0.0040	0.7261	1.29	0.29	71.63
0.0050	0.7919	1.40	0.40	79.98
Temperature: Cooled from 50°C to 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.9536	1.05	0.05	50.65
0.0020	1.0288	1.15	0.15	73.57
0.0030	1.1110	1.22	0.23	74.87
0.0040	1.1546	1.29	0.29	71.74
0.0050	1.2424	1.39	0.39	76.33

A130, pH 10.5 – 10.6**Table III-12: Viscosity data of A130 in 0.01M NaCl at pH 10.5 – 10.6 and 25°C, 35°C, 50°C**

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.9609	1.06	0.06	55.29
0.0020	1.0537	1.16	0.16	78.74
0.0030	1.1134	1.22	0.22	74.03
0.0040	1.1691	1.28	0.28	70.62
0.0050	1.2409	1.39	0.39	77.13
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.7770	1.05	0.05	47.05
0.0020	0.8451	1.14	0.14	69.53
0.0030	0.8940	1.20	0.20	68.03
0.0040	0.9435	1.27	0.27	67.52
0.0050	0.9956	1.37	0.37	73.11
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.5951	1.04	0.04	38.83
0.0020	0.6381	1.11	0.11	57.06
0.0030	0.6770	1.18	0.18	60.42
0.0040	0.7063	1.23	0.23	57.94
0.0050	0.7595	1.35	0.35	70.29

A150, Natural pH (5.1 – 7.0)**Table III-13: Viscosity data of A150 in 0.01M NaCl at natural pH and 25°C, 35°C, 50°C**

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	1.0058	1.11	0.11	111.43
0.0020	1.0886	1.22	0.22	110.15
0.0030	1.2108	1.34	0.34	112.59
0.0040	1.3171	1.46	0.46	113.77
0.0050	1.3649	1.53	0.53	105.78
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.8110	1.10	0.10	99.79
0.0020	0.8817	1.21	0.21	106.49
0.0030	0.9790	1.33	0.33	109.11
0.0040	1.0644	1.44	0.44	110.74
0.0050	1.1049	1.52	0.52	103.80
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.6189	1.09	0.09	87.16
0.0020	0.6705	1.19	0.19	97.46
0.0030	0.7561	1.33	0.33	109.34
0.0040	0.8194	1.44	0.44	109.75
0.0050	0.8409	1.50	0.50	99.51
Temperature: Cooled from 50°C to 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.9915	1.10	0.10	95.66
0.0020	1.0656	1.19	0.19	97.24
0.0030	1.1828	1.31	0.31	102.29
0.0040	1.2950	1.43	0.43	107.66
0.0050	1.3384	1.50	0.50	99.85

A150, pH 8.5 – 8.6**Table III-14: Viscosity data of A150 in 0.01M NaCl at pH 8.5 – 8.6 and 25°C, 35°C, 50°C**

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	1.0110	1.11	0.11	114.26
0.0020	1.0905	1.22	0.22	107.91
0.0030	1.2671	1.40	0.40	131.96
0.0040	1.3407	1.48	0.48	119.37
0.0050	1.4201	1.58	0.58	116.63
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.8227	1.11	0.11	112.40
0.0020	0.8861	1.21	0.21	105.86
0.0030	1.0238	1.38	0.38	127.90
0.0040	1.0760	1.46	0.46	113.71
0.0050	1.1265	1.54	0.54	108.10
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.6247	1.09	0.09	94.24
0.0020	0.6804	1.21	0.21	102.91
0.0030	0.7862	1.38	0.38	125.49
0.0040	0.8246	1.44	0.44	111.05
0.0050	0.8768	1.55	0.55	110.77
Temperature: Cooled from 50°C to 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	1.0032	1.11	0.11	105.73
0.0020	1.0774	1.20	0.20	100.60
0.0030	1.2401	1.38	0.38	126.98
0.0040	1.3104	1.44	0.44	111.04
0.0050	1.3931	1.55	0.55	110.62

A150, pH 10.5– 10.6**Table III-15: Viscosity data of A150 in 0.01M NaCl at pH 10.5 – 10.6 and 25°C, 35°C, 50°C**

