Solution Behavior of Hydrophobic Non-Ionic and Ionic Polymers

by

Sohel Shaikh

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMICAL ENGINEERING

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This thesis, written by

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Date: 25-10 1997

And say "Oh my Lord! Bestow on them Your Mercy as they did bring me up when I was small" (Al-Quran 17:24)

For my Mother

Acknowledgments

Praise be to Allah Almighty, for instilling in me the will and determination to complete the Master's Program here at KFUPM.

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Contents

List of Figures

List of Tables

Abstract

Name: **Sohel Shaikh**

Title: **Solution Behavior of**
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Degree: **Master of Science**

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Water soluble polymers have gained increasing importance in recent years. Specific structural characteristics of the macromolecular backbone determine their solution properties. Viscofication of aqueous solutions can be achieved by using amphiphilic polymers i.e. water soluble polymers bearing a few hydrophobic groups. Intermolecular association between the hydrophobes leads to a substantial enhancement in viscosity. We have sucessfuly synthesized hydrophobically modified poly(vinyl alcohol) and block copolymers of acrylamide and styrene by micellar copolymerization. A substantial enhancement in viscosity and thickening properties equivalent to those of very high molecular weight polymers have been noticed for the polymers under study. Furthermore, the reversible association -dissociation process gives rise to a shear thinning behavior which is desired in water based systems involving a viscosity control. Salt interactions have been studied. Surface tension and interfacial tension measurements have been made. Polymer characterization is done using fluorescence measurements and NMR spectroscopy.

الخلاصة

اسم الطالب : سهيل شيخ
عنوان الرساله : صفات المحاليل المائيه للمبلمرات الايونيه وغير الايونيه المعدله بجزيئات منافره للماء
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حازت المبلمرات قابلة الذوبان في الماء على اهتمام كبير خلال الاعوام الاخيره وذلك لسبب خواصها المرغوبه وتطبيقاتها المتعدده . وتتحدد خواص هذه المبلمرات في الماء حسب خواص الجزيئات المكونه لها . ويمكن زيادة لزوجة المحاليل المائية لهذه المبلمرات عن طريق اضافة نسبة معينه من السلاسل المكونه من جزيئات مفاخره للماء . وعندما تقوم هذه الاجزاء المنافره بالإتحاد في المحلول المائي ، ترتفع لزوجة المحلول بشكل كبير في هذا البحث قمنا بتصميم وتصنيع بولي فينيل الكحول معدل بسلاسل منافره للماء . كما تم تصنيع مبلمرات الأكريلامايد المحتويه على نسبة ٦٪ من الستيرين بشكل سلاسل متصله تكون جزأً من العمود الفقري للبولي اكريلامايد . وقد وجد ان هذه المبلمرات تحمل خواص اللزوجه العاليه والتي تقارن مع مبلمرات لها اوزان جزيئيه عاليه جداً . كما ان طبيعة الإتحاد بين المجموعات المفاخره للماء تؤدي إلى خاصية انخفاض اللزوجه تحت ظروف الفرك المرتفعه مما يؤدي إلى المحافظه على هذه المبلمرات من التكسر . كما تمت دراسة النشاط السطحي لهذه المبلمرات في المحلول مع الهواء ومع زيت الديكان ووجد أن لها خواص مرغوبه جداً . كما تم دراسة خواص هذه المبلمرات بالرنين النووي المغناطيسي والفلوسنس .

درجة الماجستير في العلوم
جامعة الملك فهد للبترول والمعادن
الظهران – المملكة العربية السعودية

Nomenclature

$C10$	deconyl chloride
$C13$	carbon 13
$C18$	steoryl chloride
$CTAB$	cetyl trimethyl ammonium bromide (surfactant)
DMF	dimethyl formamide
EOR	enhanced oil recovery
F	measured force, mN
$HMPVA$	hydrophobically modified poly(vinyl alcohol)
$HMWSP$	hydrophobically modified water soluble polymer
I	wetted length of plate or wetted circumference of ring
IFT	interfacial tension
K	effective permeability of the displacing fluid in the zone occupied by the fluid
M	water oil mobility ratio
NMR	nuclear magnetic resonance

$P(AS)$	poly(acrylamide/styrene) block copolymer
q	flow rate per unit c/s area
r	radius of the porous media, mm (Ch. 1)
r	radius of the ring, mm (Ch. 3)
ST	surface tension, mN/m
t	time, s
T	temperature, ^{o}C or K

Subscript

max	maximum
o	oil
r	reduced
w	water

Greek

γ	interfacial tension
σ	surface tension
μ	absolute viscosity, cp
ρ	density, g/cm^3
Δ	Differential

η	reduced viscosity
θ	angle of contact

Chapter 1

Introduction

1.1 Hydrophobically modified water soluble polymers (HMWSP)

Water soluble polymers have gained increasing importance in recent years and have been used as viscofiers and gelation agents in many processes. Viscofication or gelation can be achieved by using amphiphilic polymers i.e. water soluble polymers bearing a few hydrophobic groups. Intermolecular association of the hydrophobic groups may occur, resulting in the formation of very large macromolecular aggregates. This leads to an increase in the apparent molecular weight and a substantial enhancement of viscosity [1-5]. Thickening of solutions can be achieved by dissolving polymers of very high molecular weight. Similarly, viscofication or gelation of aqueous solutions can be achieved by using amphiphilic polymers [1][2]i.e. water soluble polymers bearing a few hydrophobic groups, typically upto 5 mol%. Aggregation of the hydrophobic parts results in an increase in the apparent molecular weight. Such thickeners control very efficiently, the flow properties of aqueous based fluids in many industrial applications and formulations e.g. in latex paints, drilling muds and enhanced oil recovery (EOR)[6]. Synthetic hydrophobically modified polyelectrolytes may also serve as models of biopolymers for studying the relationship between structure and activity in proteins and biomembranes[7]. A schematic representation of a typical hydrophobic association is shown in Figure 1.1. Here the filled circles represent hydrophobic groups on the polymer chain.

The reversible association / dissociation gives rise to a typical rheological behavior as a function of the shearing rate or shearing time. Such shear thinning or thixotropic properties are of great technological importance, especially in applications which involve a viscosity control. Solution properties of water soluble polymers are determined by specific structural character-

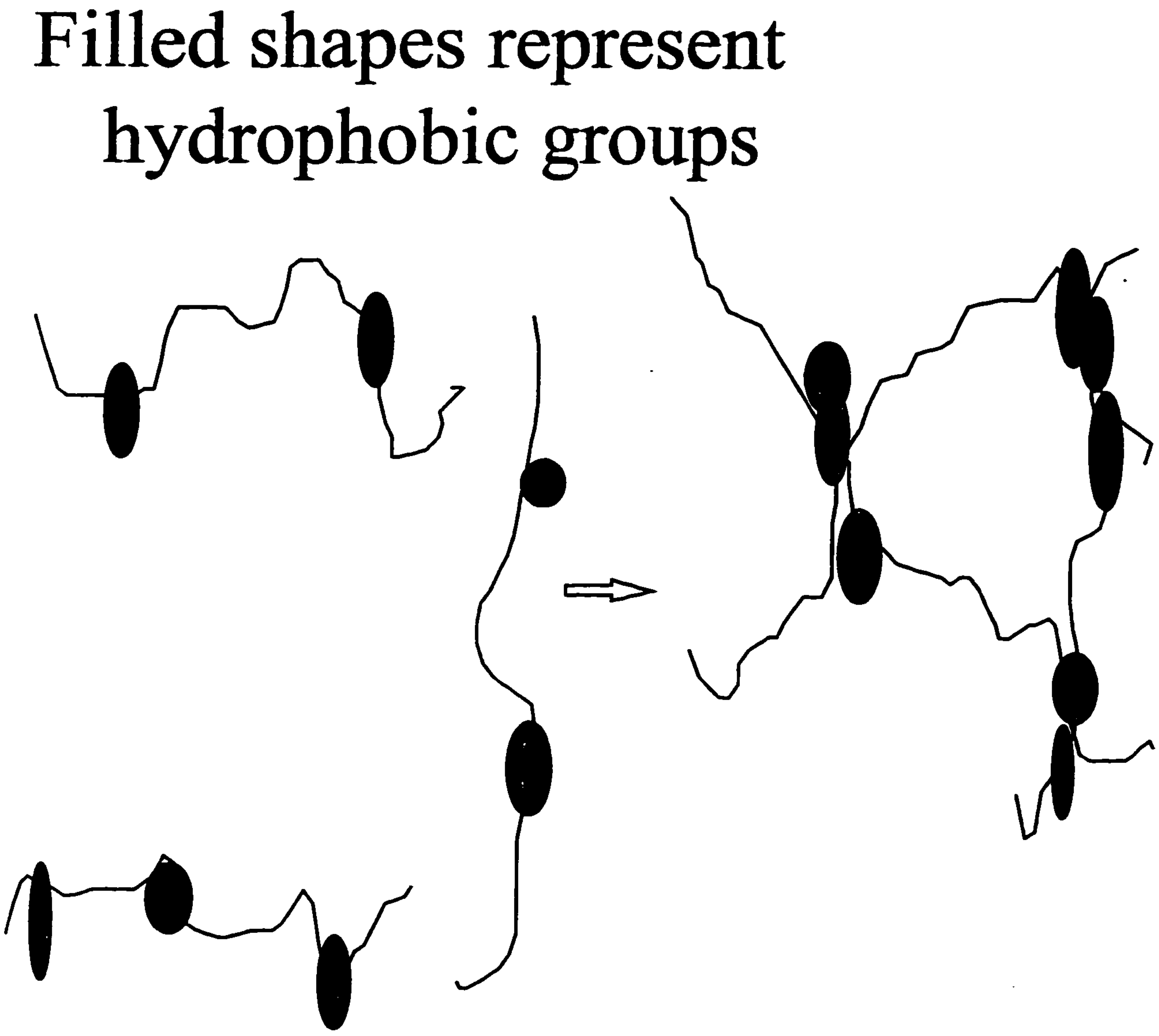


Figure 1.1: Hydrophobic Association

istics of the macromolecular backbone. Primary structure depends on the nature of the repeat units as well as their composition, location and frequency. Macromolecules may be linear or branched with repeating units arranged in random, alternating, block or graft fashion. Secondary structure in water soluble polymers is related to configurational, conformational and intramolecular effects such as hydrogen bonding and ionic interactions. Tertiary structure is defined by intermolecular interactions while quaternary structure is governed by multiple complexation.

In synthetic water soluble polymers, polar non-ionic functional groups can impart water solubility if present in large numbers along or pendant to the backbone. Acrylamide polymers and co-polymers have widespread application in rheology control, flocculation, adhesion and other varied applications. Poly (vinyl alcohol) and poly (vinyl acetate) co-polymers are used in paper-making, emulsification, thickening and cosmetic formulation.

Charged polymers are those possessing charges along or pendant to the molecular backbone. These can be classified into two main groups. Polyelectrolytes, polyanions (negative charges) or polycations (positive charges) with their associated counter-ions, normally collapse to smaller hydrodynamic dimensions with the addition of electrolytes, while polyampholytes (both positive and negative charges along the macro-molecular chain) expand in dilute solution.

Hydrophobically modified or associating polymers are synthetically derived water soluble polymers that contain a small number of oil soluble or hydrophobic groups. When these polymers are dissolved in aqueous solution, the hydrophobic groups aggregate to minimize their exposure to water, in a fashion analogous to that of surfactants above the critical micelle concentration. In aqueous solutions, hydrophobic association can dominate polymer conformation, and in turn solution rheological properties. We will now discuss a few of the applications in detail.

1.2 Technological Applications of HMWSP

1.2.1 Enhanced Oil Recovery

The production of a petroleum reservoir has different phases in its life history. The first, where the oil freely flows from the reservoir to the production well under its own pressure, is the shortest. Energy must then be supplied to the porous medium which bears the crude oil, so that oil continues to flow to the producing wells. This energy is brought into the well by the injection of water or gas. In order to recover some of this oil, tertiary methods have to be used. Figure 1.2 indicates the importance of tertiary recovery methods.

EOR Concepts

The goal of EOR processes is to mobilize the oil remaining after primary recovery. This is achieved by enhancing microscopic oil displacement and volumetric sweep efficiencies [8]. Oil displacement efficiency is increased by decreasing oil viscosity (thermal and miscible flooding) or by reducing capillary forces or interfacial tension (chemical and miscible flooding). Volumetric sweep efficiency is improved by increasing the viscosity of the displacing agent.

EOR methods are divided into three broad categories.

1. Thermal methods such as continuous steam injection, cycle steam injection (or huff-puff) and in-situ combustion.
2. Chemical flooding such as polymer, surfactant -polymer and caustic flooding.
3. Miscible displacement such as carbon dioxide, miscible hydrocarbon

and inert gas injection.

Mechanics of Polymer Flooding

The percentage of oil at the end of secondary recovery i.e. water flooding, residual oil is believed to be in the form of immobile globules distributed through the pores of the rock in the petroleum reservoir. The two major forces acting on these immobile globules are capillary forces and viscous forces. The ratio of viscous to capillary forces with the oil recovery efficiency in porous media has been correlated with the capillary number N_C.

$$N_C = \mu_w \, \phi \, \frac{q}{\gamma_{o/w}} \tag{1.1}$$

It is generally recognized that as the capillary number increases, the oil displacement efficiency also increases [9][10]. The increase in capillary number can be achieved by either increasing the viscosity of the drive water μ_w, or decreasing the interfacial tension between the oil and drive water $\gamma_{o/w}$ or both. It is also generally believed that the lower the pressure drop ΔP, across the interface of the oil and water, the higher the oil displacement efficiency. The

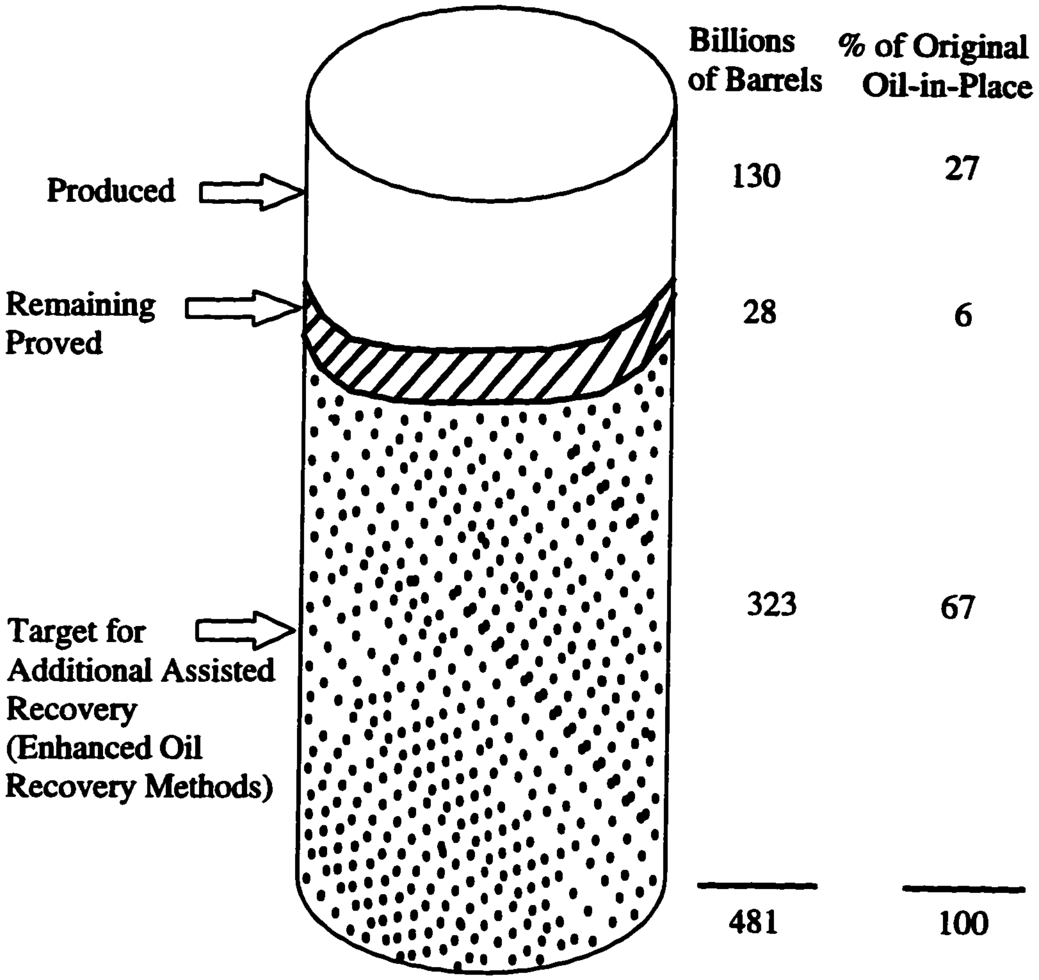


Figure 1.2: World Oil Reserves

pressure drop is related to the interfacial tension and the pore radius r, by

$$\Delta P = 2 \frac{\gamma_{o/w}}{r} \tag{1.2}$$

The pressure drop can be lowered by lowering the interfacial tension (IFT) between the oil and the drive water. For the trapped oil drops to flow, an ultra low IFT is required as it reduces the work of deformation needed for oil ganglia to move through the narrow necks of oil channels. The sweep efficiency of water flooding can be improved by lowering the water oil mobility ratio M, which is expressed as

$$M = k_w \frac{\mu_0}{k_0 \mu_w} \tag{1.3}$$

The proportion of the unswept area depends greatly on the mobility ratio which may be decreased by either lowering the viscosity of the oil μ_0 or by increasing the viscosity μ_w, of the driving fluid.

1.2.2 Applications in the Paint Industry

Components of Paint

A paint is a colloidal multicomponent system. As different substrates require different mechanical properties from paint films, the composition varies from one application to another. For example, a soft highly extensible paint film based on a low T_g latex polymer is a much better proposition on wood but totally unsuitable as a car finish. Hence desired properties are obtained by using intrinsic physical and chemical characteristics of the polymer. Other components are added to modify the physical and mechanical properties. A typical paint composition is as shown in Figure 1.3.

A paint can consist of just a dispersion of pigment in a polymer solution as exemplified by a typical oil based paint. Alternatively the film forming components of a paint may be non-solvent and present solely as a disperse phase, where both the polymer and pigment are in a colloidal suspension as in an emulsion or latex paint[11].

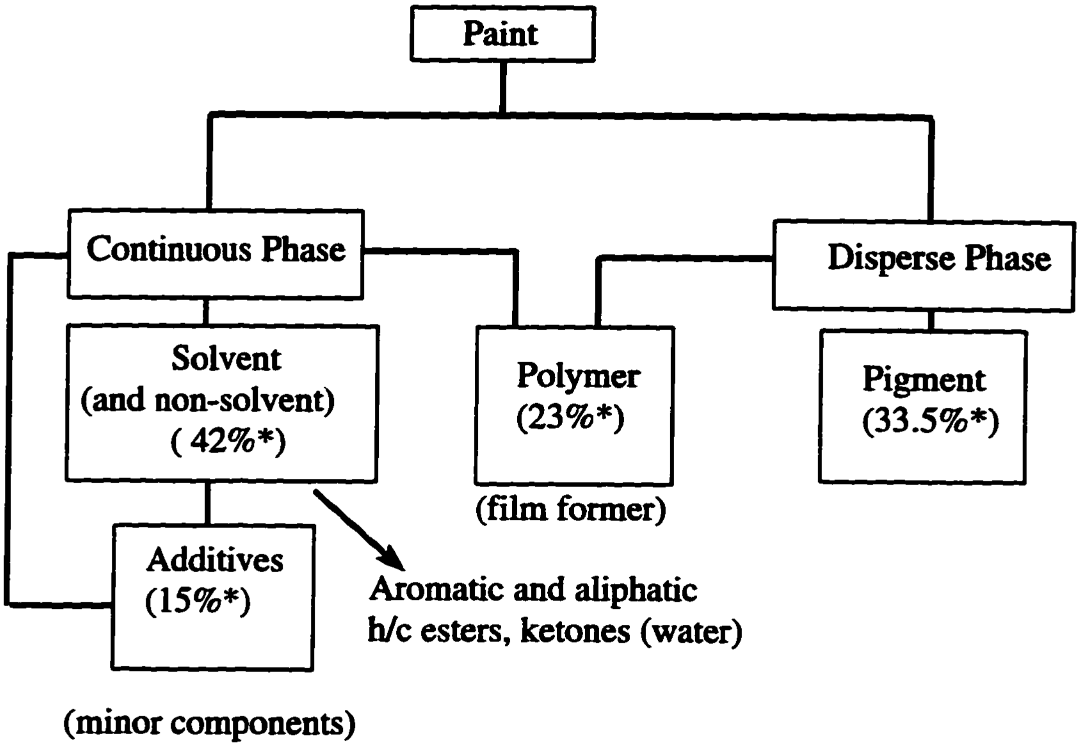
Rheological Requirements of Paint

The rheological requirements for paint can be quite contradictory since a low viscosity at high shear is necessary for application, yet a high viscosity at low shear is required to prevent pigment settlement and the paint sagging on surfaces. Both requirements can be met by careful design and incorporation of special hydrophobically modified water solube polymers[12][11].

1.2.3 Applications in protein partitioning

Polymer choice

The starting point for any aqueous two phase polymer (ATPP) system is the selection of the polymers used to generate the phases. Phase separation is seen with almost any combination of two chemically distinct polymers in a single solvent and is seen in both organic and aqueous solutions. Flory and Huggins developed the basic theory to describe this phenomenon. Albertson[13] demonstrated phase separation in a large number of aqueous systems.



* As percent by weight

Figure 1.3: Schematic overview of paint constituents

Phase forming characteristics

The Flory Huggins theory can qualititatively describe aqueous two phase partitioning. Phase separation is caused by the fact that polymer solutions have a small entropy of mixing. Hence positive enthalpic effects involving the interactions of the segments of the polymer chain lead to phase separation. Put simply, polymers prefer to self associate rather than mix with other polymer molecules. Hence two phases of different polymer compositions are formed in the mixtures. A detailed description of the Flory Huggins theory can be found in the original work or in recently published reviews [14][13].

Some Factors Affecting Two Phase Partitioning

Molecular weight

When the molecular weights of the two phase forming polymers are dissimilar, there is a driving force for proteins to partition towards the phase with the smaller molecular weight. The larger the difference in the molecular weight, the stronger is the effect.

Hydrophobicity

An important consideration is the relative hydrophobicity of the polymers [15]. Since hydrophobic effects have an impact on the interaction between the polymer and the protein, more strongly hydrophobic polymers should be expected to enhance partitioning. It has also been seen in a study by Hamad et. al. [16] that a block copolymer partitions the protein better than a random copolymer due to the concentrated attractive or repulsive interactions with proteins.

1.3 Objectives

Usually high molecular weight polymers are used in EOR and other applications. These undergo irreversible thermal as well as mechanical degradation. Surfactant solutions used in EOR applications are designed to yield ultra low IFT by decreasing the intermolecular reactions of both, the oil and water phases at their region of contact. However these decrease the polymer solution viscosity [17] and hence cause a decrease in the sweep efficieny of the polymer flood. Recent advances in synthesizing amphiphilic polymers dwell on the possibility of combining both, the mobility control and the IFT reduction properties in a single chemical compound.

Our goal is to understand the solution behavior of certain hydrophobically modified polymers, and then to incorporate it in other polymers for use in engineering applications. This goal will be achieved through the following specific objectives.

1. Synthesize hydrophobically modified poly(vinyl alcohol) (HMPVA) and characterize and study its solution properties.
2. Introduce ionic groups in the PVA and study the solution properties.
3. Synthesize multi-block co-polymers of acrylamide and styrene and measure the viscosity, surface tension and interfacial tension as a function of polymer and salt concentrations.
4. Characterize the nature of hydrophobic associationin poly (acrylamide styrene) block copolymers using fluorescence probe studies.

Chapter 2

Literature Review

2.1 Hydrophobically Modified Acrylamide Styrene Block Copolymers

Water soluble acrylamide block copolymers have been the subject of study for many researchers. Bock et. al. in their patented work[3] discussed the synthesis of a polymer containing the water soluble groups acrylamide and a salt of acrylic acid, and a higher alkylacrylamide as the water insoluble group.These showed desired solution properties such as enhanced viscofication and reduced salt sensisitivity. Copolymers of acrylamide and N-alkyl acrylamide monomers prepared by micellar copolymerization have been synthesized [18]. Hill et. al. in their work [4] discuss the influence of the method of synthesis of hydrophobically associating polyacrylamides on their solution properties. Among the different methods discussed, the micellar process was found to be most suited for synthesizing polymers with improved thickening properties not just by Hill but also by other researchers[19][4]. Biggs et. al [20] studied the effect of varying the surfactant concentration on the copolymer structure. They reported that despite the high level of surfactant and low levels of hydrophobic monomer, the reaction rate kinetics for acryamide polymerization in aqueous solution may still be applied.