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	1.0139	1.11	0.11	112.71
0.0020	1.0803	1.21	0.21	104.20
0.0030	1.2032	1.32	0.32	107.08
0.0040	1.2748	1.43	0.43	106.24
0.0050	1.3829	1.55	0.55	109.29
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.8190	1.10	0.10	102.84
0.0020	0.8776	1.20	0.20	102.16
0.0030	0.9707	1.31	0.31	102.64
0.0040	1.0280	1.41	0.41	102.42
0.0050	1.1059	1.52	0.52	103.45
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.6230	1.09	0.09	86.89
0.0020	0.6636	1.18	0.18	90.64
0.0030	0.7420	1.29	0.29	98.33
0.0040	0.7804	1.39	0.39	97.08
0.0050	0.8340	1.48	0.48	96.88
Temperature: Cooled from 50°C to 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.9974	1.10	0.10	94.68
0.0020	1.0585	1.18	0.18	92.00
0.0030	1.1615	1.28	0.28	91.80
0.0040	1.2361	1.38	0.38	95.43
0.0050	1.3263	1.48	0.48	96.64

Appendix IV: Viscosity Data of N100 and A130 in 0.01M NaCl and 0.001M CaCl₂

N100, Natural pH

Table IV-1: Viscosity data of N100 in 0.01M NaCl and 0.001M CaCl₂ at natural pH at 25°C.

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	0.9657	1.07	0.07	13.40
0.0075	0.9915	1.10	0.10	12.73
0.0100	1.0132	1.14	0.14	13.50
0.0125	1.0586	1.17	0.17	13.58
0.0150	1.0739	1.20	0.20	13.57
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	0.7878	1.07	0.07	13.62
0.0075	0.8089	1.10	0.10	12.90
0.0100	0.8266	1.14	0.14	13.66
0.0125	0.8627	1.17	0.17	13.58
0.0150	0.8761	1.20	0.20	13.67
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	0.6081	1.07	0.07	13.62
0.0075	0.6239	1.10	0.10	12.77
0.0100	0.6369	1.13	0.13	13.43
0.0125	0.6628	1.16	0.16	13.14
0.0150	0.6743	1.20	0.20	13.43
Temperature: Cooled from 50°C to 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	0.9659	1.07	0.07	13.44
0.0075	0.9914	1.10	0.10	12.71
0.0100	1.0130	1.14	0.14	13.49
0.0125	1.0553	1.17	0.17	13.29
0.0150	1.0726	1.20	0.20	13.47

N100, pH 10.5**Table IV-2: Viscosity data of N100 in 0.01M NaCl and 0.001M CaCl₂ at pH 10.5 at 25°C.**

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	0.9688	1.06	0.06	12.77
0.0075	0.9787	1.09	0.09	12.57
0.0100	1.0283	1.13	0.13	12.93
0.0125	1.0489	1.17	0.17	13.84
0.0150	1.0865	1.21	0.21	14.33
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	0.7903	1.06	0.06	12.97
0.0075	0.7987	1.10	0.10	12.74
0.0100	0.8382	1.13	0.13	12.94
0.0125	0.8557	1.17	0.17	13.91
0.0150	0.8872	1.22	0.22	14.48
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	0.6101	1.06	0.06	12.97
0.0075	0.6166	1.10	0.10	12.96
0.0100	0.6456	1.13	0.13	12.69
0.0125	0.6591	1.17	0.17	13.85
0.0150	0.6836	1.22	0.22	14.45
Temperature: Cooled from 50°C to 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0050	0.9700	1.07	0.07	13.03
0.0075	0.9811	1.10	0.10	12.92
0.0100	1.0279	1.13	0.13	12.88
0.0125	1.0493	1.17	0.17	13.88
0.0150	1.0907	1.22	0.22	14.65

A130, Natural pH

Table IV-3: Viscosity data of A130 in 0.01M NaCl and 0.001M CaCl₂ at natural pH.