The micellar synthesis of water soluble acrylamide / styrene block copolymers has been investigated by Dowling and Thomas[21]. The micellar polymerization of styrene was carried out in an aqueous solution of acrylamide to form the water-soluble copolymer. Characterization of the resulting block copolymers was done based primarily on photophysical phenomena.

2.2 Hydrophobically Modified Poly(vinyl alcohol)

Water soluble hydrophobically modified PVA has been prepared by the chemical modification of PVA[5][22]. The modification reaction is carried out on an already existing polymer. This synthesis route has mainly been applied to cellulose derivatives e.g. poly(oxy ethylene), which lead to the so called HEUR thickeners[23] i.e. hydrophobically modified ethoxylated urethane polymers. It was found that the modified polymer displayed certain rheological properties which could be exploited in EOR applications. Among the factors investigated were the effect of side chain incorporation, variation of the hydrophobic chain length, the effect of shear variation, the behavior in electrolyte solutions and temperature variations.

2.3 Ionically modified PVA

The ionic PVA was made by reacting the already prepared PVA with the sodium salt of monochloroacetic acid. The resulting ionic PVA had a higher ion incorporation as compared to a previous work[24]. Due to the high incorporation of ions on the PVA chain, the ionic PVA showed a better solubility in water than the unmodified PVA. Intrinsic viscosity measurements indicated a typical polyelectrolyte behavior.

2.4 Micellar Copolymerization : Process description

Several methods for the synthesis of water soluble block copolymers have been used in research. Of these, the micellar copolymerization technique has shown promising results for the preparation of polymers with improved thickening properties [4] [19]. Hydrophobically associating acrylamides are an increasingly important type of associating polymers. We aim to copolymerize acrylamide with a hydrophobic comonomer by micellar copolymerization, where a surfactant provides a medium for the polymerization of styrene, the hydrophobic monomer.

Above a certain concentration known as the critical micelle concentration (C.M.C) surfactant molecules aggregate to form structures called micelles. These can be visualized as structures having a core made of a solvent incompatible medium and a shell region consisting of solvent compatible strands. The micelles are capable of solubilizing within their cores other monomeric or polymeric substances that are insoluble in the bulk solvent where the micelles are dispersed. This phenomenon is known as solubilization.

While a random copolymer results in the case of a solution copolymerization, the use of a micellar process leads to a blocky structure due to the microheterogenous dispersion of the hydrophobe. Here the surfactant not only ensures the solubilization of the hydrophobic monomer but also induces the formation of hydrophobic sequences whose length depends on the number of hydrophobic blocks per micelle. In this polymerization technique, the hydrophobic monomer is solubilized within surfactant micelles, whereas acrylamide is dissolved together with the potassium persulfate initiator in the aqueous continuous medium. The surfactant used in this study was cetyltrimethylammoniumbromide (CTAB). The reaction mixture which is optically transparent is in reality a microheterogenous system. Major differences exist between this technique and the conventional emulsion polymerization. These are outlined below :

1. The surfactant to hydrophobe ratio in micellar polymerization is quite

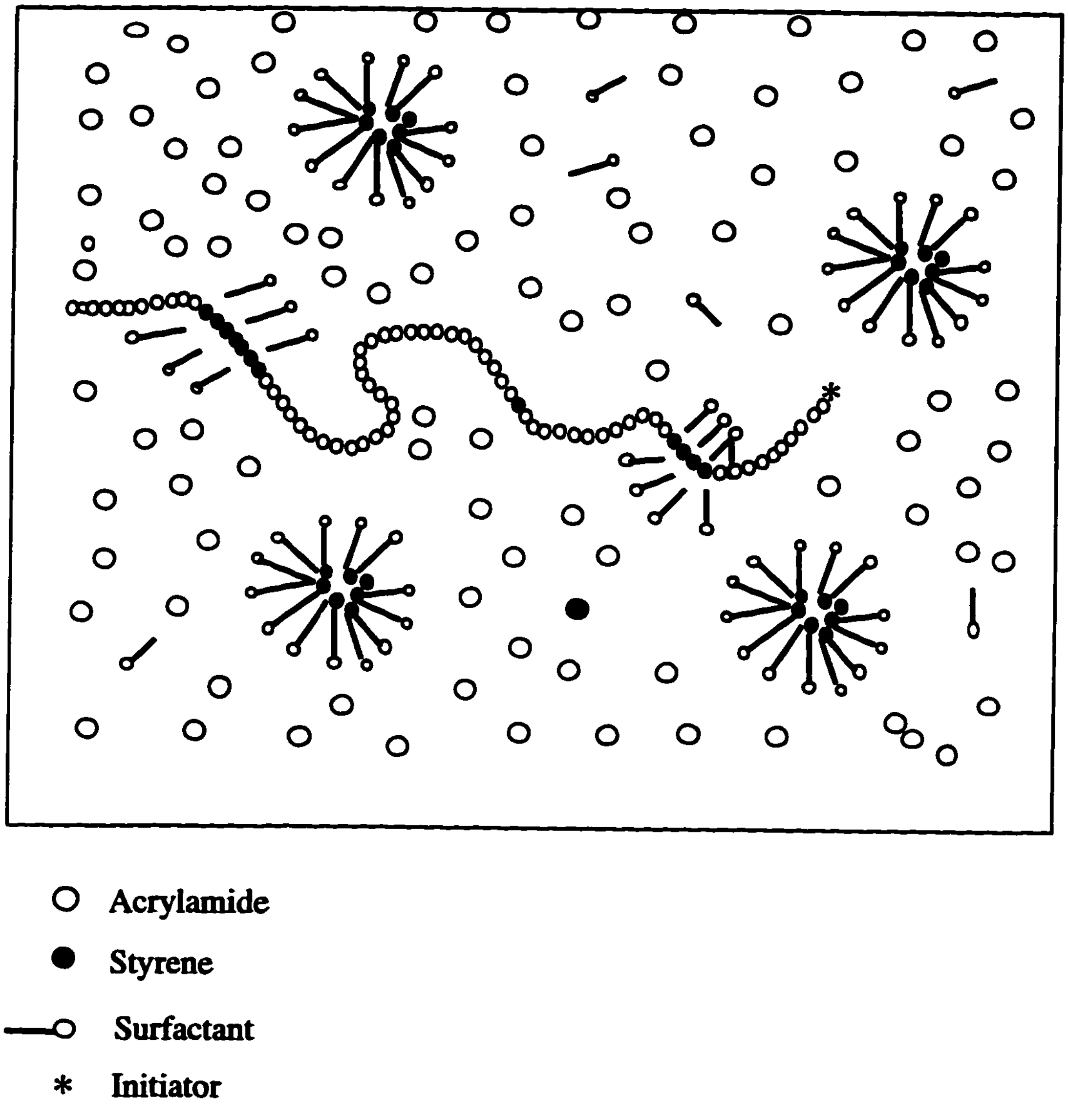


Figure 2.1: Schematic representation of the reaction medium for the micellar copolymerization

high (in the range of 15/1 to 70/1 by weight) as compared to that of aqueous emulsion polymerization.

2. A direct emulsion copolymerization implies a low water solubility of the monomers;i.e., the monomers are essentially located in the dispersed phase(large monomer droplets and small micelles). The situation is quite different for the micellar copolymerization , since the major part of the monomeric species i.e., acrylamide, is soluble in the aqueous continuous phase. The hydrophobic monomer located within the micelles represents only a very small fraction of the total monomer feed (2-7 wt%)

3. In the micellar process, the two monomers are segregated into two distinct phases due to their solubilities. This situation affects the mechanism of polymerization.

4. In the micellar process, the copolymerization reaction occurs both in the continuous phase and the dispersed phase. Therefore although this process is called "micellar polymerization", it involves in fact a combination of a micellar and a solution polymerization. In this respect, the name "micellar polymerization" is somewhat ambiguous since a

true micellar polymerization actually occurs when all of the monomer is actually located within the swollen micelles.

5. The final reaction mixture is not a latex(i.e., a fluid dispersion of insoluble polymer particles in water), but a homogenous clear and strongly viscous polymer solution. Besides, the copolymerization of a hydrophilic monomer and a hydrophobic monomer by an emulsion process gives a latex functionalized with hydrophobic groups because of the reverse proportion of the two monomers.

2.5 Mechanism for polymerization

The most probable mechanism should be similar to that proposed by Hill et. al.[4].

1. Potassium persulfate initiates the polymerization of acrylamide in the aqueous phase.
2. When a growing macroradical encounters a monomer swollen micelle, it adds several hydrophobe molecules inside the micelle to form a short hydrophobe block.

3. The radical head group may then leave the micelle and the polymerization proceeds with acrylamide until another micelle is encountered to form again a hydrophobic block. These steps are repeated many times because the average lifetime of a growing polyacrylamide radical is relatively high. This is due to the high ratio of the rate constants for propagation over termination and to a small chain transfer constant in water.

The polymer chain will be blocky in nature. The important parameter in the scheme proposed above is the number of hydrophobe molecules per micelle. By varying the surfactant to hydrophobe ratio, both the number and length of the hydrophobic blocks could be modified. In fact it could be argued that a random copolymer structure might result if there is just one hydrophobe per surfactant micelle.

2.6 Rheological Behavior Studies

Studies of the rheological behavior of hydrophobically modified polymers[25][26][27][28] can help in guiding the choice and number of groups that need to be incorporated in the polymer molecule to produce aggregates of size large enough to give the desired viscosity. Viscosity is a measure of the energy dissipated by a fluid in motion as it resists an applied shearing force. The dissipation is a form of friction and in an adiabatic system, results in an increase in the temperature of the system. This friction becomes apparent when a layer of fluid is made to move in relation to another. The greater the friction, the greater the amount of force required to cause this movement which is called shear. Shearing occurs whenever the fluid is physically moved or disturbed as in pouring, spraying, spreading, mixing etc. Hence highly viscous fluids require more force to move than less viscous materials. In laminar unidirectional flow, the shear stress τ, and the rate of shear γ are used to indicate the applied force and the response of the fluid. A certain force per unit area " f/A " is required to maintain a constant velocity gradient, which in this case is "u/y". These quantities of interest are expressed as,

$$\begin{aligned} \tau &= Shear\ stress = \frac{f}{A} \\ \gamma &= rate\ of\ Shear = \frac{u}{y} \\ \eta &= Shear\ viscosity = \frac{\tau}{\gamma} \end{aligned} \tag{2.1}$$

For many liquids of lower molecular weight, the Newton's law applies i.e. the viscosity is a constant independent of τ or γ. For many polymer solutions, the shear stress and shear rate are not proportional over all ranges so that the non-newtonian viscosity as described by equation (2.4) is not a constant. In other words, if the shear rate is varied, the shear stress does not vary in the same proportion. The viscosity of the fluids will therefore change as the shear rate is varied. Thus the experimental parameters of the viscometer model, the spindle and the speed all have an effect on the measured viscosity of non-newtonian fluids. This measured viscosity is the apparent viscosity' of the fluid and is accurate only when explicit experimental parameters are furnished and adhered to.

Most polymer solutions display a pseudoplastic i.e. shear thinning behavior. There have been many studies on the rheological measurements, preparation, characterization, rheological behavior and properties of water soluble polymers. Other than the ability of the hydrophobically modified associative polymers to increase solution viscosity, they also show an unusual dependance on concentration as compared to conventional polymers [18]. In their study of the synthesis and aqueous solution behavior of associative acrylamide/N-alkylacrylamide copolymers, McCormick et. al. observed that the polymers showed a remarkable increase in apparent viscosity at low mole fractions of N-alkyl acrylamide. Wang et. al.[25] observed a substantial increase in the viscosity of hydrophobically modified poly(sodium acrylate), an ionic polymer, when NaCl was added to the aqueous polymer solution. The same observation was made when hydrophobically associating polymers containing N-vinyl-pyrrolidone was dissolved in an aqueous brine solution[3]. The initial increase in viscosity could be attributed to the screening of the charge repulsion among the polymer main chains actually causing the increase. The decrease in the viscosity with a further addition of sodium chloride could be due to the formation of compact network of micelles beyond a certain value of salt concentration[25]. In another study by Hamad et. al., the decrease in viscosity of a hydrophobically modified polymer was observed upon the addition of a surfactant solution[17]. It can be surmised here that the added surfactant solution associated with the hydrophobic segments on individual surfactant molecules, thereby leading to a suppression in the intermolecular association of the polymers. This finding advocates against mixing polymers with hydrophobic polymers in enhanced oil recovery. Several other polymers have been studied. These include acrylamide surfactant copolymers [26], sulfonated styrene-butadienestyrene block co-polymers [27], alkylhydroxyethyl celluloses [28], copolymers of acrylamide with N-(4-butyl)phenylacrylamide and sodium-3-acrylamido-2-methybutanoate (NaAMB) and copolymers of acrylamide with sodium-2-acrylamido-2-methyl-propane sulfonate (NaAMPS) [18]. All these show an improved salt tolerance. The fluorocarbon copolymers of acrylamide have also shown viscosity enhancement in the presence of NaCl [29].

2.7 Surface And Interfacial Tension Behavior Studies

The amphiphilic character of hydrophobically associating polymers makes them surface active. Bektruov et. al. in their work [30], studied the surface tension behavior of the associating polymers. Ultra low surface tension in a surfactant system is usually associated with the formation of a middle phase microemulsion. Windsor in his work [31], referred to it as a type III phase diagram. Micellar two phase systems have also exhibited an ultra low interfacial tension [32]. The very low interfacial tension in surfactant systems have been attributed to the balance between the hydrophobic and hydrophilic surfactant molecules which cause the molecules to concentrate at the interface and lower the interfacial tension. This idea has been quantified by defining a quantity 'R' which is defined as the ratio of solvent attraction between surfactant and water [33] and may be expressed as,

$$R = \frac{A_{co}}{A_{cw}} \tag{2.2}$$

Other interactions have been included in the definition of 'R' [31][33]. The value of 'R' has been very close to unity before a middle phase microemulsion. This is the reason for the ultralow surface tension obtained. Other variables such as the temperature salinity and oil type could also have an influence on 'R'. It could also be affected by internal variables such as the structure of the surfactant molecules and the nature and the relative size of the hydrophilic and hydrophobic groups. Hence for a given fixed set of variables such as temperature, salinity etc., the concept of a hydrophobic-hydrophilic balance may be applied in selecting groups comprising a polymer chain. The surface tension behavior for a polymer chain is expected to be similar to surfactant molecules because they are simply surfactant molecules bonded together. Most surface tension studies conducted on polymers are at the air water interface [34][35]. Yahya et. al. in their work[36] have studied the surface tension and interfacial tension of poly(vinyl alcohol) at the oil water interface. It was observed that the surface and interfacial activity of hydrophobically modified polymers was clearly more than that of their unmodified counterparts. However the surface tension was only moderate as compared to conventional surfactant which exhibit ultimate surface tension values in the range of 20-40 mN/m.

Chapter 3

Materials and Methods

3.1 Synthesis of the PAS Block Copolymer

3.1.1 Materials

Acrylamide was used as received from Fluka A. G., Chemische Fabrik. Styrene from the same company was distilled prior to use. The surfactant, Cetyl trimethylammonium bromide (CTAB), and the potassium persulfate initiator were purchased from BDH Ltd. Poole, England. Deionized water was used exclusively for all aqueous solutions. Methanol was obtained from BDH Ltd. Poole, England.

3.1.2 Distillation of Styrene

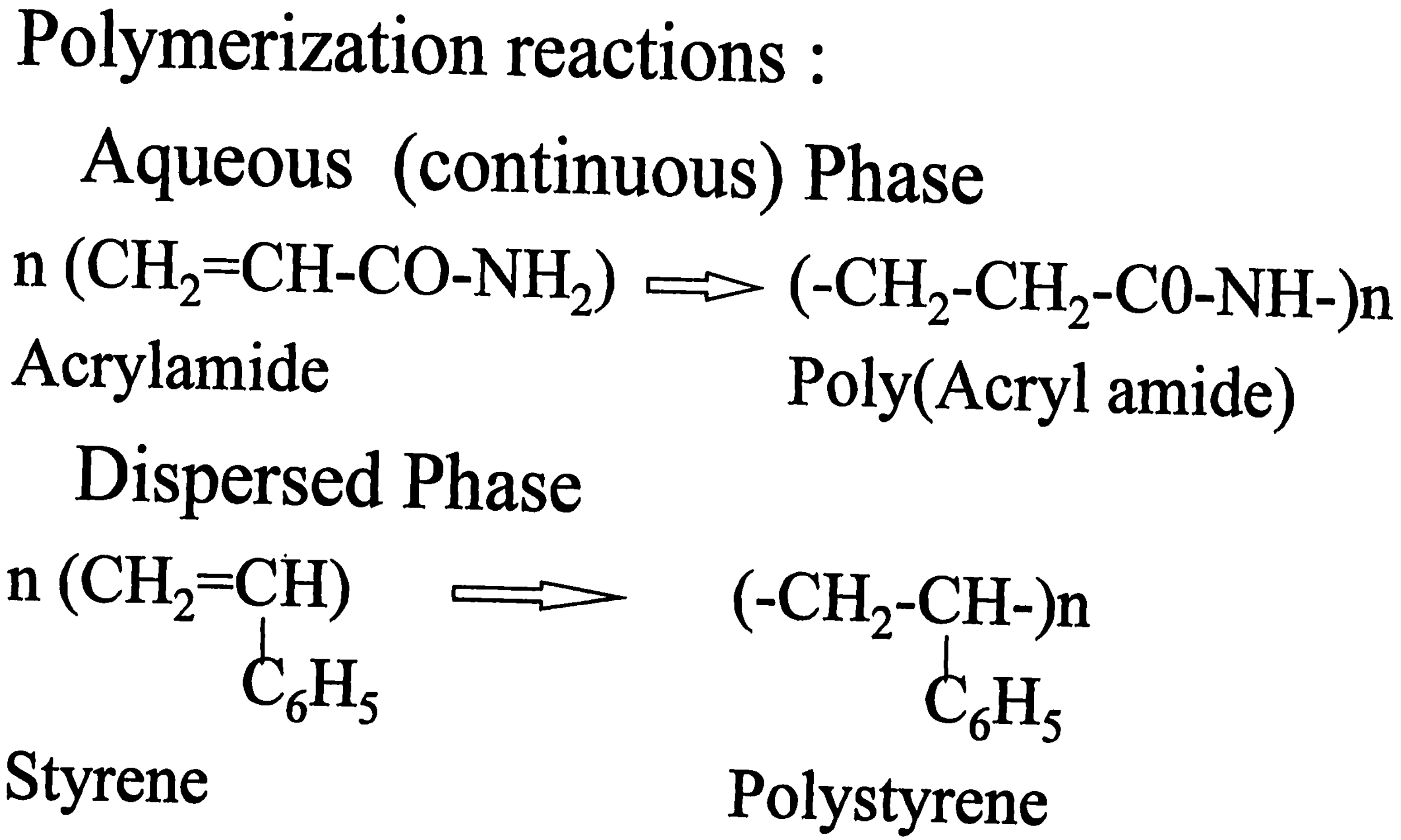
Styrene was washed with 5% NaOH solution and dried (Na_2SO_4). Distillation was carried out under vacuum. The sample withdrawn was purged with nitrogen gas and stored at a temperature of 5 ^{o} C

3.1.3 Polymer Synthesis

The experimental procedure used for the micellar process is as follows: The composition of the reaction mixture is as shown in Table 3.1.

Aqueous solutions of acrylamide were placed in 500 ml round bottom flasks covered with septum caps and were degassed with gentle bubbling with nitrogen for 30 minutes. The surfactant CTAB was added followed by injection of styrene with a syringe into the reaction mixture and stirring was continued for about 0.5 to 1 hour until a homogenous solution was obtained. The flask containing the reaction mixture was then placed into the temperature controlled oil bath at 50 ^{o} C under constant stirring. Polymerization was initiated by the addition of potassium persulfate solution . The reaction time for all reactions was kept constant at 96 hours.

The polymers were precipitated by slowly pouring into methanol (1L)



Polymerization reactions :

Aqueous (continuous) Phase

$$n\,(CH_2{=}CH\text{-}CO\text{-}NH_2) \Longrightarrow (\text{-}CH_2\text{-}CH_2\text{-}C0\text{-}NH\text{-})n$$

Acrylamide — Poly(Acryl amide)

Dispersed Phase

$$n\,(CH_2{=}\underset{\displaystyle C_6H_5}{\underset{|}{CH}}) \Longrightarrow (\text{-}CH_2\text{-}\underset{\displaystyle C_6H_5}{\underset{|}{CH}}\text{-})n$$

Styrene — Polystyrene

Figure 3.1: Polymerization Reactions for the PAS Block Copolymers

Polymer	CTAB (g)	init (mg)	yield (g)	Viscosity* (cps)	Viscosity** (cps)	Nature of solution
P(AS)64	0.00	150	-	-	-	Insoluble
P(AS) 63	4.70	150	5.6	320	2026	cloudy
P(AS)60	5.95	150	9.1	775	4306	cloudy
P(AS)59	7.94	150	9.5	320	1627	cloudy
P(AS)61	10.94	150	3.6	3	-	cloudy
P(AS)62	14.00	150	1.7	-	-	Insoluble
P(AS)86	14.00	353	10.6	907	5375	clear***
P(AS)87	14.00	253	8.1	-	2080	clear

* @0.79/s at 0%Nacl

** @ 5%Nacl

*** On slight heating

Table 3.1: Mixture compositions and solubility results for AM-ST block copolymers

at constant stirring. The polymer was then filtered, redissolved in water and reprecipitated in methanol. This process is repeated 4 times in order to ensure complete removal of surfactant and residual monomer. The white polymer was then dried under vacuum (18 - 20 hrs.) at 60-70 ^{o} Cuntil a constant weight of the polymer was obtained.

3.2 Synthesis of the Hydrophobically Modified Poly(vinyl alcohol)

3.2.1 Materials

The preparation of water soluble hydrophobic associative polymers can be carried out either by chemical modification of a preformed reactive polymer or by copolymerization of the appropriate monomers or by a combination of both methods. The former synthesis route has traditionally been used for the modification of cellulose derivatives leading to the so called HEUR thickeners [23]. i.e., hydrophobically modified ethoxylated urethane polymers. This procedure may be applied to modify poly(vinyl alcohol), as it contains hydroxyl groups which lend themselves easily for modification.

Hydrophobically modified PVA can be obtained by reacting acid chlorides of long chain fatty acids (hydrophobic moieties) with PVA to from ester linkages. Hydrophobically modified PVA can exhibit enhanced viscofication as a result of intermolecular association which causes an increase in the hydrodynamic volume. Furthermore, as a result of the polymeric amphiphilic structure i.e., consisting of hydrophilic groups (hydroxyl and urethane groups) and hydrophobic moieties (long chain fatty acid groups), the polymer is expected to exhibit high surface and interfacial activities.

In the present work, chemical modification of PVA by esterification reaction of different combinations of long chain fatty acid chlorides such as decanoic acid chloride, docosanoic acid chloride and stearic acid chloride with urethanized PVA will be carried out. Partly urethanized PVA was used as it is found that urethanized PVA was more stable and more soluble in solvents such as water, dimethylformamide(DMF), and dimethyl sulfoxide(DMSO)[37]. The long chain fatty acid chlorides were obtained were obtained directly from Fluka Chemie AG and was used as received.