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.9296	1.03	0.03	27.15
0.0020	0.9558	1.07	0.07	35.49
0.0030	0.9887	1.11	0.11	36.05
0.0040	1.0422	1.15	0.15	37.89
0.0050	1.0720	1.20	0.20	40.29
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.7553	1.02	0.02	24.10
0.0020	0.7736	1.06	0.06	31.94
0.0030	0.7991	1.10	0.10	33.08
0.0040	0.8403	1.14	0.14	34.84
0.0050	0.8635	1.19	0.19	37.54
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.5844	1.03	0.03	26.47
0.0020	0.5916	1.05	0.05	26.94
0.0030	0.6089	1.08	0.08	28.29
0.0040	0.6358	1.12	0.12	29.18
0.0050	0.6536	1.16	0.16	32.89

A130, pH 10.5**Table IV-4: Viscosity data of A130 in 0.01M NaCl and 0.001M CaCl₂ at pH 10.5**

Temperature = 25°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.9311	1.02	0.02	22.46
0.0020	0.9801	1.08	0.08	38.12
0.0030	1.0073	1.11	0.11	35.42
0.0040	1.0437	1.17	0.17	41.68
0.0050	1.0857	1.21	0.21	42.86
Temperature = 35°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.7572	1.02	0.02	20.25
0.0020	0.7920	1.07	0.07	33.53
0.0030	0.8114	1.09	0.09	31.10
0.0040	0.8408	1.15	0.15	38.26
0.0050	0.8728	1.20	0.20	39.51
Temperature = 50°C				
Concentration [g/dL]	Kinematic viscosity [mm ² /s]	Relative viscosity	Specific viscosity	Reduced viscosity [dL/g]
0.0010	0.5859	1.02	0.02	22.69
0.0020	0.6040	1.05	0.05	27.11
0.0030	0.6175	1.08	0.08	25.94
0.0040	0.6367	1.13	0.13	33.20
0.0050	0.6590	1.17	0.17	34.58

Appendix V: Intrinsic Viscosities of Flocculants at different pH and Temperature.

Tables V-1 and V-2 show intrinsic viscosity data of flocculants obtained from relative viscosity and reduced viscosity data presented in Appendices II and III.

Table V-1: Intrinsic viscosity data of flocculants in distilled water at different pH and temperature.

25°C	Intrinsic Viscosity [dL/g]				
	N100	A100	A110	A130	A150
Natural pH (4.9-7.2)	42.6	217.4	250.0	243.9	333.3
pH 8.5-8.6	40.5	142.9	212.8	222.2	285.7
pH 10.5-10.6	18.2	61.4	111.1	89.3	185.2
35°C					
	N100	A100	A110	A130	A150
Natural pH (4.9-7.2)	44.9	227.3	256.4	250.0	333.3
pH 8.5-8.6	40.9	147.1	212.8	217.4	277.8
pH 10.5-10.6	18.5	57.8	112.4	88.5	185.2
50°C					
	N100	A100	A110	A130	A150
Natural pH (4.9 - 7.2)	47.4	243.9	256.4	256.4	322.6
pH 8.5-8.6	40.6	156.3	212.8	208.3	277.8
pH 10.5-10.6	18.8	55.0	104.2	82.6	175.4
Cooled from 50°C to 25°C					
	N100	A100	A110	A130	A150
Natural pH (4.9-7.2)	45.6	227.3	250.0	256.4	322.6
pH 8.5-8.6	39.9	142.9	208.3	200.0	270.3
pH 10.5 - 10.6	21.1	56.8	99.0	82.6	163.9

Table V-2: Intrinsic viscosity data of flocculants in 0.01M NaCl at different pH and temperature.

25°C	Intrinsic Viscosity [dL/g]					
	N100	A100	A110	A130	A150	
Natural pH (5.1-7.0)	9.9	28.7	35.7	66.2	111.1	
pH 8.5-8.6	10.0	25.3	59.5	55.6	111.1	
pH 10.5-10.6	9.1	32.5	44.1	51.6	113.6	
35°C		N100	A100	A110	A130	A150
Natural pH (5.1-7.0)		9.9	28.3	31.8	55.3	97.1
pH 8.5-8.6		9.9	25.0	55.3	47.2	111.1
pH 10.5-10.6		9.2	31.7	39.1	43.1	102.0
50°C		N100	A100	A110	A130	A150
Natural pH (5.1-7.0)		9.6	28.0	31.4	43.5	82.6
pH 8.5-8.6		9.8	25.3	49.3	39.8	89.3
pH 10.5-10.6		9.3	33.9	31.3	34.8	84.0
Cooled from 50°C to 25°C						
		N100	A100	A110	A130	A150
Natural pH (5.1-7.0)		9.7	27.3	29.2	52.4	93.5
pH 8.5-8.6		9.8	25.3	54.6	46.3	102.0
pH 10.5-10.6		9.4	32.7	33.3	40.8	94.3

Appendix VI: FTIR Spectra of Flocculants at Natural pH and pH 3.

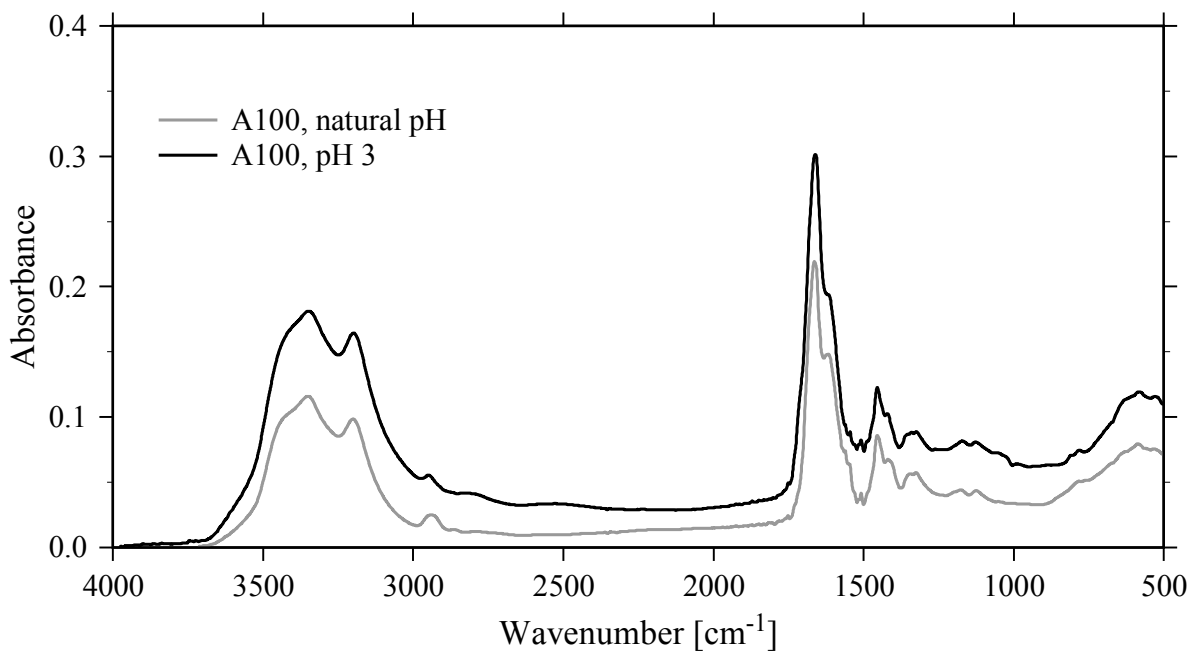


Figure VI-1: FTIR spectra of A100 prepared at natural pH and pH 3.