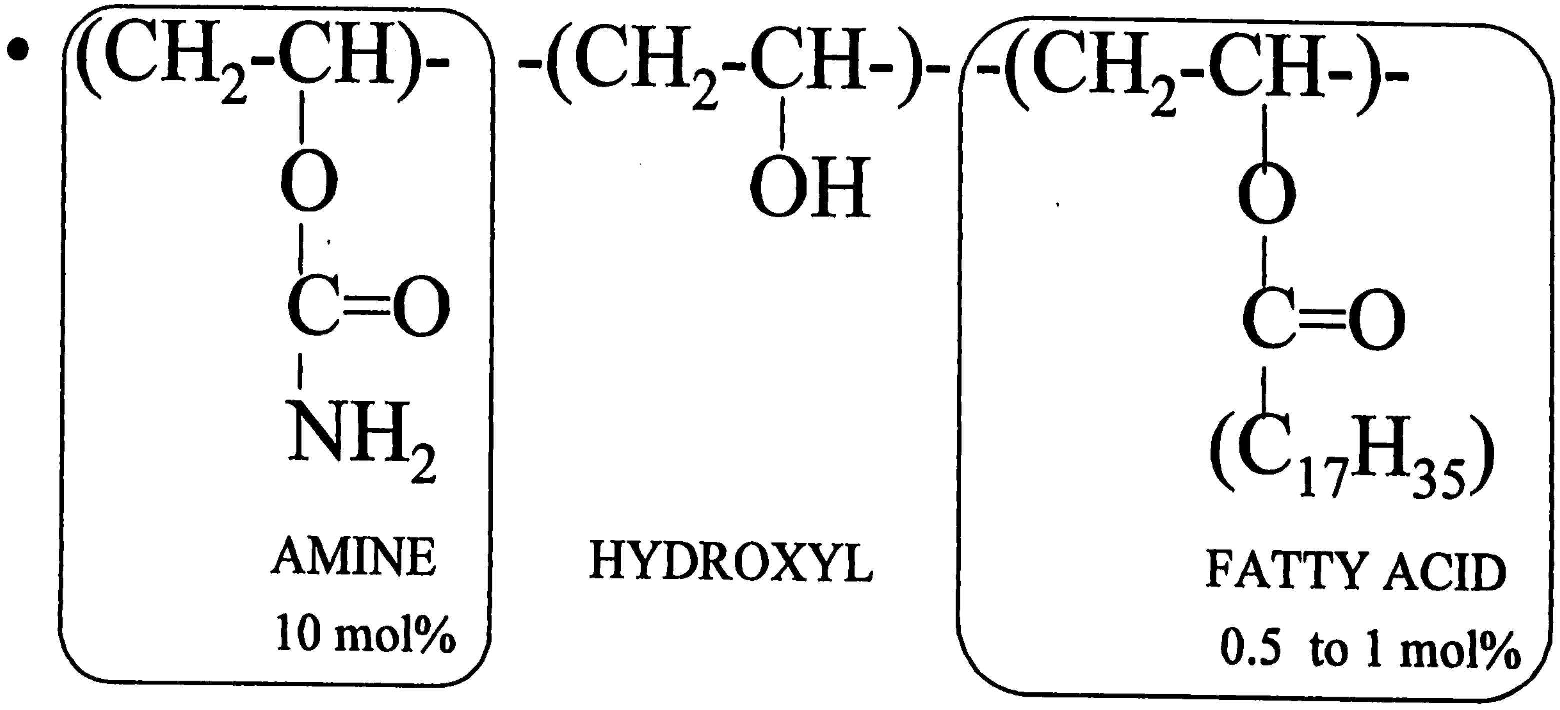


Figure 3.2: Structure of the Hydrophobically Modified PVA

3.2.2 Methods

Poly(vinyl alcohol) with its free hydroxyl groups along the polymer backbone offers considerable scope for chemical reactions such as etherification , esterification and acetalization. Partly urethanized PVA can be obtained by adding urea to PVA having a degree of polymerization of 1,600 and a molecular weight of 72,000 and with a degree of hydrolyzation of 97.5 - 99.5 mol% in distilled DMF at about 150 ^{o} C. 10.0 gms PVA was placed in a 100 ml: round bottom flask, equipped with a thermometer, a condenser, and a magnetic stirrer. The flask was maintained at a temperature of 148 to 152 ^{o} C, under N_2 gas to stop O_2 free radicals from degrading the polymer. The reaction mixture becomes homogenous within a few minutes and proceeds with the evolution of gas. The reaction mixture is left for 2.5 hrs after which the resulting polymer is precipitated into methanol, purified twice in excess methanol and then dried in vacuo at 70 ^{o} C until a constant weight is obtained.

Different combinations and ratios of the acid chlorides are reacted with the urethanized PVA. Some of the modified polymers obtained were found insoluble in water even after heating to an elevated temperature for several hours. The results obtained for the polymer solution such as the solubility in water, and viscosity are given in Table A.1.

An example of one of the modification reactions is as follows:

4 g of urethanized PVA having a degree of polymerization of 1600 and a molecular weight of 72,000 was mixed with 40 ml of distilled DMF and heated to 140 ^{o} C. It was maintained at this temperature until a clear homogenous solution was obtained. Then 0.5 mol% Steoryl Chloride and 0.5 mol% Decanoyl Chloride in DMF(2 cm^3) was mixed and added dropwise to the reaction mixture, along with vigorous stirring. The reaction was carried out under N_2 gas to stop O_2 free radicals from degrading. After 2 minutes of reaction time, the resulting polymer was precipitated into methanol, purified twice in excess methanol and then dried in vacuo at 70 ^{o} C.

3.3 Synthesis of the Ionic PVA

3.3.1 Materials

Ionic PVA was prepare by reacting unmodified PVA (molecular weight : 72000) by the sodium salt of monochloroacetic acid. The dialysis was done using a thin dialysis membrane by which the modified polymer could be segregated from the salt solution. The solution was neutralized by the addition on Sodium Hydroxide and pure products were reprecipated using methanol and acetone.

3.3.2 Methods

8.8 gms. of PVA was heated till soluble in 200 ml. of deionized water and then cooled to a temperature of $15^o\ C$. A solution of Na OH is prepared by adding 80 gms of NaOH to 120 ml. of water. This is then added to the PVA solution maintaining the tempperature at $15^o\ C$ to $25^o\ C$. The mixture is then stirred for 24 hrs. at a temperature of $25^o\ C$ to give saponified PVA. The sodium salt of monochloroacetic acid (MCA-Na) is added to the saponified PVA (233 gms.) such that the composition of the reaction mixture is 1 : 10 : 10 by weight of PVA : NaOH : MCA-Na. The etherification reaction is allowed to run for 84 hrs. at a temperature of $25^o\ C$. Th reaction mixture is then dialyzed using a dialysis membrane. The size of the semipermeable membrane is chosen such that the salt molecules are allowed to escape whle the polymer molecules remain inside due to their large size. A constant concentration gradient across the membrane aids in the difussion of salt across the membrane. The dialysis process takes about 24 hrs. for the polymer solution to be completely salt free. The solution is neutralized by the addition of slight NaOH and crude products are precipitated by acetone. These are then reprecipitated in methanol to obtain the pure products.

3.4 Viscosity Measurements

3.4.1 The Brookfield Digital Viscometer - DV2

The Brookfield thermal system consists of a Brookfield viscometer with accessories such as spindles, leg guard, extracting tool, temperature controller etc. as seen in Figure 3.3. Viscosity measurements are done using the coaxial spindle geometry. The temperature is controlled by a solid state, triac output proportioning controller, which maintains the spindle, chamber and sample material at the desired temperature. The system is designed for measuring liquid viscosities over a temperature range of upto 300 ^{o}C. The lower limit of temperature control is 15 ^{o}C. above ambient temperature. The designed viscosity range is from 1 cps to 8,000,000 cps. depending on the viscometer, and the SC4 and UL adapter spindles used.

The Brookfield UL Adapter accessory has been developed for use with Brookfield viscometers to allow accurate and reproducible viscosity measurements to be made on low viscosity materials for viscosities as low as 1 cp. At 60 rpm, the LVT model has a full scale range of 1 -10 cps with the UL adapter.The UL adapter consists of a precision cylindrical spindle rotating inside an accurately machined tube. Its correct cylindrical geometry provides accurate viscosity measurements and shear rate determinations. The tube has a removable cap. With the cap removed, the open ended tube can be used in a beaker or tank. With the cap in place, the closed tube holding a 16 ml sample can be immersed in a temperature bath.the working temperature range is from -10 $^o\,C$ to 100 $^o\,C$. All the immersed parts are stainless steel.

The Brookfield digital viscometer is a laboratory viscometer which can be utilized with with all Brookfield accessories such as the UL Adapter, small sample adapter, thermosel and helipath stand. We have a continuous display of the basic viscometer reading, a display of the calculated shear stress, Autozero for automatically zeroing the viscometer, Autorange for displaying full scale viscosity and shear stress range for any spindle/speed combination and for verifying special spindle entries and low indicator for readings below

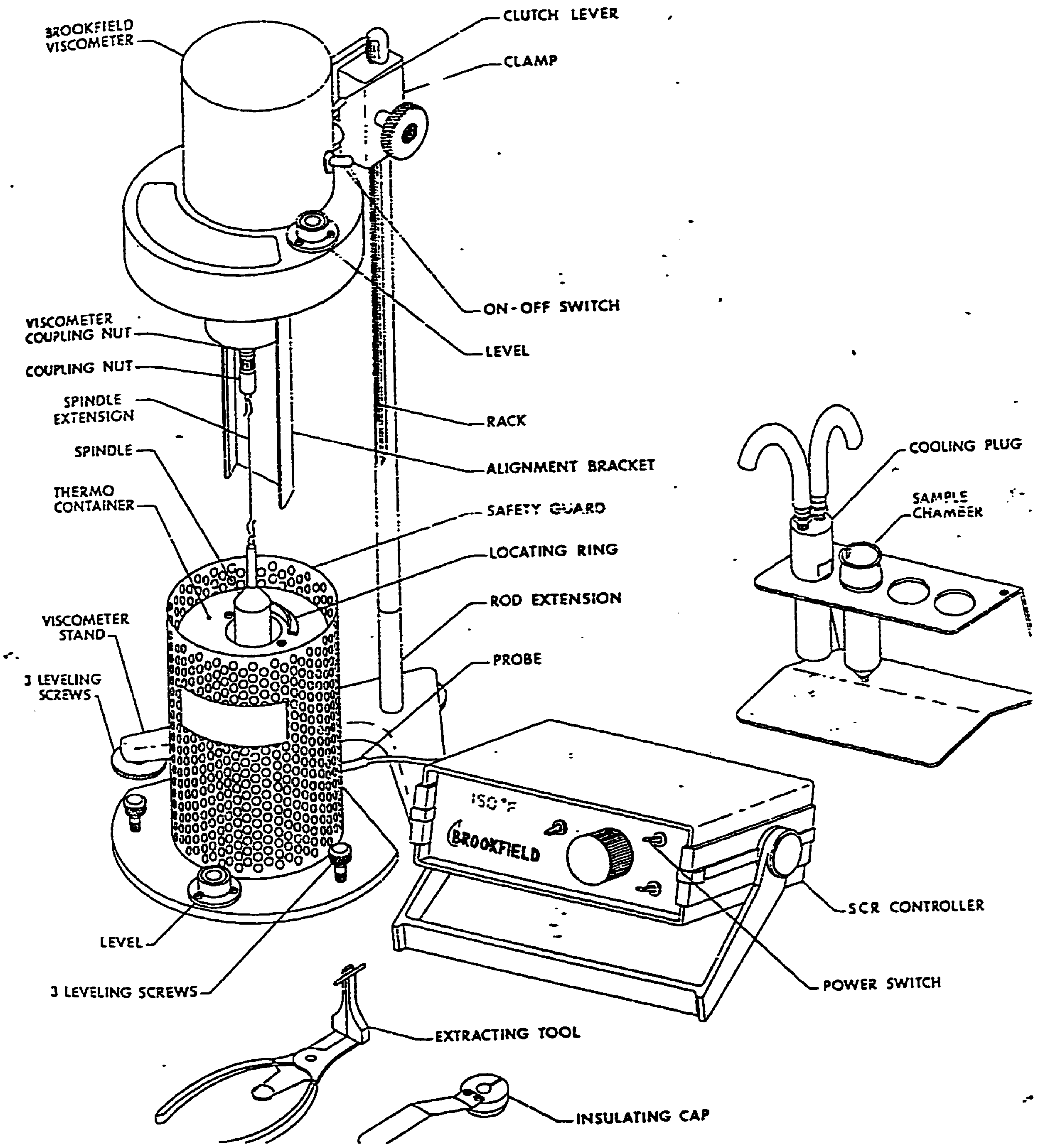


Figure 3.3: The Brookfield Digital Viscometer

10% of full scale range.

The Brookfield digital viscometers rotate a sensing element in a fluid and measures the torque necessary to overcome the viscous resistance to the induced movement. this is accomplished by driving the immersed element which is called a spindle, through a beryllium copper spring. The degree to which the spring is wound, detected by a rotational transducer, is proportional to the viscosity of the fluid. The minimum viscosity range is obtained by using the largest spindle at the highest speed, the maximum range by using the smallest spindle at the slowest speed.

3.4.2 Procedure for Viscosity Measurement

The instrumentation was placed on a firm level surface. The viscometer stand was set up by connecting the rod extension to the bottom of the upright rod. The viscometer assembly was levelled using level screws provided at the base of the assembly. The chamber was then inserted into the thermo-container using the extracting tool. The chamber was rotated until it locked in place preventing further rotation. Instrumentation was assembled as per the procedure of the Brookfield digital viscometer manual [38]. By the use of a pippete, the appropriate volume of polymer solution was poured into the sample chamber. Using the extracting tool, the loaded chamber was put back into the thermo-container. the viscometer was then lowered and the thermo-container was properly aligned. The appropriate spindle was then inserted into the polymer solution in the chamber and was coupled to the viscometer. The temperature controller was turned on and the set point knob adjusted to the desired set point at which the viscosity measurements are to be made. The viscometer was them left running for a period of about 30 minutes and viscosity readings were then taken at different shear rates and temperatures.

3.5 Interfacial and Surface Tension Measurements

The tensiometer consists of a measuring instrument and a processor control unit. The balance system situated in the head part of the instrument has an accuracy of 0.0001g and 0.01 mN/m respectively. It incorporates a servo system for fully automated calibration and taring. The solid metal housing provides an instrument with great stability and shock resistance, therefore a weighing table is usually unnecessary. Due to the rigid connection of the plate or ring to the balance system, a measurement is possible in both push and pull directions. A measurement in the push direction is necessary whenever the lighter phase has a higher affinity to the measuring body (ring or plate) than the heavier phase. The temperature of the sample is optionally controlled using a circular bath measured by the built in pt-100 thermoresistor and is displayed digitally. The force which is detected when a measuring device of known circumference is moved into the interface of two immiscible phases (liquid/liquid or liquid/gas) is directionally proportional to the surface and interfacial tension between these phases.

$$\sigma \simeq \frac{F}{L} \ (mN/m) \tag{3.1}$$

Depending on the individual needs, the platinum ring or the platinum plate are force used as the 'force pick up'.

To minimize temperature changes and air circulation, plexiglass doors have been installed to isolate the measuring area. Yet complete access is possible just by opening the doors. Integrated in the thermostat vessel is a magnetic stirrer which can be operated either manually or automatically by the processor. This feature generates reproducible starting conditions when measuring samples of the same solution at different concentrations. The combination of an electronic balance system and a processor control unit enables fully automated measurements.

3.5.1 The Ring Method

The measuring device is a platinum ring which is suspended horizontally for the measurement. The geometry of the ring has to be known. It determines the wetting length, I_b=119.95 of the ring, calculates the mean radius R=9.545 mm and the radius of cross section of the wire, r=0.185 mm (for the standard kruss ring). The platinum ring is dipped into the sample liquid and immediately removed afterwards as seen from Figure 3.4. The maximum force k_{max} which is necessary to pull the wetted circumference I_b of the ring through the surface of the liquid is measured. The surface of interfacial tension σ is calculated according to

$$\sigma = k_{max} \frac{F_{cf}}{I_b} \tag{3.2}$$

The correction factor F_{cf} takes into account, the weight of the liquid which is lifted by the ring. The main disadvantage of the ring is the necessity of correction of the measured values. It not only determines the force on the ring caused by the surface tension but also the weight force of the liquid volume of the lamella at the bottom of the ring as seen in Figure 3.4. The automatic correction of the process tensiometer K12 is based on the publication by Zuidema et. al.[39]. The equation was interpolated using the tables formulated by Harkins[40].

3.5.2 The Plate method

The measuring device is a vertically suspended platinum plate of exactly known geometry. The surface of the plate is roughened for a better wetting property. The lower edge of the plate is brought into contact with the sample liquid. The liquid 'jumps' to the plate and pulls the plate into the liquid. The force K caused by this wetting is measured by pulling out the plate upto the level of the liquid as shown in Figure 3.5. The measuring procedure is static, which means that the plate can stay at zero level for a long period. Thus a continuous measurement of the surface tension is possible without the problem of forming a new surface all the time as is necessary with the ring method. The measured values do not need a correction, which is another advantage of the plate method. The surface tension of the liquid is determined according to the wetted length I_b as

$$\sigma = \frac{K}{I_b \, cos\Theta} \tag{3.3}$$

The above equation can be used for the determination of the surface tension only if the contact angle is zero i.e. $\cos\theta = 1$. This implies a total wetting of the plate. This condition is complied with the roughened and clean platinum plates, which are usually used for the measurement.

3.5.3 Procedure for surface and IFT measurements

For measurements by the ring method,we first clean the ring by acetone and distilled water. The ring is then heated to red hot, then cooled and fixed into the measuring area. This is done by sliding carefully into the guiding mechanism situated at the top part of the measuring area. The guidance of the clamping device is locked by turning clockwise, the small wheel on the left at the outside of the measuring unit. Options are available either for making a single measurement or a series of measurements[41]. In the IFT measurement, liquid decane was used as the light phase or oil phase. The same procedure as for surface tension was followed. Measurements can be made both in the push and pull directions. Density of both, the heavy phase (polymer solution) and the light phase (decane) are needed as input data. A circulating water bath was to used to maintain a constant temperature during the measurements.

The plate method is used for the measurement of surface tension only. Essentially the procedure is the same as the ring method. In this case however, the plate is dipped 2 mm deep into the liquid the liquid surface before the start of the measurements and then lifted upto the level of the liquid surface. Most of the surface tension measurements were made at a temperature of 30 ^{o} C.

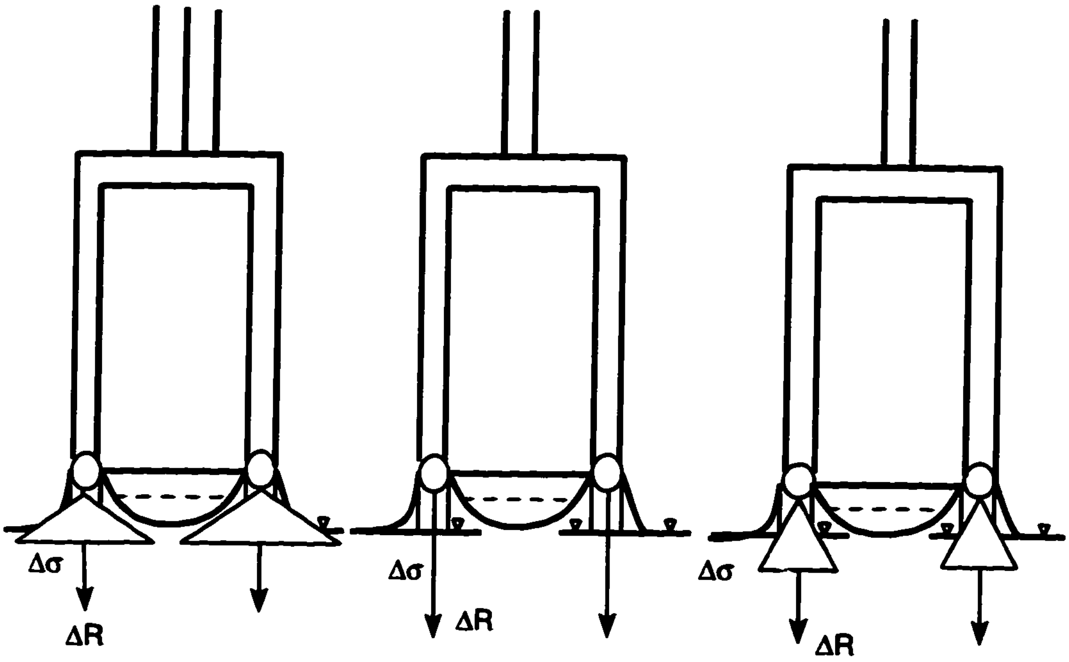
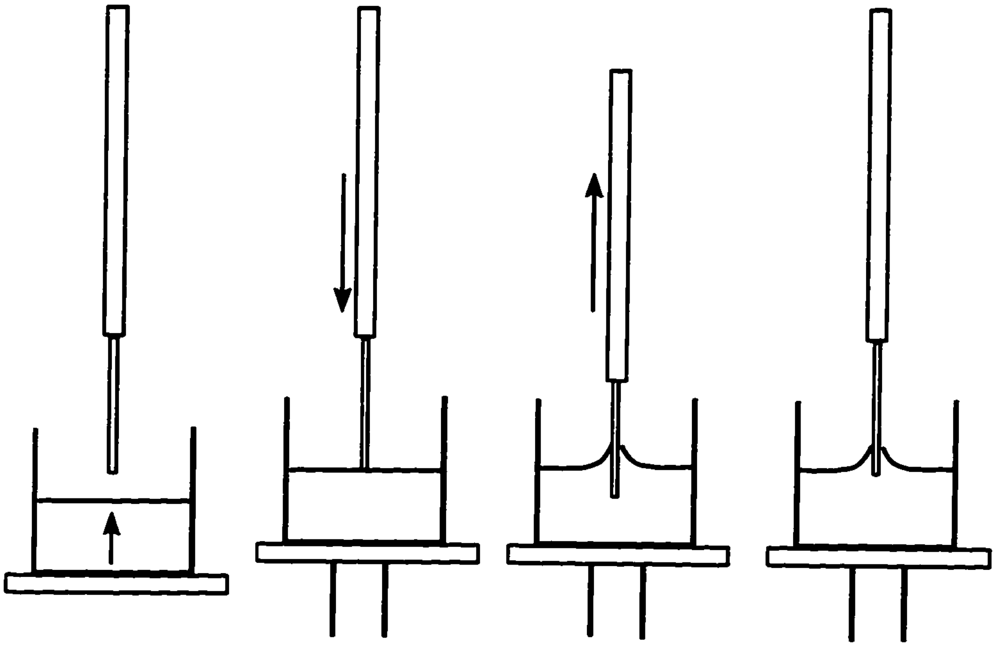


Figure 3.4: The ring method for Surface and IFT Measurement



Test vessel is raised towrds the lower edge of the plate

The lowest edge makes contact and the plate is drawn into the liquid by surface tension.

The plate is drawn up to the zero level by the tensiometer.

Figure 3.5: The Plate Method for Surface tension measurement

3.6 Characterization

3.6.1 Fluorescence

Solubilization may be defined as the preparation of thermodynamically stable isotropic solutions of substances normally insoluble or sparingly soluble in the solvent made possible by the addition of an amphiphilic component or components [42]. Of the various spectrometric techniques used to study solubilization of probe molecules such as UV Visible spectroscopy, laser light scattering, ESR spectroscopy and NMR techniques, fluorescence spectroscopy is found to be particularly versatile and one of the most informative.

The Spectrofluorophotometer

Fluorescent measurements were made using a spectrofluorophotometer (Model - RF5000, Shimadzu). The entire assembly consists of the photometer, the controller and the graphic display unit. The excitation monochromator wavelength was set constant at 330 nm and emission was recorded between a wavelength of 340 to 550 nm.

Fluorescence measurements

Pyrene and its derivatives are widely used as probes in solubilization studies. Pyrene is chosen as a probe because of its fine monomer fluorescence structure in solution. The vibrational fine structure intensities show significant variation when the environment changes from a non-polar solvent to a polar one with a high dipole moment and a high di-electric constant. The fluorescence intensity ratio of the fluorescence bands, I at 372 nm and III at 383 nm is a good indicator of the environment of the probe. A lower I/III ratio indicates a more hydrophobic environment of the pyrene label.

3.6.2 NMR Spectroscopy

When certain types of nuclei such as protons, C13 and F19 are placed in a strong magnetic field, they can absorb electromagnetic radiation in the radio-frequency range. Such nuclei are said to be spin active and said to resonate. The precise frequencies at which spin active nuclei resonate can be picked up and displayed by instruments called nuclear magnetic resonance or NMR spectrometers. The information contained in an NMR spectrum as chemical shifts, coupling constants and integration ratios can be converted to structural information. This translation of information or interpretation of spectral data involves the use of several logical and empirical rules of thumb or "heuristics". All peaks in an NMR spectrum can be assigned to structural features in the molecules under study. Exceptions may be very complex molecules such as proteins or nucleic acids

NMR Characterization of Macromolecules in solution

The NMR method is the most effective available way for studying the microstructure. The method is now routinely employed to characterize and to identify the structures present in polymer molecules. The NMR parameter that is sensitive to the structural issues is the chemical shift, commonly measured in ppm from an internal reference. It senses readily information on the framework of the polymer -its connectivity - by providing information on the number and type of atoms linked to each particular nucleus and also senses such factors as the relative chirality of pairs of such centers and cis/trans isomerism within double bonds.

The nucleus most often employed for synthetic and natural macromolecules is C13, despite its being rather dilute(only 1% natural abundance of the C-13). The dispersion of chemical shifts is rather large in a C-13 spectrum

. Hence much detail is encountered that is directly related to the polymer structure itself and signal intensity is rarely a problem with modern high field instruments.

Chapter 4

Results and Discussion

4.1 Hydrophobically Modified PVA

4.1.1 Solubility

The primary factor governing the solubility of a water soluble polymer is the presence of hydrophilic and hydrophobic groups on the polymer chain. Urethanized PVA is better soluble than ordinary PVA due to the presence of the hydrophilic urethane groups on the polymer chain. The hydrophobic fatty acid chlorides contribute towards enhancing the viscosity. The correct balance between hydrophilic and hydrophobic groups leads to a polymer which is water soluble and at the same time possesses a high viscosity.

In the modified polymer under study it was found that the maximum hydrophobe incorporation was 0.5 mol% C18 (Stearoyl Chloride) and 0.5 mol% C10 (Decanoyl Chloride). Beyond this , say for a hydrophobe content of 0.75 mol% C18 and 0.5 mol% C10, it was found that the polymer sample was insoluble in water even after 2 days of continuous stirring. A summary of the solubility results is as shown in Table A.1. Thus we see that the limiting factor for the solubility is the hydrophobe incorporation in the polymer side-chains.

4.1.2 Viscosity Behavior

The solution viscosity of HMPVA was determined using a Brookfield digital viscometer. It can be seen from Figures 4.1 and 4.2 that the hydrophobically modified polymers with a hydrophobe incorporation of 0.5 mol% C18 and 0.5 mol% C10 (PVA1) and 0.5 mol% C18 and 0.25 mol% C10 (PVA2) show a typical shear thinning behavior so often found in hydrophobically associating polymers. This can obviously be attributed to the rupture of intermolecular associations and a disentanglement of the macromolecular chains at high shear. Viscosity rises sharply from a value of 189 cP at 2.2% to a value of about 2200 at 3% polymer concentration indicating an increasing association between hydrophobic moieties. The incorporation of hydrophobic groups is primarily responsible for the increase in viscosity of the unmodified polymer. Interchain association between the hydrophobes leads to the polymer chain occupying a larger hydrodynamic volume and an enhancement in viscosity. This phenomenon is consistent with studies reported in literature. Viscosity of the polymer solution decreases with decreasing chain length of the fatty acid chlorides. This is very logical because it is easy for longer hydrophobic chains to associate and they also occupy a larger hydrodynamic volume.

The HMPVA viscosity decreases with increasing salt concentration . It can be seen from Figure 4.3 that the viscosity decreases steadily upto a concentration of 4.5% NaCl after which there is a sharp drop in the viscosity and the polymer precipitates out of the solution. A similar behavior is seen for PVA2 (Figure 4.4) where a sharp drop in viscosity is noted at an NaCl concentration of 4%. The decrease in viscosity could be attributed to a contraction of the polymer chain. The repulsion amongst the partial charges on the hydroxyl groups along with interchain hydrophobic association is the reason for the high viscosity in water. The salt molecules shield the charges

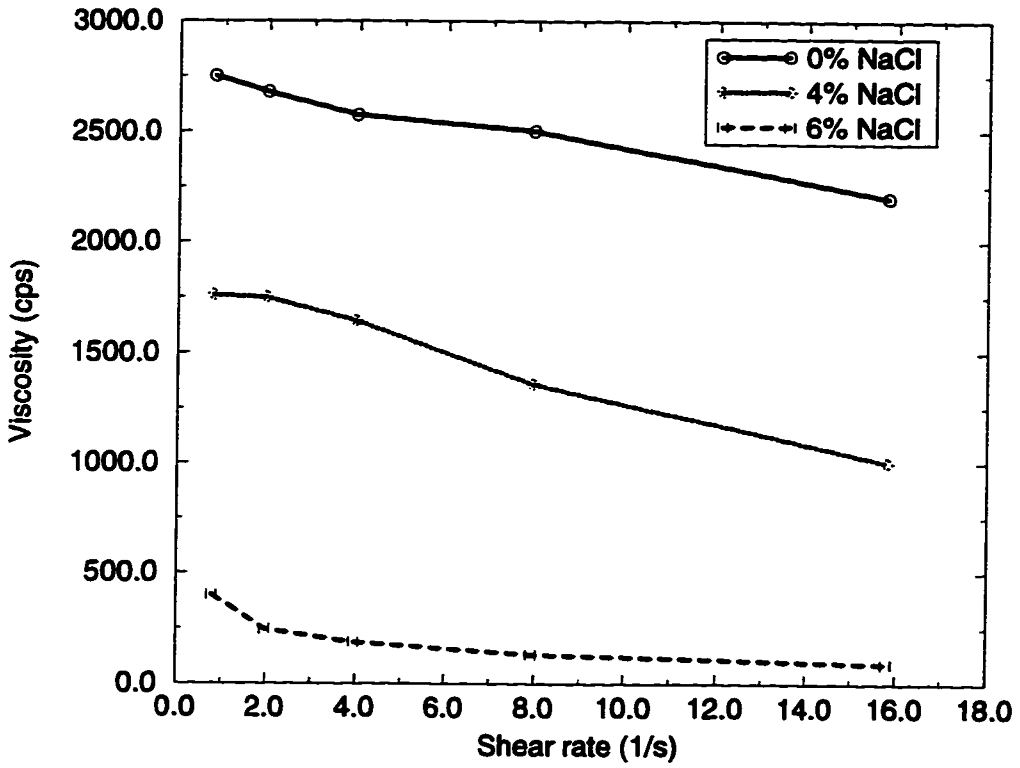


Figure 4.1: Plot of Shear rate Vs Viscosity for HMPVA with 0.5 mol% C18 and 0.5 mol% C10 (PVA1)

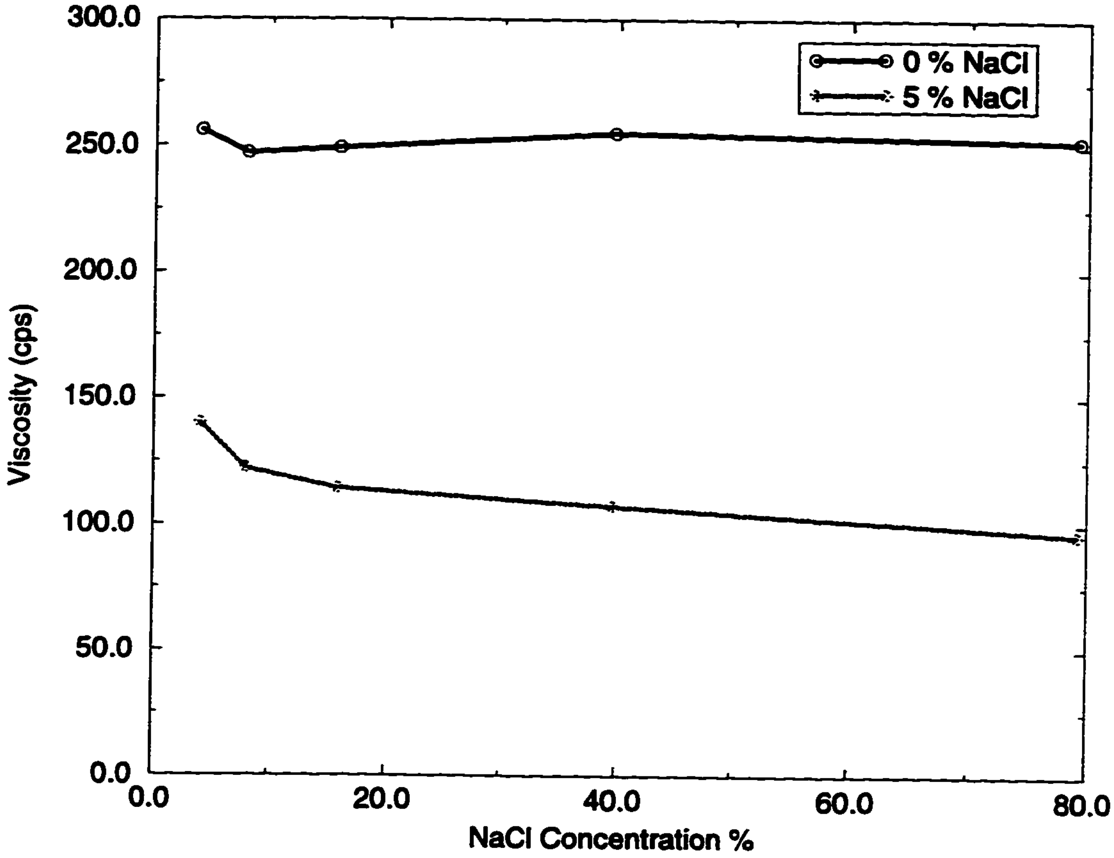


Figure 4.2: Plot of Shear rate Vs Viscosity for HMPVA with 0.5 mol% C18 and 0.25 mol% C10 (PVA2)

from each other causing the chain to collapse to smaller hydrodynamic dimensions.

4.1.3 Surface and Interfacial Tension Behavior

The series of water soluble hydrophobically modified PVA show high surface and interfacial activity. It is seen form Figure 4.5 that the surface tension value decreased to about 50 mN/m from that of 72 mN/m (ST value for water) at polymer concentrations as low as 0.1 %, after which it remained invariant. In a 5% NaCl solution also, a similar behavior was obtained although a slight increase was noted at 0.5% polymer concentration (Figure 4.6). The interfacial tension value decreased to about 23 mN/m from about 45 mN/m, the IFT value noted for the n-decane / water system (Figure 4.7). The IFT remains invariant with increasing NaCl concentration as is expected for non-ionic polymers as there are no charged groups present on the macromolecular chain which may influence the polymer chain behavior (Figure 4.8).

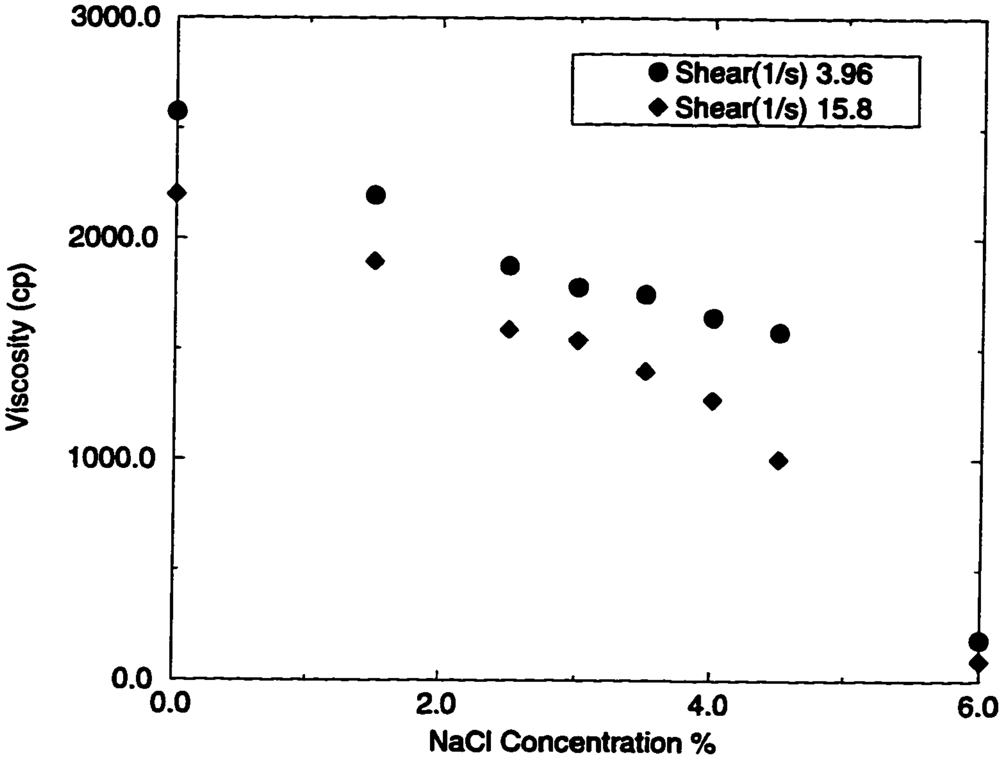


Figure 4.3: Plot of NaCl concentration Vs viscosity for HMPVA with 0.5 mol% C18 and 0.5 mol% C10 (PVA1)

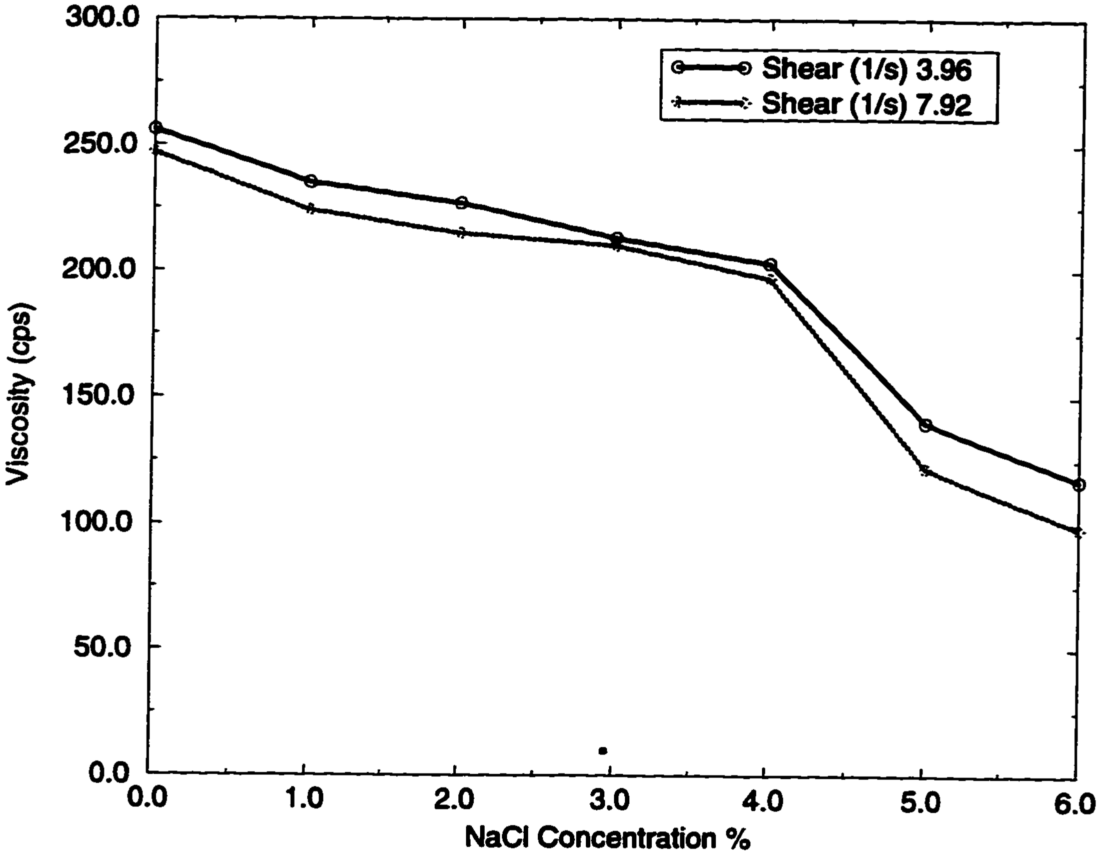


Figure 4.4: Plot of NaCl concentration Vs Viscosity for HMPVA with 0.5 mol% C18 and 0.25 mol% C10 (PVA2)

4.1.4 Fluorescence Spectroscopy

In hydrophobic media, the I / III ratio i.e. the ratio of the emission spectrum of the 1st to the 3rd peak decreases to a value of about 1.2 to that of about 1.75, the value for pyrene in water. The I/III values for the hydrophobically modified PVA show very similar trends with increasing polymer concentration for both, the 0% and 5% NaCl solutions. This confims that salt has little effect on molecular interactions. The I/III value decreases to about 1.2, the value for pyrene in hydrophobic media at an HMPVA concentration of 0.4-0.5%.

4.2 Ionic PVA

Ionic PVA was synthesized as discussed earlier by the incorporation of negative charges on the PVA chain. The incorporation of charges has been high as indicated by the results of Elemental Analysis.

As with non-ionic polymers the viscosity behavior of ionic polymers is important from both practical as well as theoretical considerations. The intrinsic viscosity directly relates to the hydrodynamic volume of the polymer molecule and can provide an idea of the conformation of the macromolecular

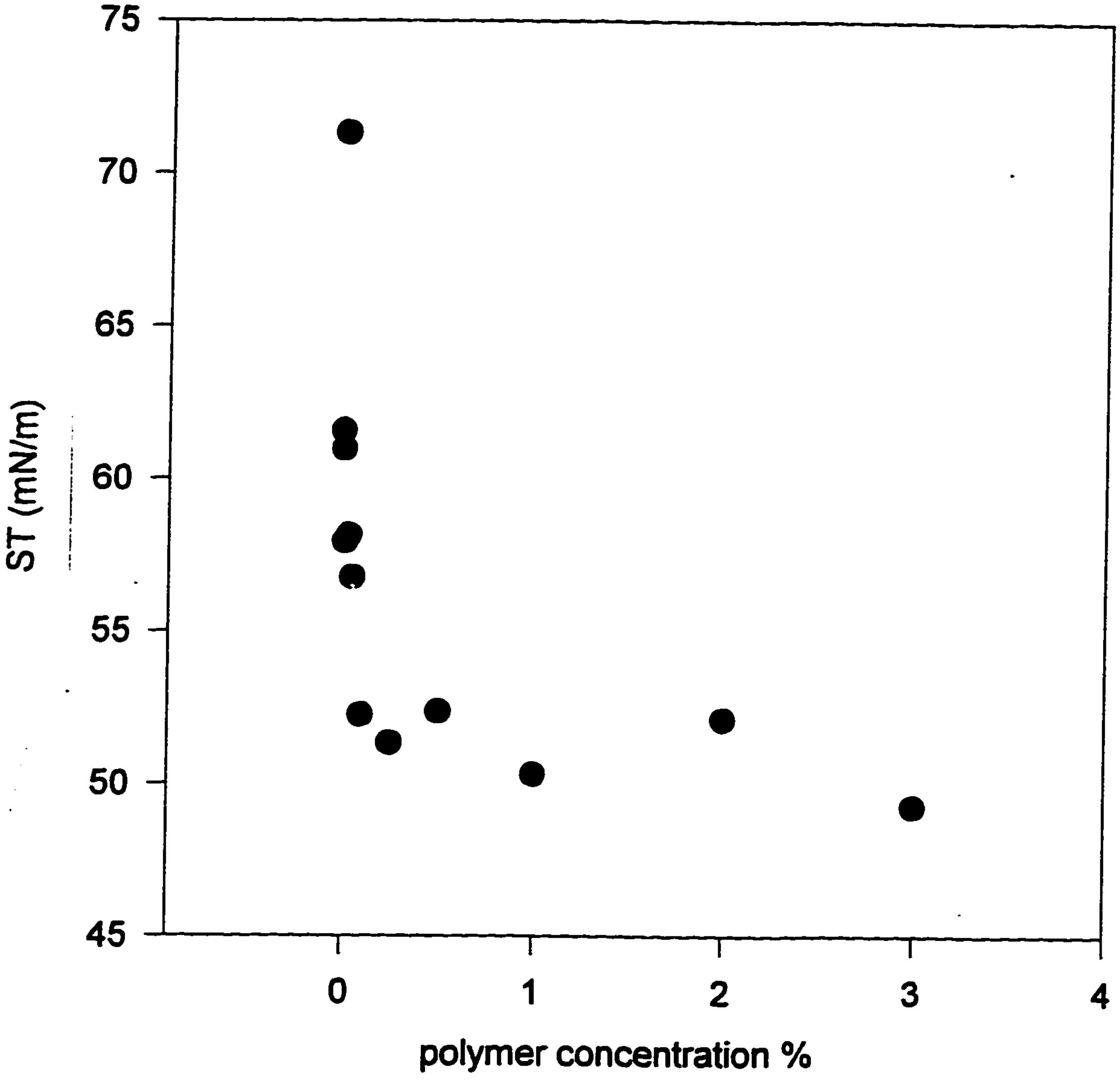


Figure 4.5: Surface tension behavior at varying polymer concentration for PVA1 (0% NaCl)

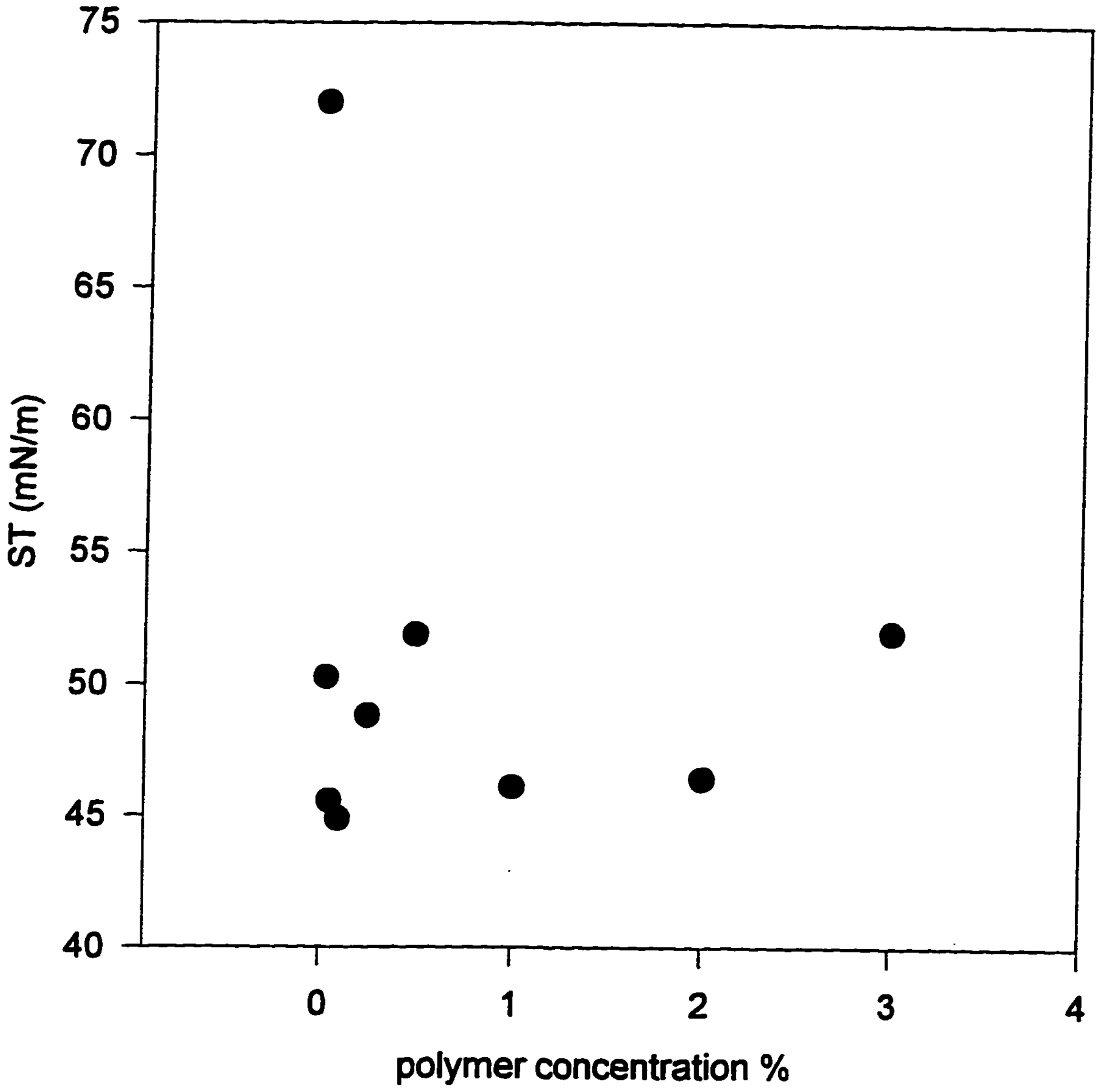


Figure 4.6: Surface tension behavior at varying polymer concentration for PVA1 (5% NaCl)