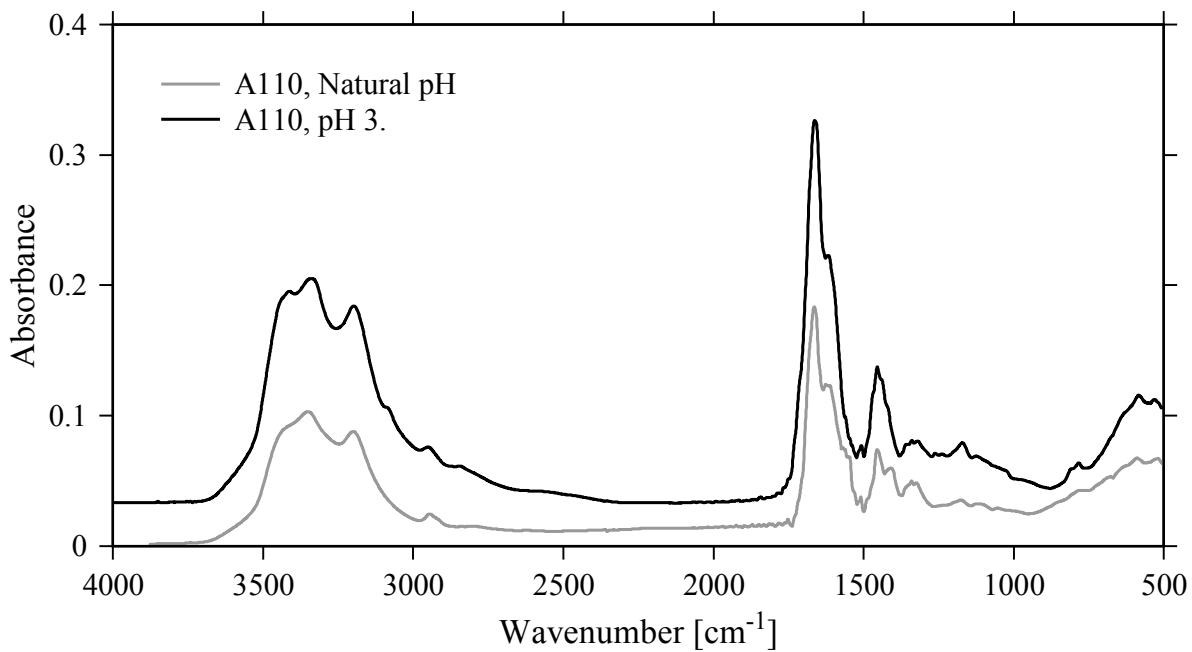


Figure VI-2: FTIR spectra of A110 prepared at natural pH and pH 3.

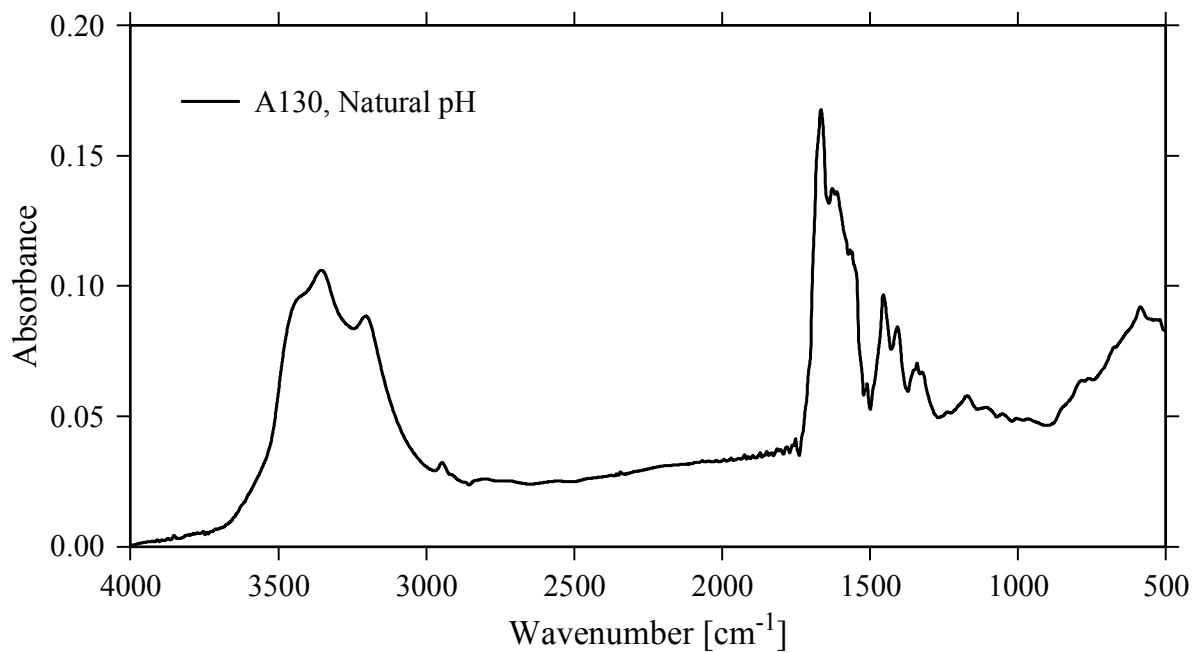


Figure VI-3: FTIR spectra of A130 prepared at natural pH.