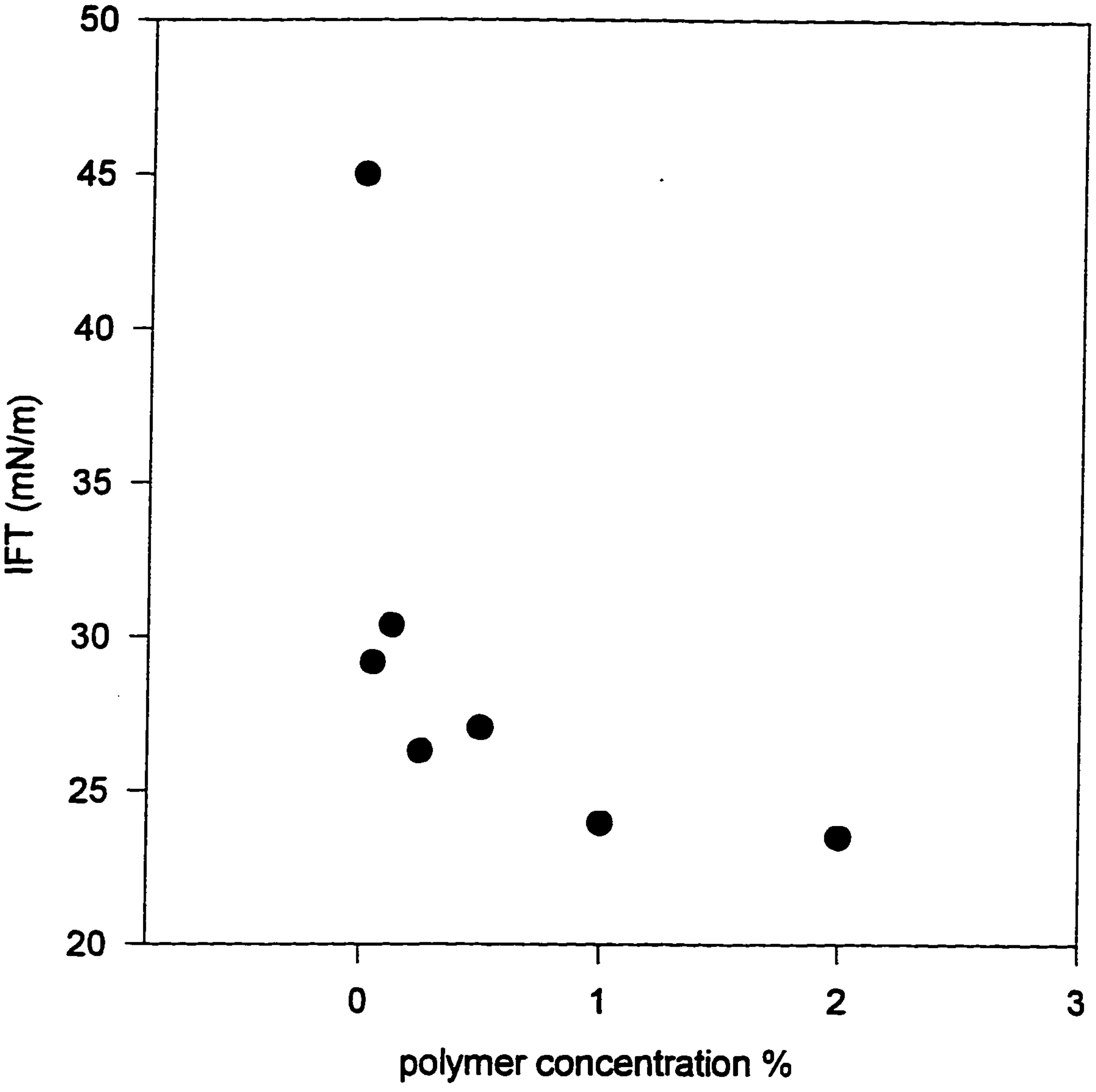


Figure 4.7: Interfacial tension behavior at varying polymer concentration for PVA1 (0% NaCl)

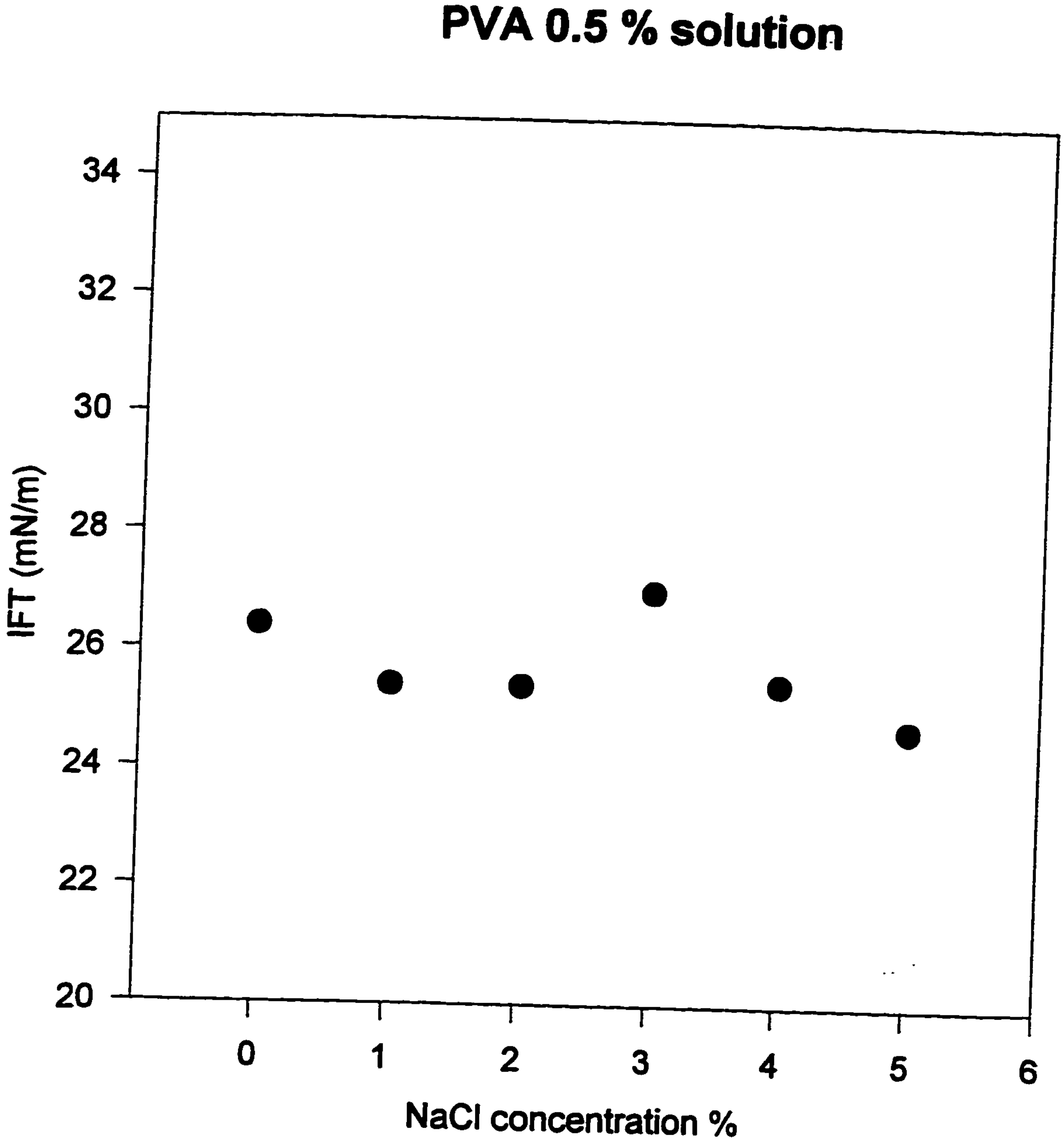


Figure 4.8: Interfacial tension behavior at varying salt concentration for PVA1 (0.5% polymer concentration)

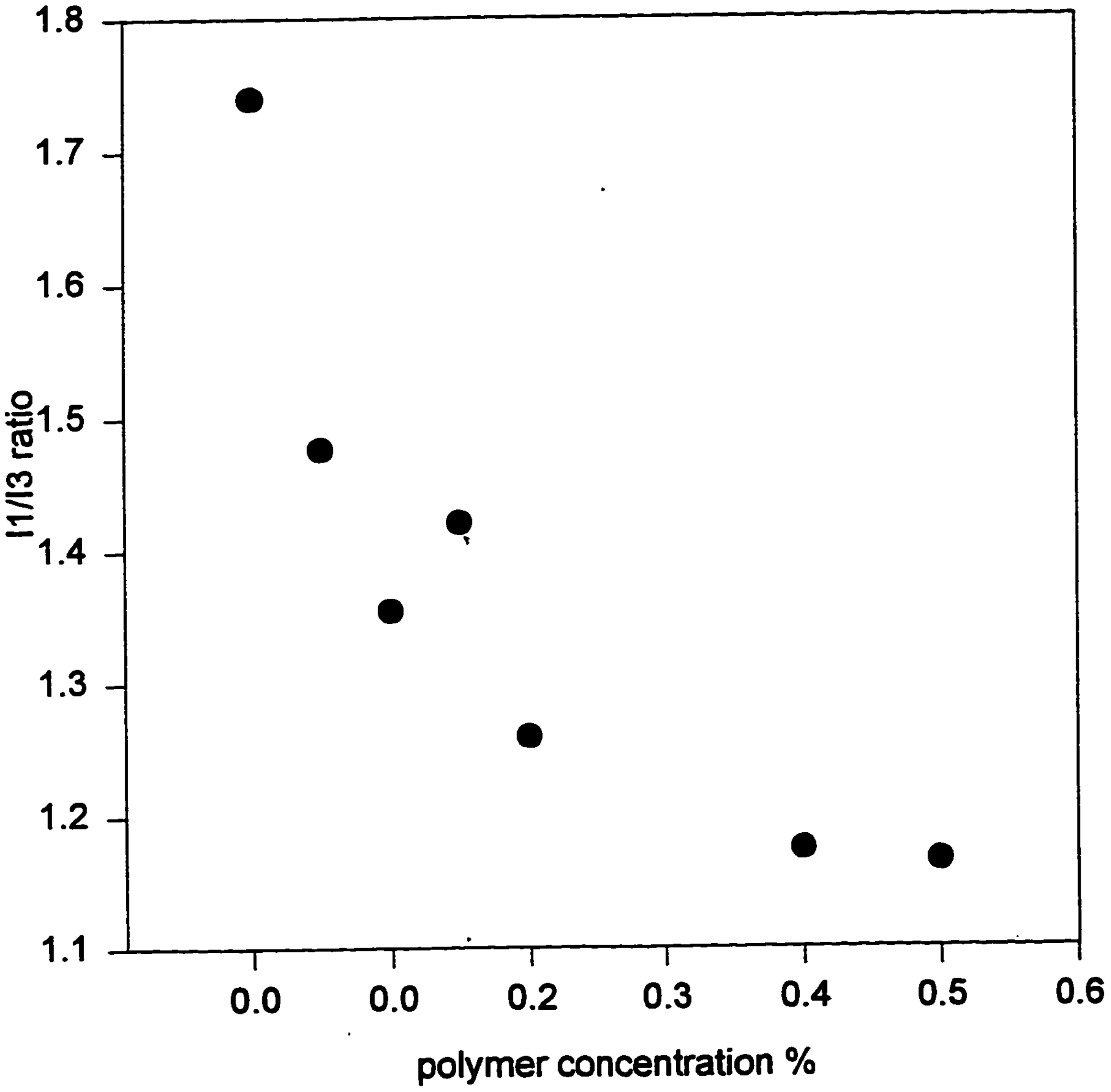


Figure 4.9: I1/I3 ratio at varying polymer concentration for PVA1 (NaCl concentration 0%)

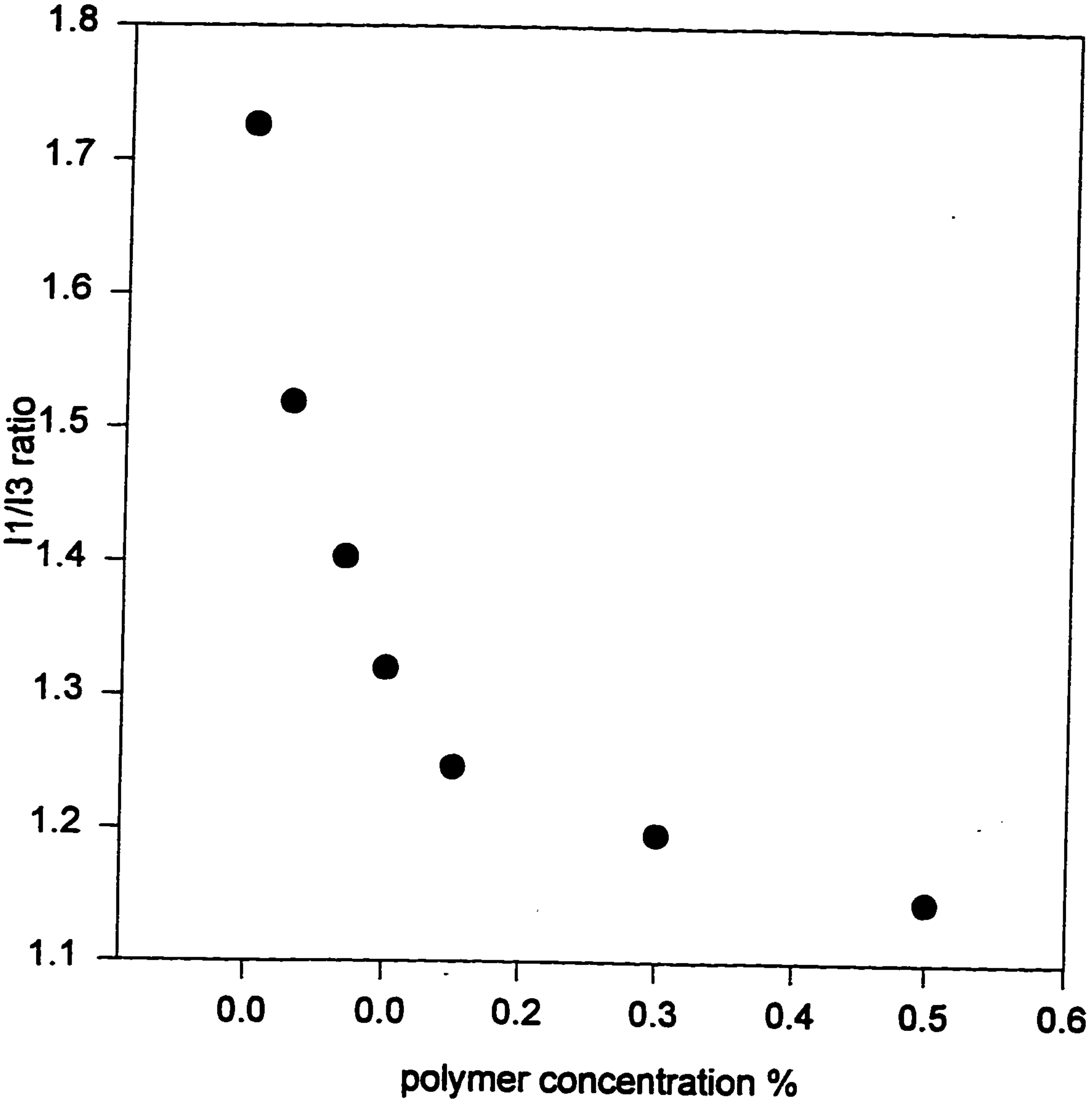


Figure 4.10: I1/I3 ratio at varying polymer concentration for PVA1 (NaCl concentration 5%)

chain in varying experimental conditions such as changes in temperature, degree of ionization, nature and concentration of added small electrolytes etc.

The viscosity behavior of a polyelectrolyte is markedly different from that of a non-ionic polymer. In the plot of η_R versus concentration, the reduced viscosity η_R cannot be extrapolated to zero. It increases as concentration decreases and approaches infinity as we approach zero concentration. The ionic PVA under study shows a typical electrolyte behavior(Figure 4.11). In aqueous solution , the chain expands due to repulsion between the fixed sodium ions resulting in a higher solution viscosity. A viscosity behavior more similar to that of the non-ionic PVA is obtained in a 0.1 N NaCl solution. The addition of the NaCl solution may be done in a way such that the total ionic strength remains constant during dilution. For this case, the Huggins plot (η_R versus concentration) which when extrapolated to zero shear gave the value for intrinsic viscosity as shown in Figure 4.12.

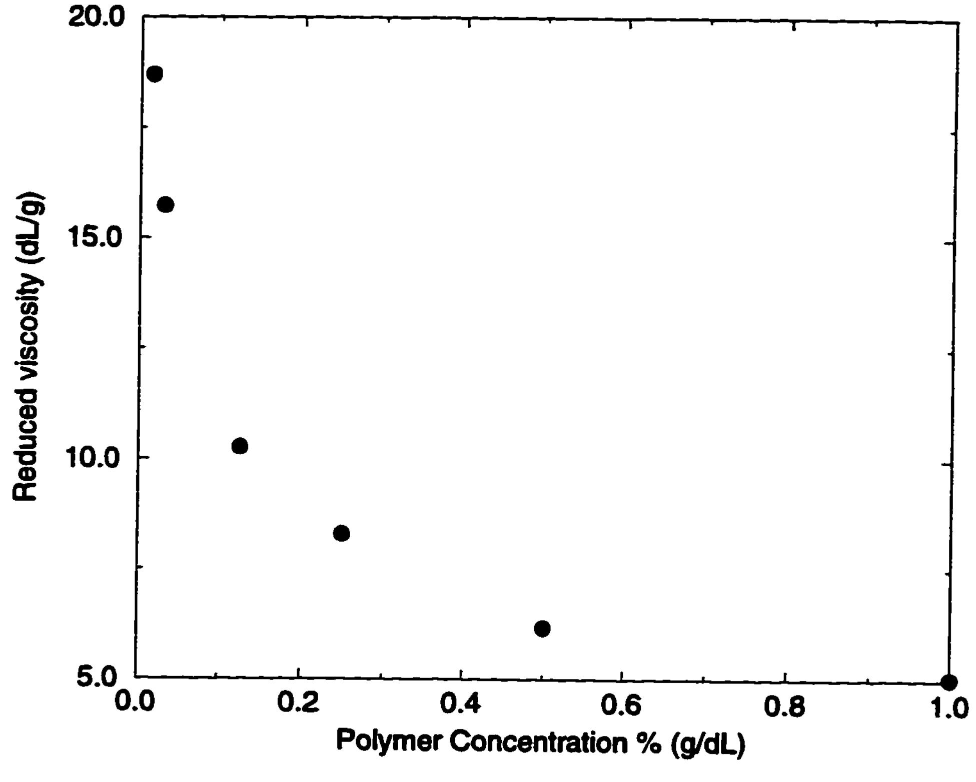


Figure 4.11: Polymer concentration Vs Reduced Viscosity for Ionic PVA

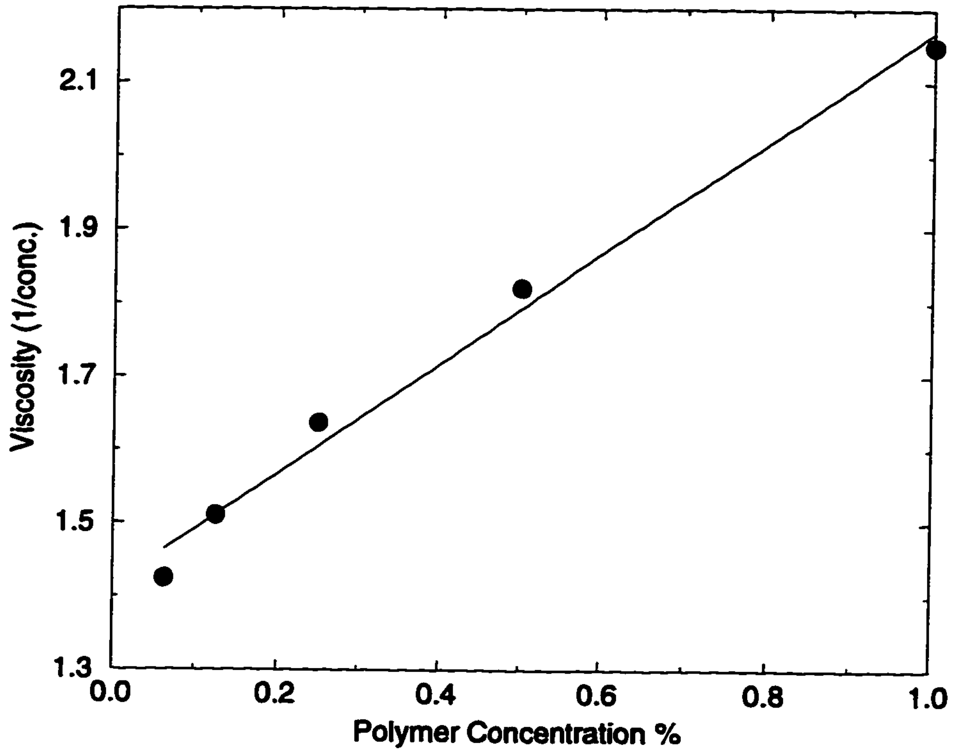


Figure 4.12: Polymer concentration Vs Reduced Viscosity for Ionic PVA 0.1 N NaCl solution

4.3 Acrylamide/Styrene Block Copolymers

4.3.1 Viscosity measurements

Acrylamide-styrene copolymers were synthesized using the micellar copolymerization technique. These showed substantial viscosity enhancement in the presence of NaCl. The ratio of the acrylamide to styrene monomer was kept constant in all runs i.e. it was aimed to incorporate 6 mol% styrene in the copolymer structure.

Experiments were conducted for a constant initiator concentration of 150 mgs, varying the surfactant (CTAB) concentration. It can be seen from Figure 4.13 that the viscosity for a 2 % polymer solution is at a maximum at a CTAB concentration of 5.95 gms. Initiator concentration was varied keeping the CTAB concentration constant at 5.95 gms. Experiments were conducted at initiator concentrations ranging from 50 to 250 mgs. The viscosity was at a maximum again at 150 mgs.

Although the polymer samples P(AS)59 and P(AS)60 showed encouraging results, it was found that on dissolution of these polymers in water, a two phase solution was obtained on centrifuging the sample, thus indicating that

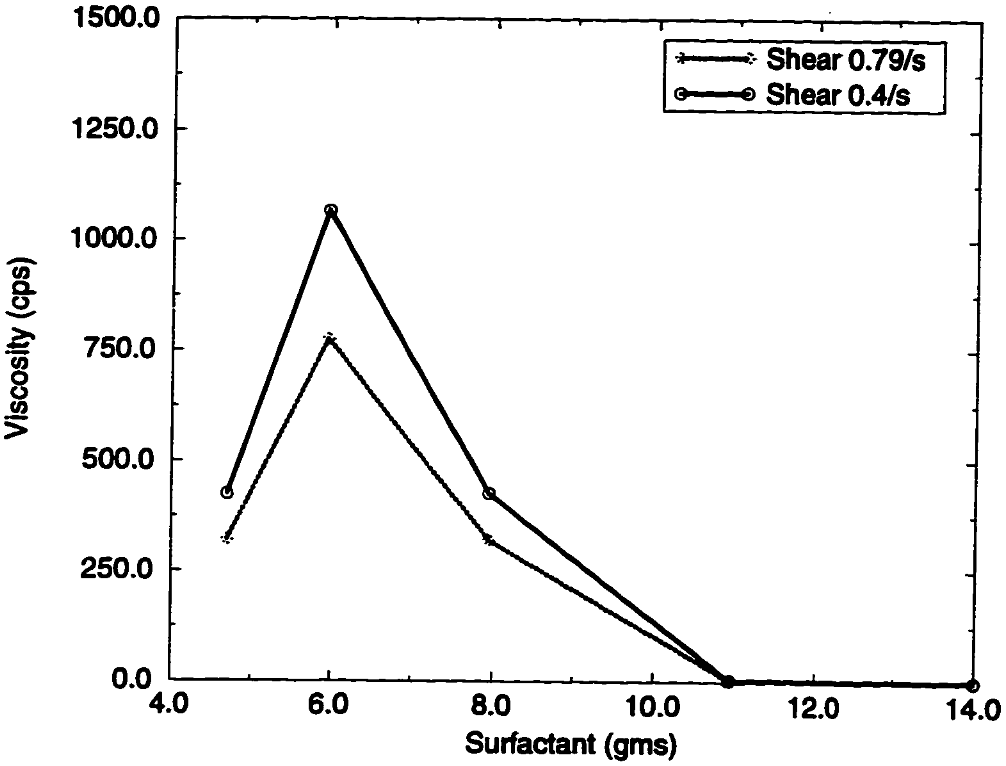


Figure 4.13: Surfactant Vs Viscosity Behavior for a constant initiator concentration of 150 mgs. at 2% polymer solution.

the polymer solution is partly soluble in water. Hence maintaining the same styrene to acrylamide ratio, we increased the quantity of the surfactant to 14 gms. At low initiator concentrations (150 mgs), we obtained very low yields but at high initiator concentrations (253 and 353 mgs) we obtained a highly viscous polymer solution.

4.3.2 Salt effect

All the polymer samples studied, showed an enhancement in viscosity in the presence of NaCl. A similar phenomenon has been observed before for Acrylamide/N-alkylacrylamide block copolymers [18]. The NaCl enhances intermolecular association. A plausible explanation could be that the addition of salt makes the environment more hostile for the polystyrene blocks pushing them towards one another and hence promoting the formation of large macromolecular aggregates.

Viscosity enhancement was most pronounced in the polymer sample P(AS)86 as seen from Figures 4.17 and 4.18. A sharp viscosity rise was noticed at an NaCl concentration of 3%. Shear thinning behavior was observed for all the AM-ST block copolymers as seen from Figure 4.19 for polymer P(AS)86 and from Figure 4.14 for polymers P(AS)59 and P(AS)60. The decrease in viscosity is more sharp at a higher salt concentration. This is because the salt induced hydrophobic associations tend to disintegrate at high shear. The viscosity increases non-linearly with increasing polymer concentration and shows a sharp rise at a polymer concentration of about 1.5% for the polymers P(AS)59 and P(AS)60 (Figures 4.15 and 4.16).