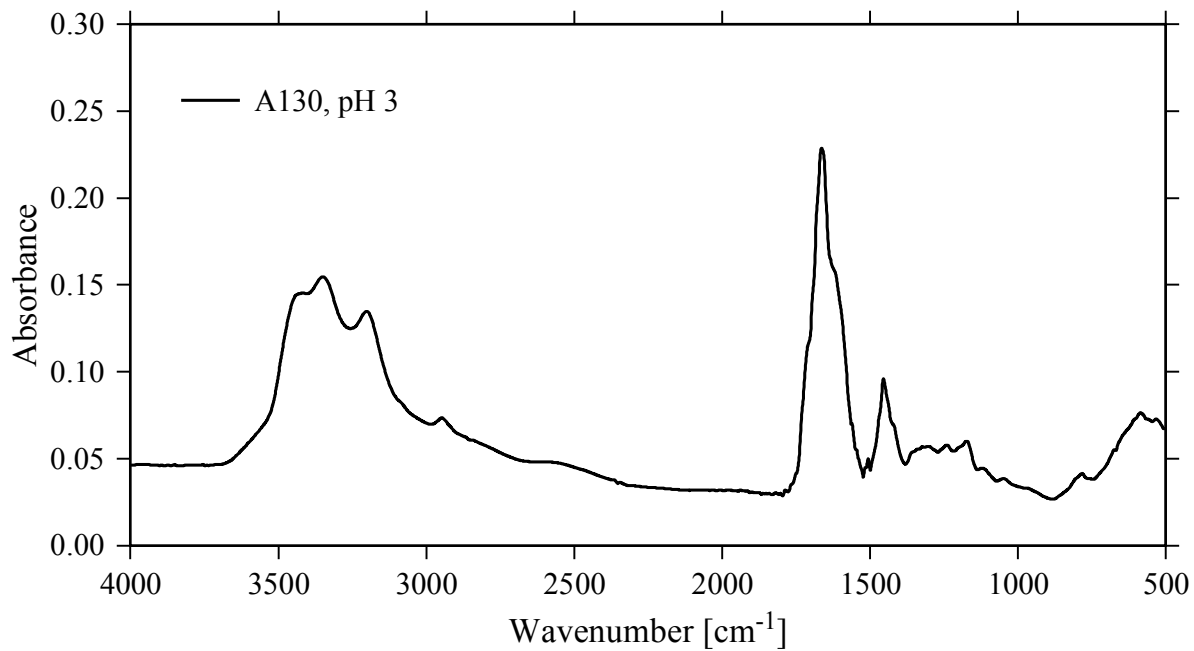


Figure VI-4: FTIR spectra of A130 prepared at pH 3.

Appendix VII: Standard Deviation between Intrinsic Viscosity Values for the N100 and A110 flocculants

The repeatability of the intrinsic viscosity results was measured by performing separate experiments on separately prepared stock and dilute flocculant solutions. Table VII-1 shows three sets of intrinsic viscosity values and standard deviations for the N100 (nonionic) and A110 (anionic) flocculants. The A110 flocculant was chosen because it gave the largest relative decrease in intrinsic viscosity when tested in 0.01M NaCl. The standard deviation was calculated using the equation below:

$$\sigma = \sqrt{\frac{\{[\eta] - \overline{[\eta]}\}^2}{n-1}}$$

Where;

σ - Standard deviation

$[\eta]$ - Intrinsic viscosity

$\overline{[\eta]}$ - Mean of the intrinsic viscosity values

n - Number of intrinsic viscosity values

Table VII-1: Intrinsic viscosity values and standard deviations for the N100 and A110 flocculants.

Flocculant	Intrinsic viscosity [dL/g]	Standard deviation [dL/g]
N100	42.6	2.1
	38.4	
	41.1	
A110	250.0	10.3
	270.3	
	263.2	

It can be seen that the standard deviation of the nonionic flocculant is less than that of the anionic flocculant, but the percent errors are almost the same (5.2% for the N100 and 3.9 % for the A110 flocculant). It was generally difficult to measure kinematic viscosities for the flocculants even though great care was taken in cleaning glassware, preparing solutions and performing the measurements. It must be said that *dilute* solutions of PAM in distilled water are

extremely difficult to handle compared to those in NaCl and in most cases, kinematic viscosities at one concentration had to be repeated twice or thrice to obtain reliable values. This difficulty was also reported by Kulicke and Kniewske (1981) and Munk et al. (1980).