4.3.3 Temperature Behavior

An increase in temperature causes a sharp decrease in viscosity. The phenomenon shown in figures , indicates a rupturing of the associating hydrophobic domain with increasing temperature both at 0% and 5% NaCl concentrations as a result of increased polymer miscibility.

4.3.4 Surface and Interfacial Tension Behavior

The polyacrylamide-styrene block copolymers have high surface and interfacial activity due their amphiphilic nature. Amphiphilic polymers aggregate in aqueous solutions to form micelles and have an enhanced ability to adsorb at an interface, in addition to the thickening properties possessed by

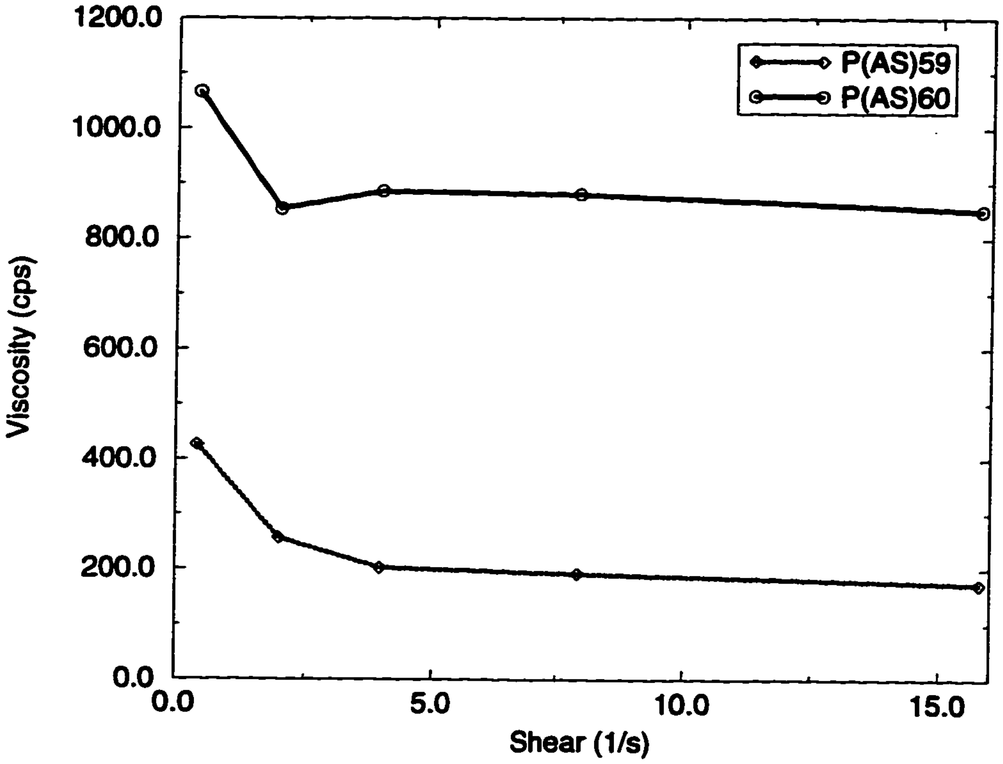


Figure 4.14: Shear Vs Viscosity Behavior of polymers P(AS)59 and P(AS)60

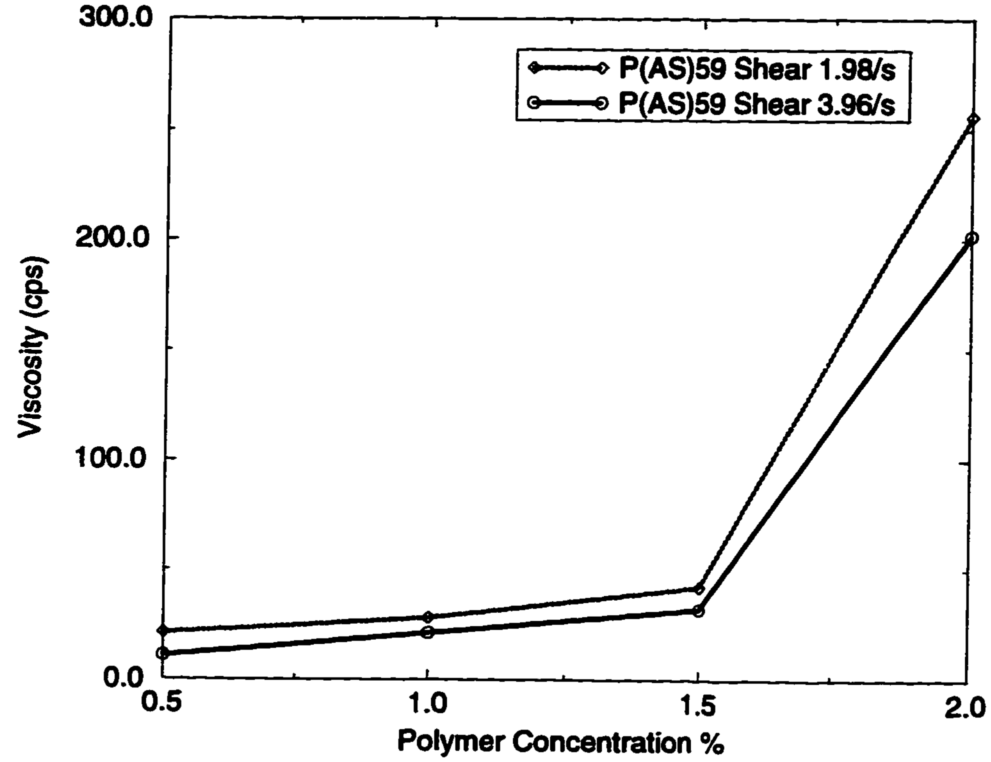


Figure 4.15: Polymer Concentration Vs Viscosity Behavior of polymer P(AS)59

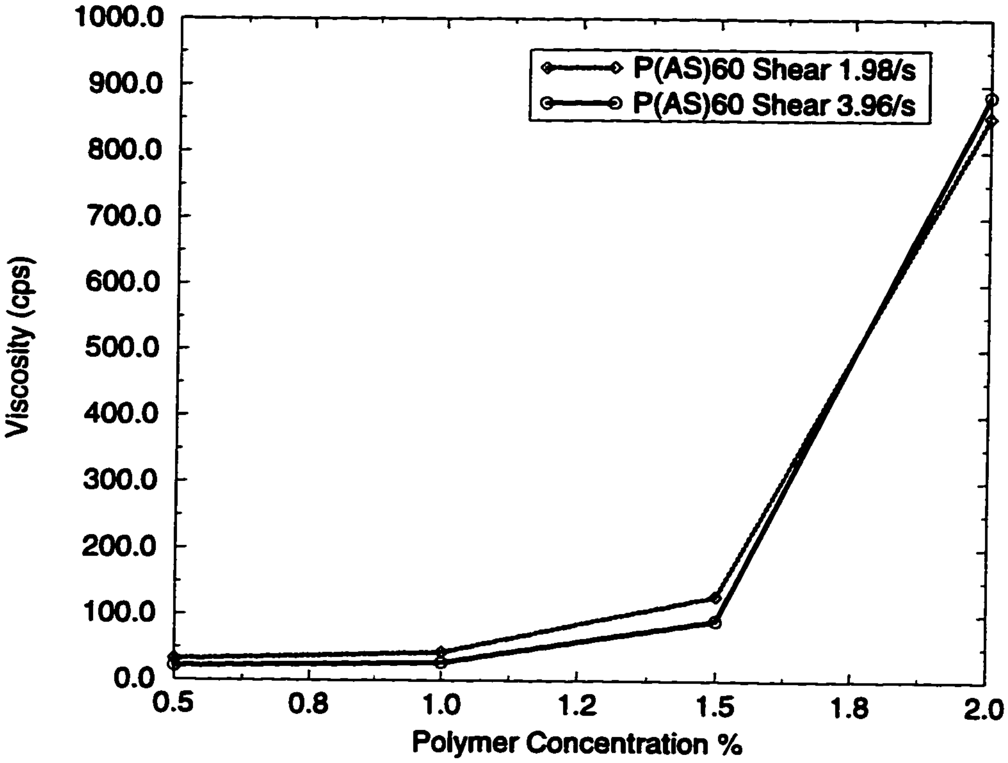


Figure 4.16: Polymer Concentration Vs Viscosity Behavior of polymer P(AS)60

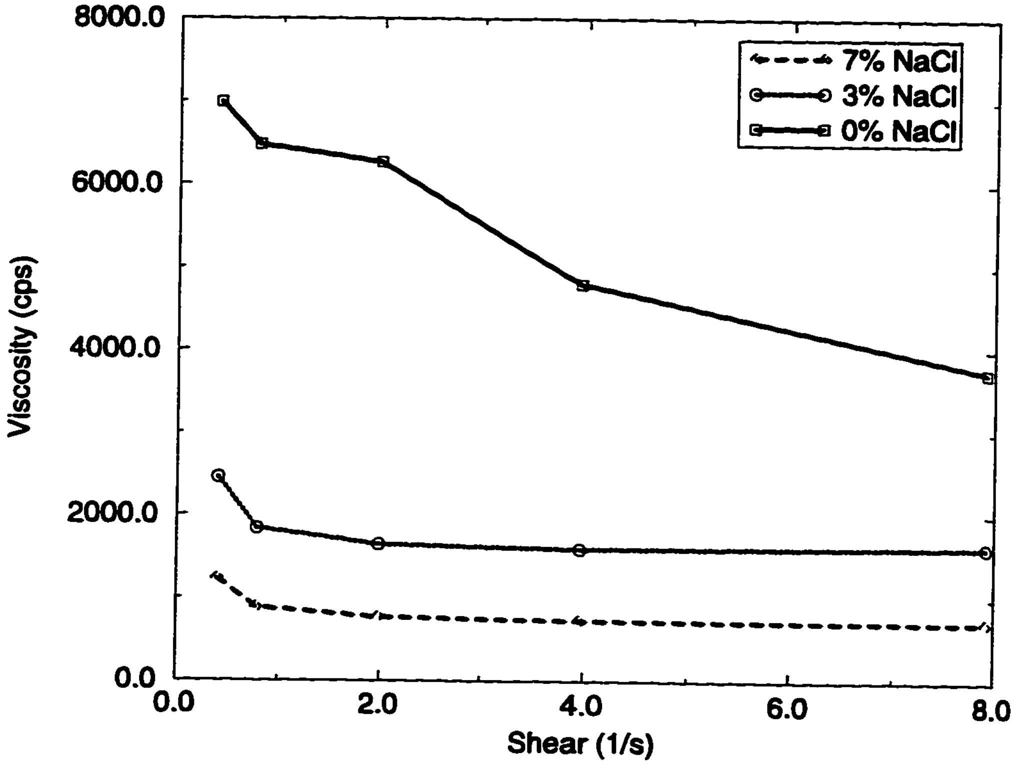


Figure 4.17: Shear Rate Vs Viscosity Behavior of polymer P(AS)86 at varying NaCl concentrations

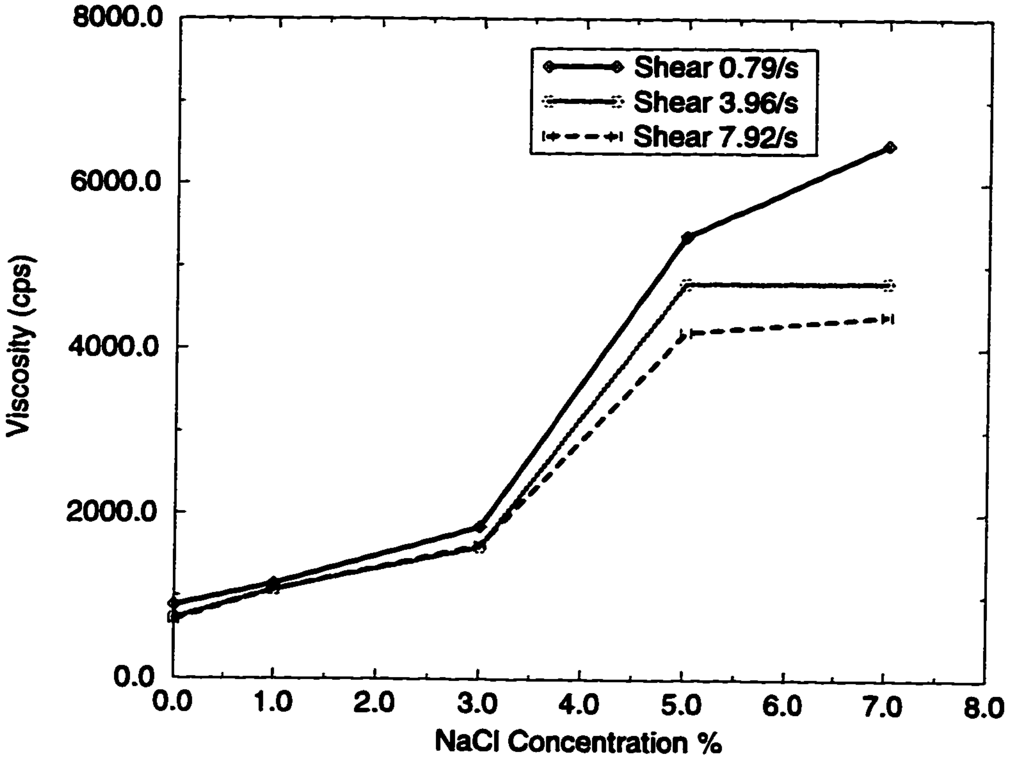


Figure 4.18: NaCl concentration Vs Viscosity Behavior of polymer P(AS)86

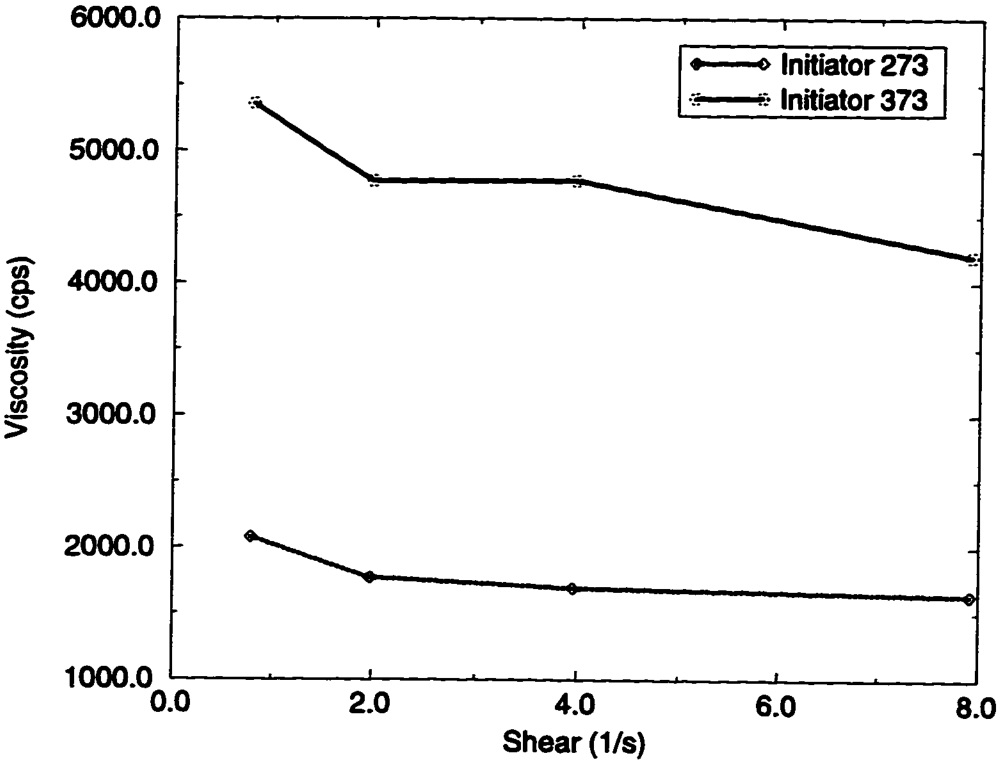


Figure 4.19: Shear Rate Vs Viscosity Behavior of polymers P(AS)86 & P(AS)87

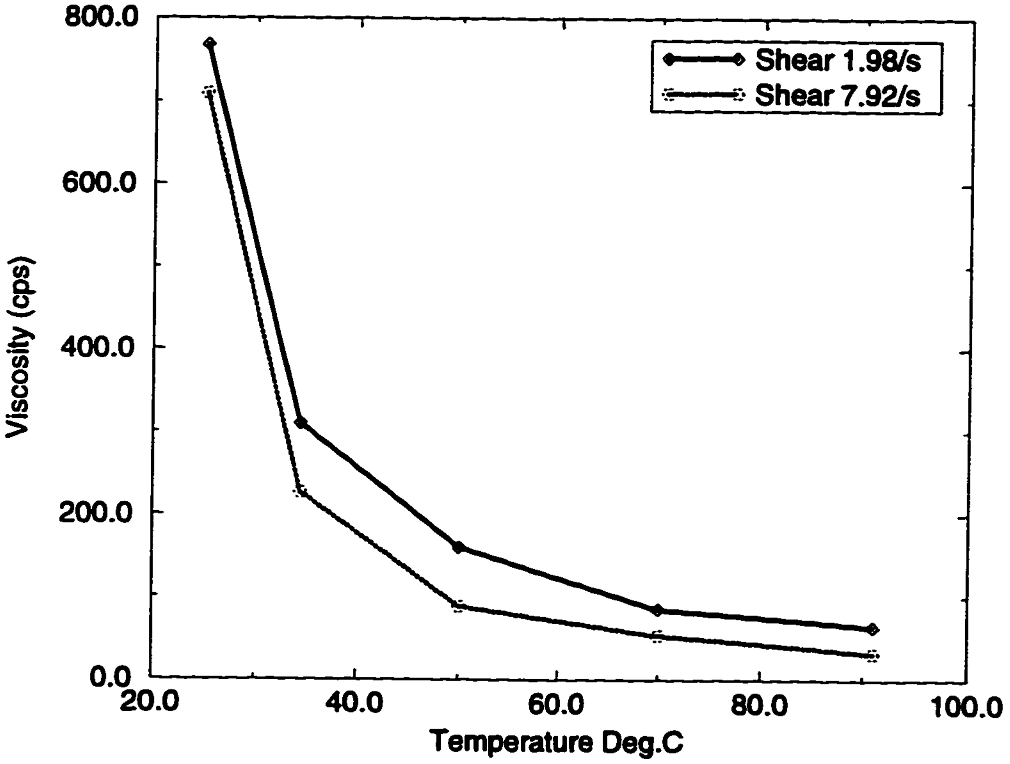


Figure 4.20: Temperature Vs Viscosity for polymer P(AS)86 at 0% NaCl

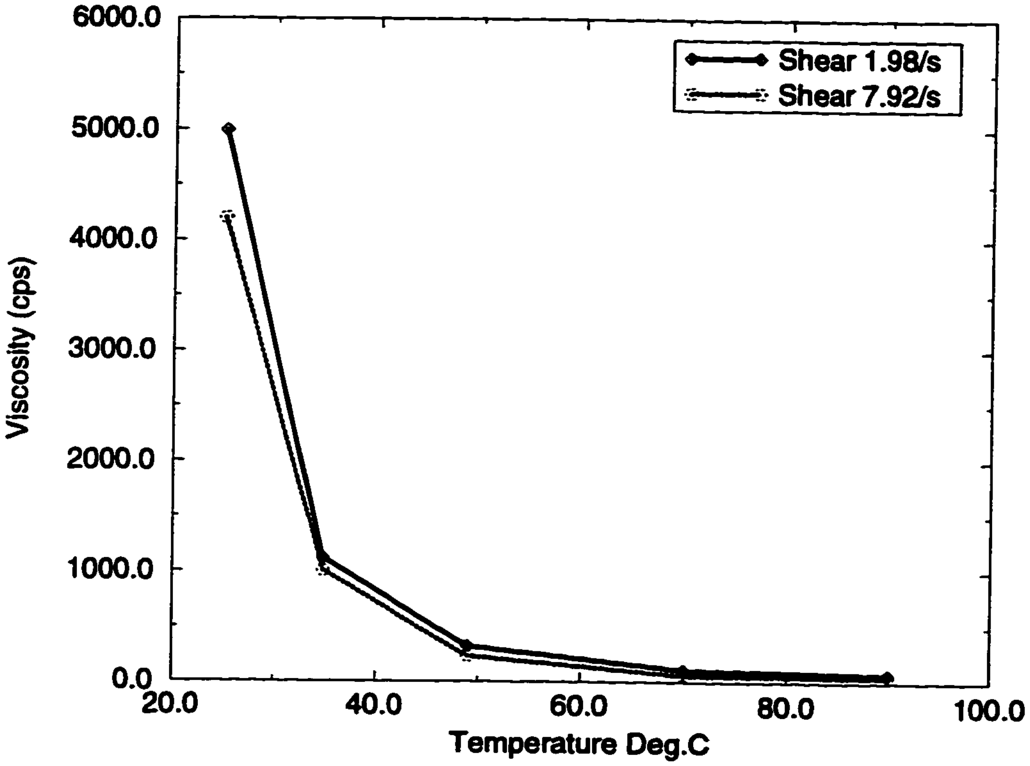


Figure 4.21: Temperature Vs Viscosity for polymer P(AS)86 at 5% NaCl

them due to polymolecular associations. The surface tension behavior of the polymer P(AS)86 was investigated with respect to increasing NaCl concentration. An average value of 50 mN/m was observed. It remained invariant with increasing salt concentration which is the normal behavior for non-polyelectrolytes. The surface and interfacial tension showed similar trends with increasing NaCl concentration. A decrease in the value was seen at polymer concentrations of about 0.15% after which the value increased to a maxima and then decreased as seen from Figures 4.23 and 4.24. The initial decrease in ST or IFT could be attributed to the hydrophobe molecules moving either towards the free surface or the oil/water interface. After a certain concentration however, there is competition among the hydrophobes to remain either in the solution to form polymeric micelles or move towards the oil/water interface causing a slight increase in ST or IFT values. The ST or IFT value finally decreases again when the micelles are saturated with hydrophobes and any increase in the styrene molecules will only cause an increase in the free hydrophobe concentration at the interface.

4.3.5 NMR Spectroscopy

NMR spectra were taken for both P(AS)86 and P(AS)87 samples. A spectra of homopolyacrylamide was also taken for comparison. The incorporation of styrene was found to be about 5.5 mol%, close to the actual 6 mol% styrene used initially.

4.3.6 Fluorescence Spectroscopy

In hydrophobic media, the I/III ratio i.e. the ratio of the emission spectrum of the 3rd and 1st peaks decreases with increasing polymer concentration. This indicates the formation of hydrophobic microdomains in the solution. The I/III ratio for pyrene solubilized in hydrophobic microdomains is much lower than that in water. This could be attributed to a longer florescence lifetime of fluorine in a hydrophobic environment.

For the polymer P(AS)86, the I/III ratio decreased from a value of 1.75 for that of pyrene in water to 1.2 in a hydrophobic environment, indicating the movement of pyrene from the aqueous into the hydrophobic microdomains and a commencement of domain ordering. It may be noted that the critical concentration for domain ordering is much lower than the C.M.C obtained through viscosity measurements.

The decrease in the I/III ratio is sharper in a 5% NaCl concentration compared to that without salt for the P(AS)86 block copolymer (Figures 4.25 and 4.26) indicating that the salt promotes hydrophobic aggregation as also confirmed by viscosity measurements.

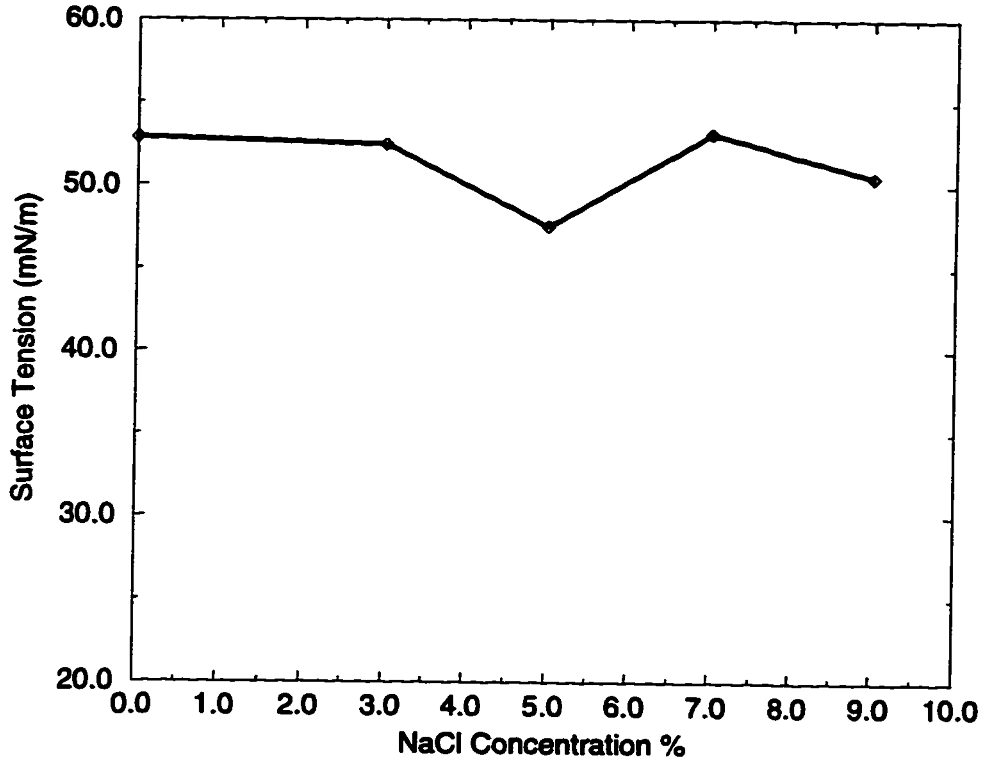


Figure 4.22: Surface tension Behavior Vs salt concentration for polymer P(AS)86 (polymer concentration 2%)

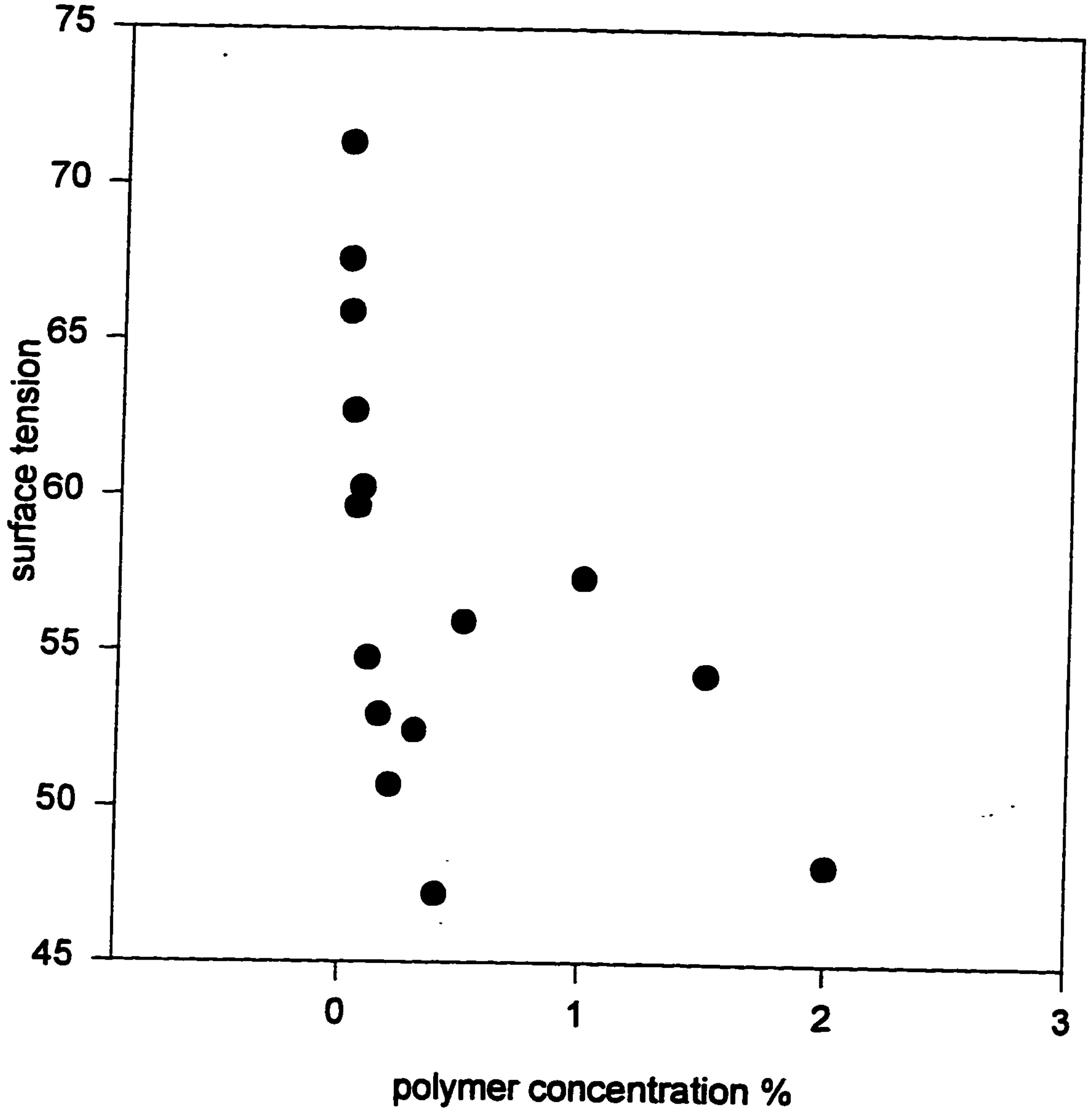


Figure 4.23: Surface tension behavior at varying polymer concentration for P(AS)86 (0% NaCl)

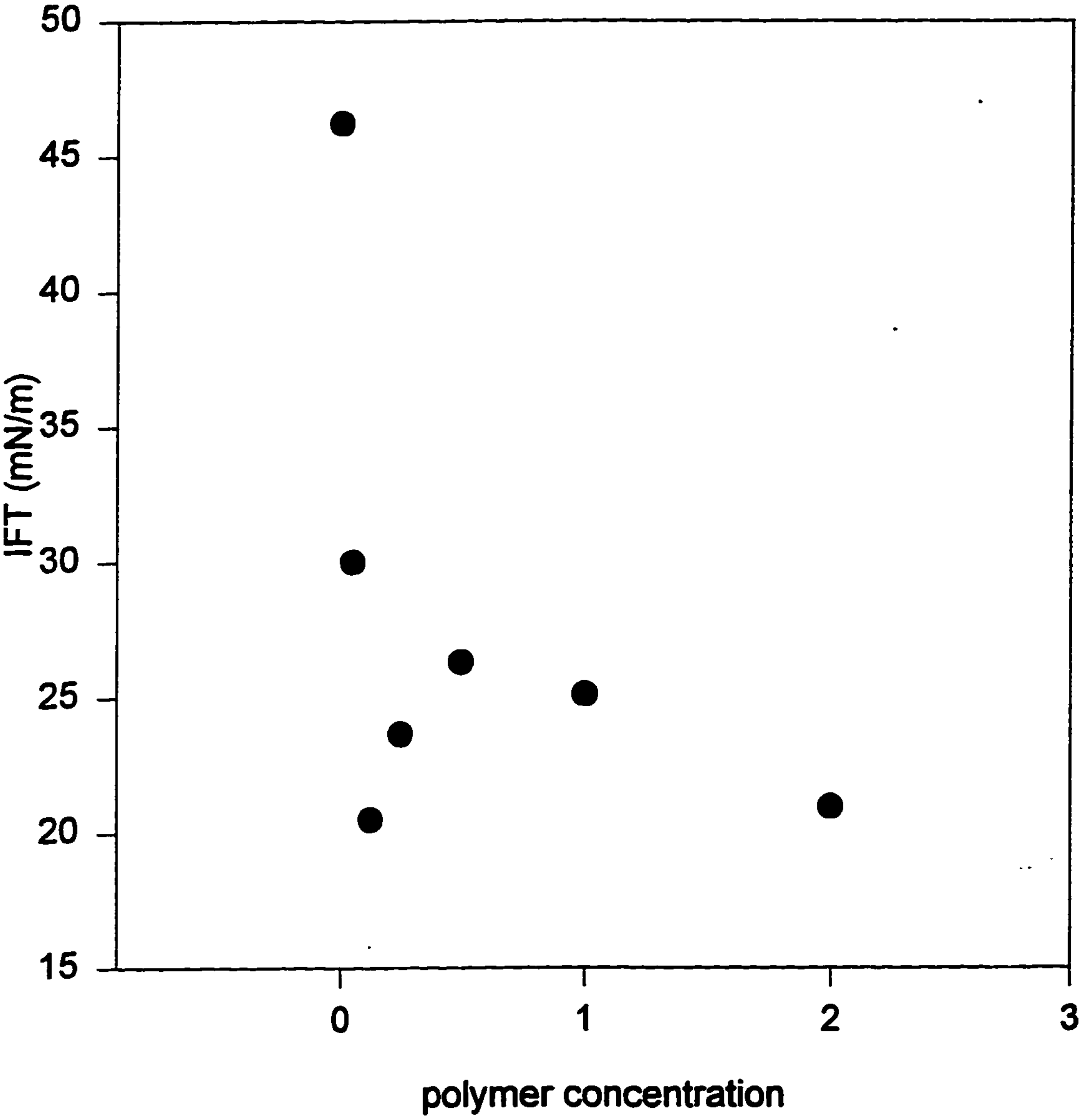


Figure 4.24: Interfacial tension behavior at varying polymer concentration for PAS(86) (0% NaCl)

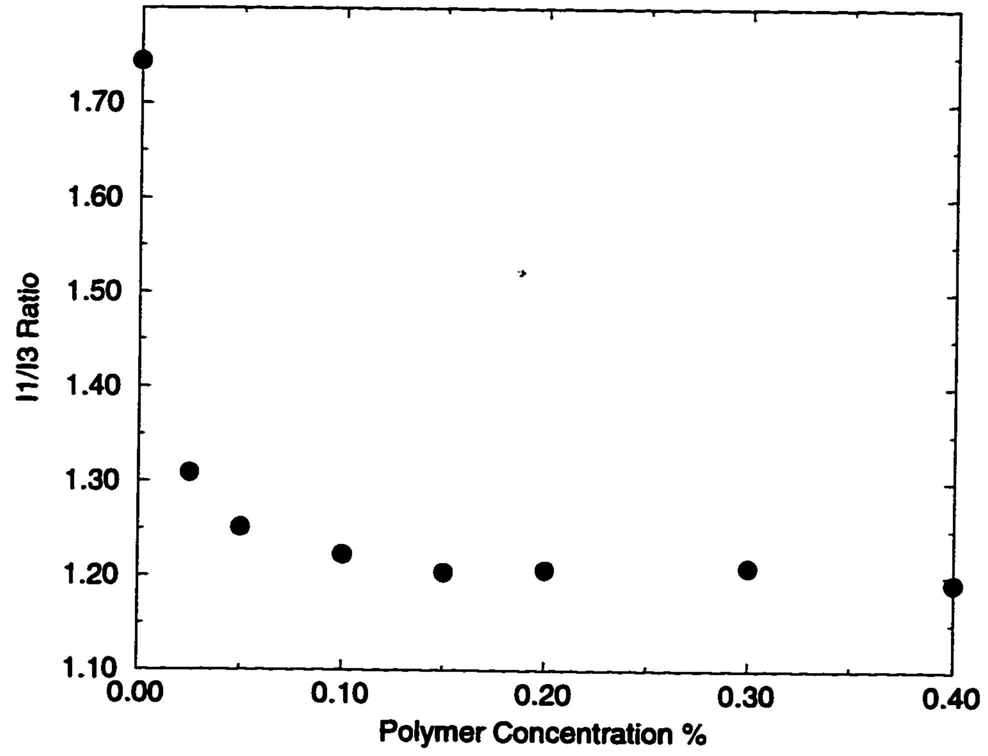


Figure 4.25: I/III ratio Vs Polymer concentration at 0%NaCl

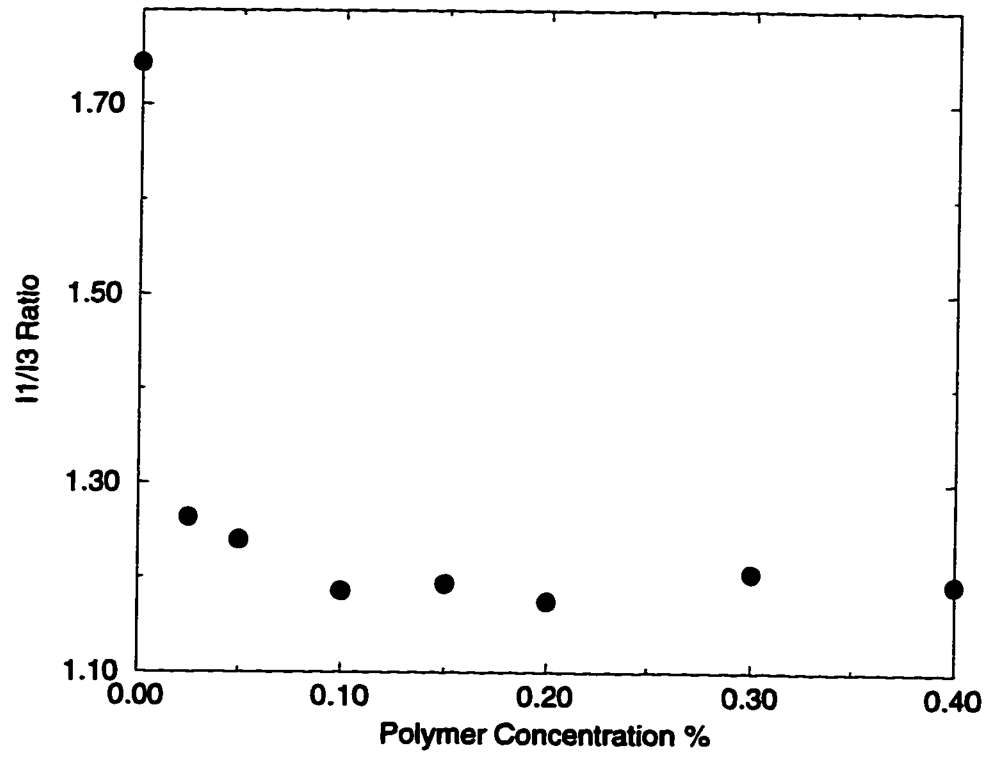


Figure 4.26: I/III ratio Vs Polymer concentration at 5%NaCl

Chapter 5

Conclusions and Recommendations

5.1 Conclusions

Water soluble hydrophobically modified PVA samples were prepared by the chemical modification of PVA via urethanization - esterification reactions of different combinations of long chain fatty acid chlorides. Because of the uniqueness of the polymer chain, it was found to exhibit a very high viscosity (about one hundred fold more) as compared to the unmodified polymer. A gradual decrease in viscosity was observed with increasing salt concentration for all the synthesized polymers upto NaCl concentration of about 4 to 4.5%, when there was a sudden drop in viscosity. All polymer samples showed a typical shear thinning behavior. The polymer should be a good candidate for viscofication applications and in EOR for wells of low salinity.

Ionic PVA was synthesized by incorporating charges on the PVA chain. Charge content on the polymer chain was much higher than that earlier found in literature. The viscosity behavior was that of a typical polyelectrolyte i.e. the reduced viscosity approached infinity as the concentration approaches zero. The behavior is markedly different from that of the non-ionic PVA because of the expanded conformation of the macromolecular backbone. A literature model for flexible-chain electrolytes described well, the behavior of the polymer solution in water. In a 0.1 N NaCl solution, the viscosity behavior of the electrolyte approached that of the non-ionic PVA due to the shielding of the charges from one another.

Acrylamide styrene block copolymers have been investigated in detail. Studies revealed that polymer viscosity varies with initiator concentration i.e. it increased upto a certain minimum concentration and then decreased. Viscosity increased with increasing salt concentration for all the samples analysed and were particularly encouraging for certain combinations where the viscosity reached values as high as 5000 cP at a 5% NaCl concentration and a polymer concentration of 2%. This property makes the finding especially attractive for polymer flooding applications in EOR, especially in wells of high salinity. The styrene incorporation of 6 mol% is very high and hence provides us with a wide range over which aqueous solution properties may be tailored. NMR studies confirm the presence of the hydrophobe in the polymer backbone. Florescence studies have been conducted to give an insight into the exact nature of hydrophobic aggregation. Pyrene has been used as a probe molecule. Results prove that domain ordering starts at very low polymer concentrations and a critical value is reached much earlier than the corresponding value found for viscosity enhancement.

5.2 Recommendations

1. Studies should be conducted on reservoir cores to study the practical utility of the findings in this research.
2. Applications in the field of protein partitioning hold promise, especially in light of higher incorporation of hydrophobe in the acrylamide / styrene copolymer.

3. Hydrophobic modification for the ionic polymer of PVA should be conducted in order to study and model the behavior of hydrophobically associating polyelectrolytes in solution.
4. Time resolved florescence studies should be conducted to compare theoretically and experimentally determined hydrophobe block size.

Appendix A

Experimental Results

Table A.1: Solubility of Hydrophobically modified PVA (3 wt % polymer solution)

Hydrophobe Content	Solubility
C_{18} 1 mol% : C_{10} 1 mol%	Insoluble (2 days stirring)
C_{18} 1 mol% : C_{10} 0.5 mol%	Insoluble (2 days stirring) cloudy, not viscous
C_{18} 0.75 mol% : C_{10} 0.5 mol%	Insoluble (2 days stirring) foamy, slightly viscous
C_{18} 0.5 mol% : C_{10} 0.5 mol%	Soluble (2 days stirring) highly viscous

Table A.2: Viscosity of Hydrophobically modified PVA (3 wt% polymer solution) Hydrophobe content C_{18} 0.5 mol% : C_{10} 0.5 mol%

shear(1/s)	0%	1.5%	2.0%	2.5%	3.0%	3.5%	4.0%	4.5%	6%
0.79	2750	2240	1830	1866	1760	1760	1760	1760	400
1.98	2677	2197	1830	1877	1770	1790	1749	1706	245
3.96	2575	2197	1824	1877	1781	1749	1646	1578	186
7.92	2501	2122	1770	1802	1696	1600	1360	1264	130
15.8	2200	1898	1590	1541	1402	1272	1002	925	90.7

Table A.3: Viscosity of Hydrophobically modified PVA (3 wt% polymer solution) Hydrophobe content C_{18} 0.5 mol% : C_{10} 0.25 mol%

shear(1/s)	0%	1.0%	2.0%	3.0%	4.0%	5.0%	6.0%	7.0%
3.96	256	235	227	213	203	140	117	117
7.92	247	224	215	210	197	122	98	98
15.8	249	224	214	217	200	114	97	99
39.6	255	228	216	218	195	107	88	83
79.2	252	226	207	205	177	96	77	68

Table A.4: Polymer P(AS)59. Shear vs viscosity at varying polymer concn.

shear(1/s)	0.5%	1.0%	1.5%	2.0%
0.40	-	-	106	426
0.79	42	-	53	320
1.98	21	28	42	256
3.96	10.7	21	32	202
7.92	5.33	16	-	192
15.8	-	-	-	173

Table A.5: Polymer P(AS)60. Shear vs viscosity at varying polymer concn.

shear(1/s)	0.5%	1.0%	1.5%	2.0%
0.40	106.7	106.7	320	1066
0.79	53.3	53.3	182	774
1.98	32	42.7	128	853.3
3.96	21.3	27.0	91	885
7.92	10.7	16.0	80	880
15.8	9.0	10.7	73	850.7
39.6	4.0	8.1	-	-

Table A.6: Polymer P(AS)60. Shear vs viscosity '0%' NaCl .

Polymer	CTAB	Initiator	yield	Shear(1/s)	viscosity(cps)
P(AS)60	5.95	150	9.1	0.4	1066
				0.79	774
				1.98	853.3
				3.96	885
				7.92	880
				15.8	850.7

Table A.7: Polymer P(AS)59. Shear vs viscosity '0%' NaCl .

Polymer	CTAB	Initiator	yield	Shear(1/s)	viscosity(cps)
P(AS)59	7.94	150	9.5	0.4	426.7
				0.79	320
				1.98	256
				3.96	202
				7.92	192
				15.8	173

Table A.8: Polymer P(AS)61. Shear vs viscosity '0%' NaCl .

Polymer	CTAB	Initiator	yield	Shear(1/s)	viscosity(cps)
P(AS)61	10.94	150	3.61	15.8	2.67

Table A.9: Polymer P(AS)62. Shear vs viscosity '0%' NaCl .

Polymer	CTAB	Initiator	yield	Shear(1/s)	viscosity(cps)
P(AS)62	14.0	150	1.7	-	Insoluble

Table A.10: Polymer P(AS)63. Shear vs viscosity '0%' NaCl .

Polymer	CTAB	Initiator	yield	Shear(1/s)	viscosity(cps)
P(AS)63	4.7	150	5.67	0.4	425
				0.79	320
				1.98	266
				3.96	245
				7.92	227
				15.8	209

Table A.11: Polymer P(AS)64. Shear vs viscosity '0%' NaCl .

Polymer	CTAB	Initiator	yield	Shear(1/s)	viscosity(cps)
P(AS)64	0.0	150	9.8	0.79	53.3
				1.98	21.3
				3.96	10.7
				7.92	5.33

Table A.12: Polymer P(AS)73. Shear vs viscosity '0%' NaCl .

Polymer	CTAB	Initiator	yield	Shear(1/s)	viscosity(cps)
P(AS)73	5.95	50	-	-	no rxn.

Table A.13: Polymer P(AS)72. Shear vs viscosity '0%' NaCl .

Polymer	CTAB	Initiator	yield	Shear(1/s)	viscosity(cps)
P(AS)72	5.95	100	-	-	no rxn

Table A.14: Polymer P(AS)71. Shear vs viscosity '0%' NaCl .

Polymer	CTAB	Initiator	yield	Shear(1/s)	viscosity(cps)
P(AS)71	5.95	200	7.51	0.4	155
				0.79	76
				1.98	53
				3.96	38
				7.92	30

Table A.15: Polymer P(AS)74. Shear vs viscosity '0%' NaCl .

Polymer	CTAB	Initiator	yield	Shear(1/s)	viscosity(cps)
P(AS)74	5.95	250	10.2	0.4	106.7
				0.79	53.3
				1.98	21.3
				3.96	16.7
				7.92	11

Table A.16: Polymer P(AS)76. Shear vs viscosity '0%' NaCl .

Polymer	CTAB	Initiator	yield	Shear(1/s)	viscosity(cps)
P(AS)76	10.94	276	9.2	0.4	320
				0.79	213.3
				1.98	170.7
				3.96	160
				7.92	154.7
				15.8	152

Table A.17: Polymer P(AS)77. Shear vs viscosity '0%' NaCl .

Polymer	CTAB	Initiator	yield	Shear(1/s)	viscosity(cps)
P(AS)77	14	353	7.9	0.4	700
				0.79	533.3
				1.98	451
				3.96	421
				7.92	437.3
				15.8	478

Table A.18: Viscosity of Polymer P(AS)86. (2 wt% polymer solution) at varying salt concentration

shear(1/s)	0%	1.0%	3.0%	5.0%	7.0%	9.0%
0.4	1227	1333	2453	-	6987	-
0.79	880	1147	1840	5360	6477	-
1.98	768	1056	1643	4771	6261	-
3.96	725	1077	1595	4778	4800	5050
7.92	709	1074	1616	4200	3738	4400
15.8	-	-	1632	-	-	-

Table A.19: Viscosity of Polymer P(AS)86 Vs temperature. (2 wt% polymer solution) at '0%' NaCl

temp. $^o C$	shear(1/s)	viscosity
25	1.98	768
25	3.96	725.3
25	7.92	709.3
34.4	1.98	310
34.4	3.96	256
34.4	7.92	227
50	1.98	160
50	3.96	128
50	7.92	88
70	1.98	85
70	3.96	64
70	7.92	53
91	1.98	64
91	3.96	42.7
91	7.92	32

Table A.20: Viscosity of Polymer P(AS)86 Vs temperature. (2 wt% polymer solution) at '5%' NaCl

temp. ^{o}C	shear(1/s)	viscosity
25	1.98	4992
25	3.96	4778
25	7.92	4200
34.8	1.98	1120
34.8	3.96	1056
34.8	7.92	1008
49	1.98	320
49	3.96	266.7
49	7.92	229.3
70	1.98	106.7
70	3.96	85.3
70	7.92	58.7
90	1.98	74
90	3.96	59
90	7.92	45

Table A.21: Polymer P(AS)60. Shear vs viscosity '5%' NaCl .

Polymer	CTAB	Initiator	yield	Shear(1/s)	viscosity(cps)
P(AS)60	5.95	150	9.1	0.79	4306
				1.98	4254
				3.96	4220
				7.92	3909

Table A.22: Polymer P(AS)59. Shear vs viscosity '5%' NaCl .

Polymer	CTAB	Initiator	yield	Shear(1/s)	viscosity(cps)
P(AS)59	7.94	150	9.5	0.79	1627
				1.98	1578
				3.96	1467
				7.92	1338
				15.8	1403

Table A.23: Polymer P(AS)63. Shear vs viscosity '5%' NaCl .

Polymer	CTAB	Initiator	yield	Shear(1/s)	viscosity(cps)
P(AS)63	4.7	150	5.67	0.79	2026
				1.98	1995
				3.96	1962
				7.92	1866
				15.8	1630

Table A.24: Polymer P(AS)71. Shear vs viscosity '5%' NaCl .

Polymer	CTAB	Initiator	yield	Shear(1/s)	viscosity(cps)
P(AS)71	5.95	200	7.51	0.79	267
				1.98	203
				3.96	186
				7.92	179

Table A.25: Polymer P(AS)74. Shear vs viscosity '5%' NaCl .

Polymer	CTAB	Initiator	yield	Shear(1/s)	viscosity(cps)
P(AS)74	5.95	250	10.2	0.79	78
				1.98	64
				3.96	48
				7.92	30

Table A.26: Polymer P(AS)76. Shear vs viscosity '5%' NaCl .

Polymer	CTAB	Initiator	yield	Shear(1/s)	viscosity(cps)
P(AS)76	10.94	276	9.2	0.79	457
				1.98	384
				3.96	357
				7.92	352

Table A.27: Polymer P(AS)87. Shear vs viscosity '5%' NaCl .

Polymer	CTAB	Initiator	yield	Shear(1/s)	viscosity(cps)
P(AS)87	14.0	253	8.15	0.79	2080
				1.98	1770
				3.96	1691
				7.92	1637
				15.8	1509

Appendix B

Florescence Spectra

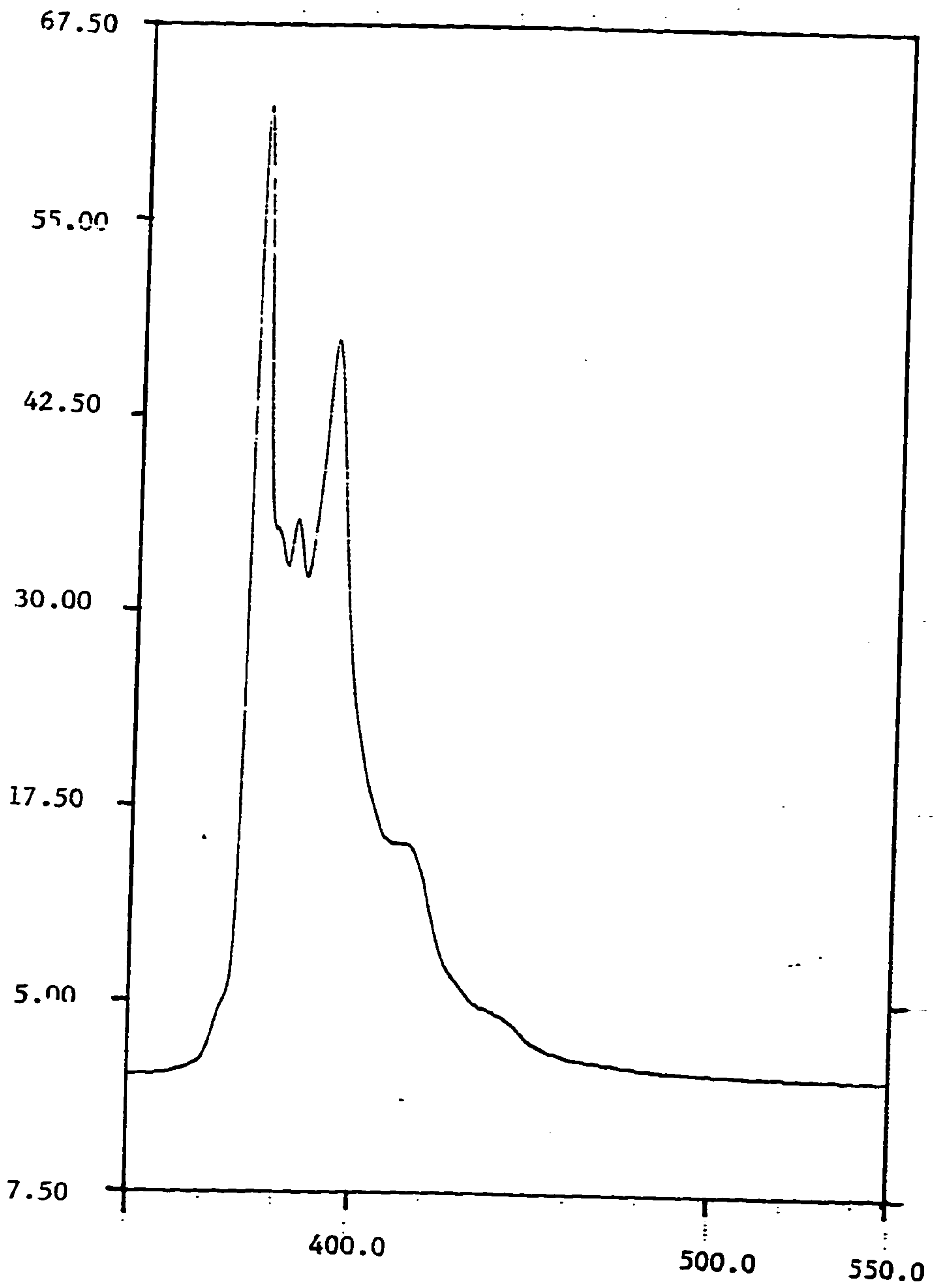


Figure B.1: Florescence Spectrum for Pyrene in Water

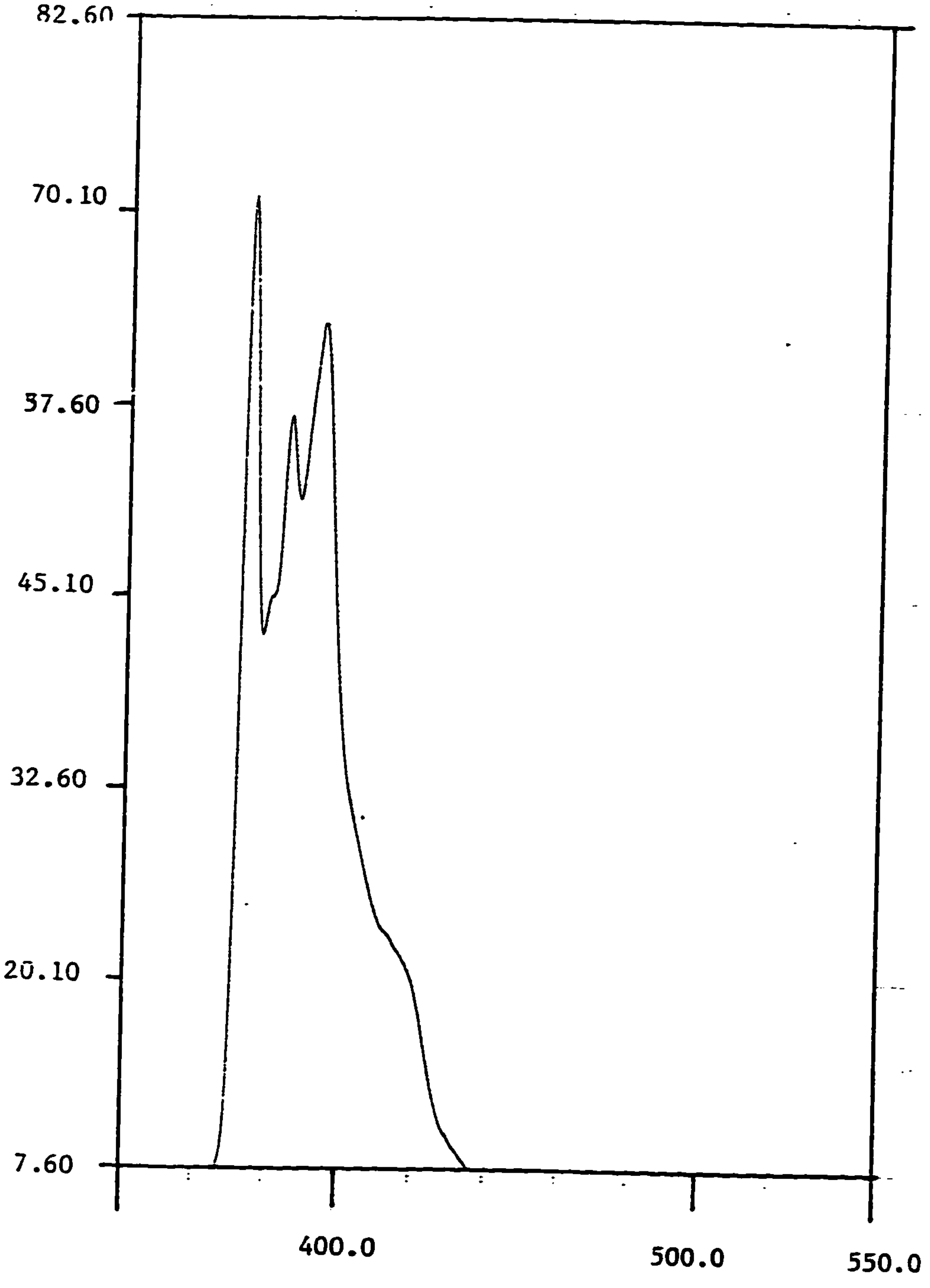


Figure B.2: Florescence Spectrum for P(AS)86 at 0% NaCl and a polymer concentration of 0.05%

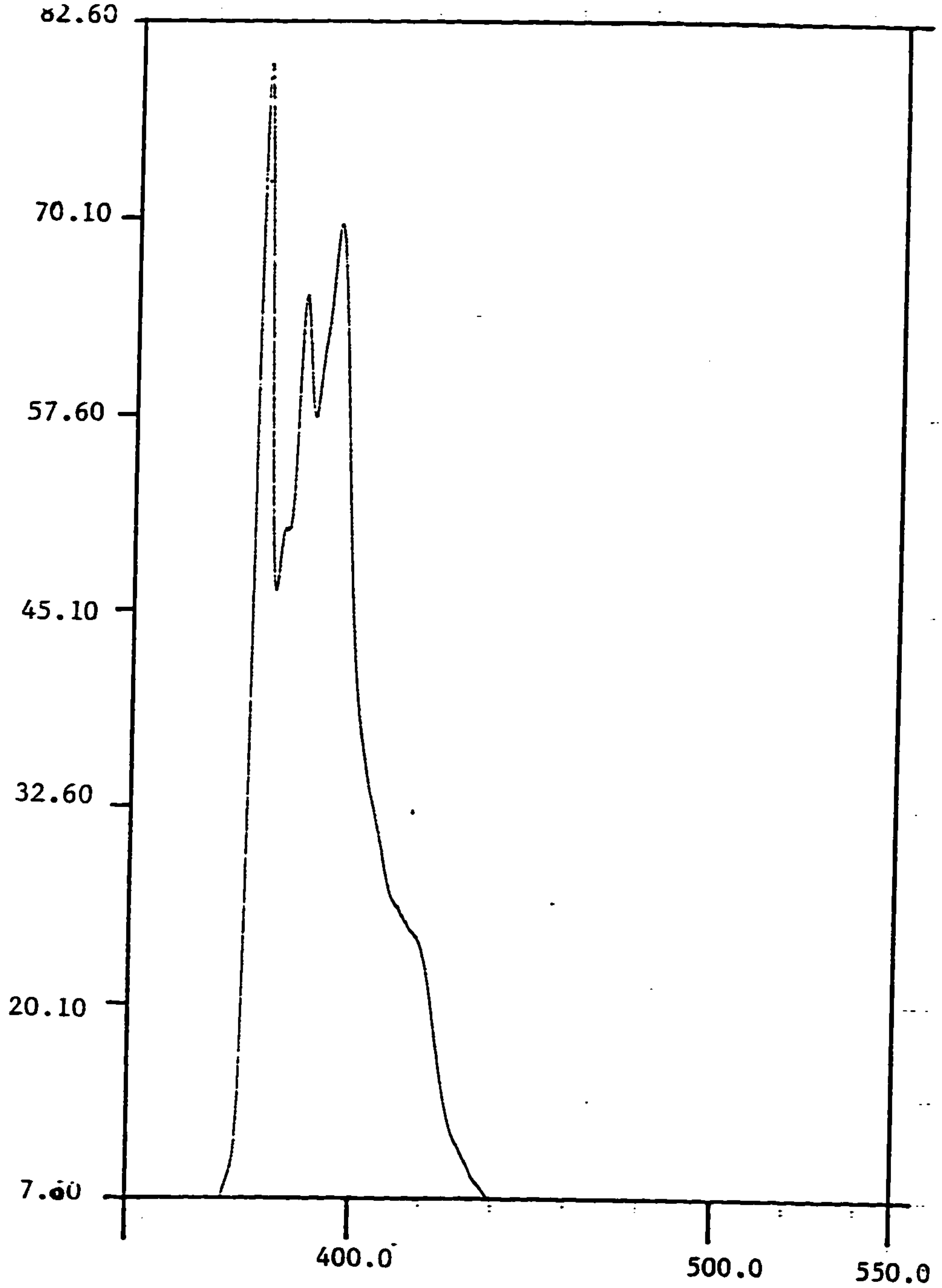


Figure B.3: Florescence Spectrum for P(AS)86 at 0% NaCl and a polymer concentration of 0.1%

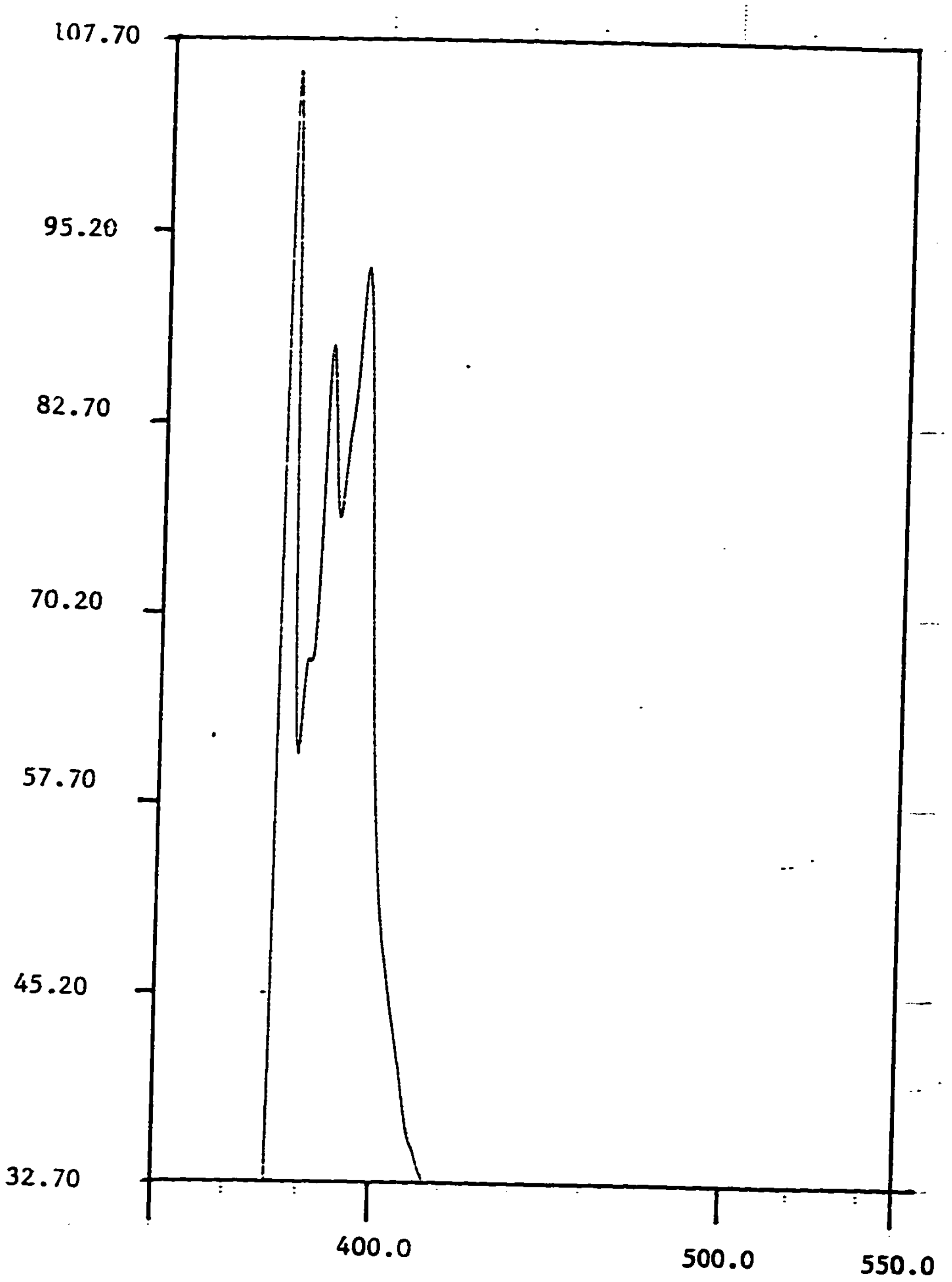


Figure B.4: Florescence Spectrum for P(AS)86 at 0% NaCl and a polymer concentration of 0.15%

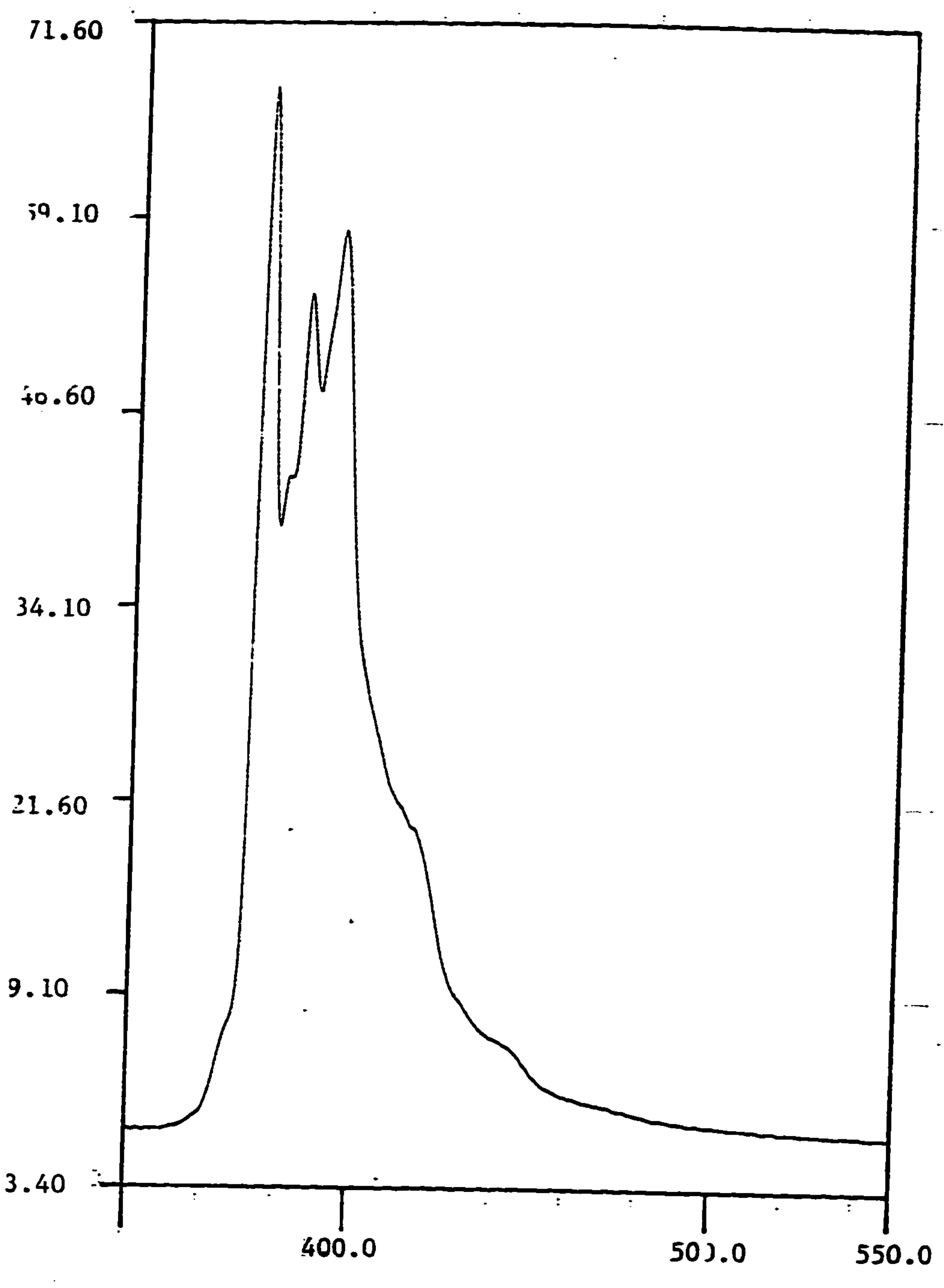


Figure B.5: Florescence Spectrum for P(AS)86 at 5% NaCl and a polymer concentration of 0.05%

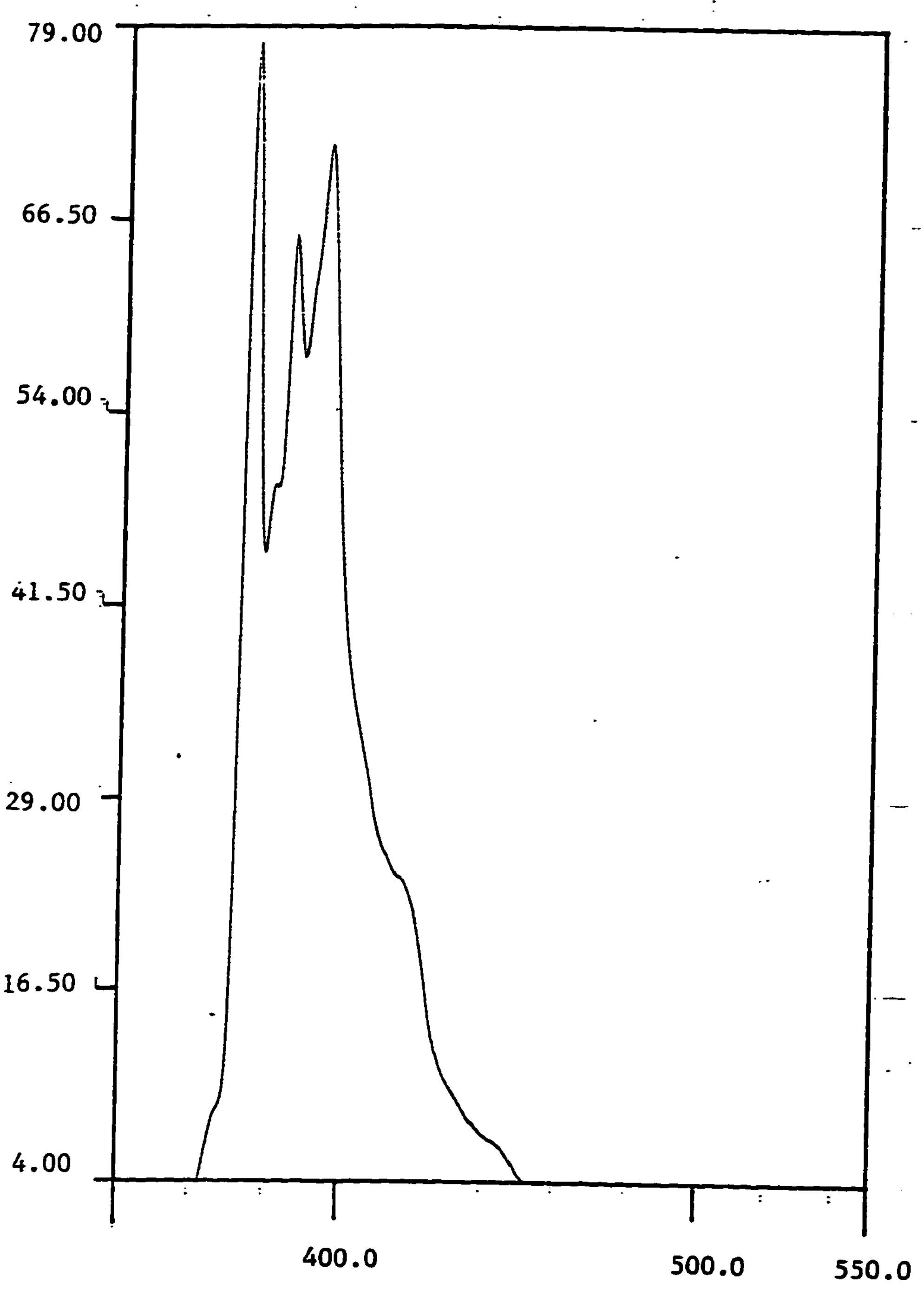


Figure B.6: Florescence Spectrum for P(AS)86 at 5% NaCl and a polymer concentration of 0.1%

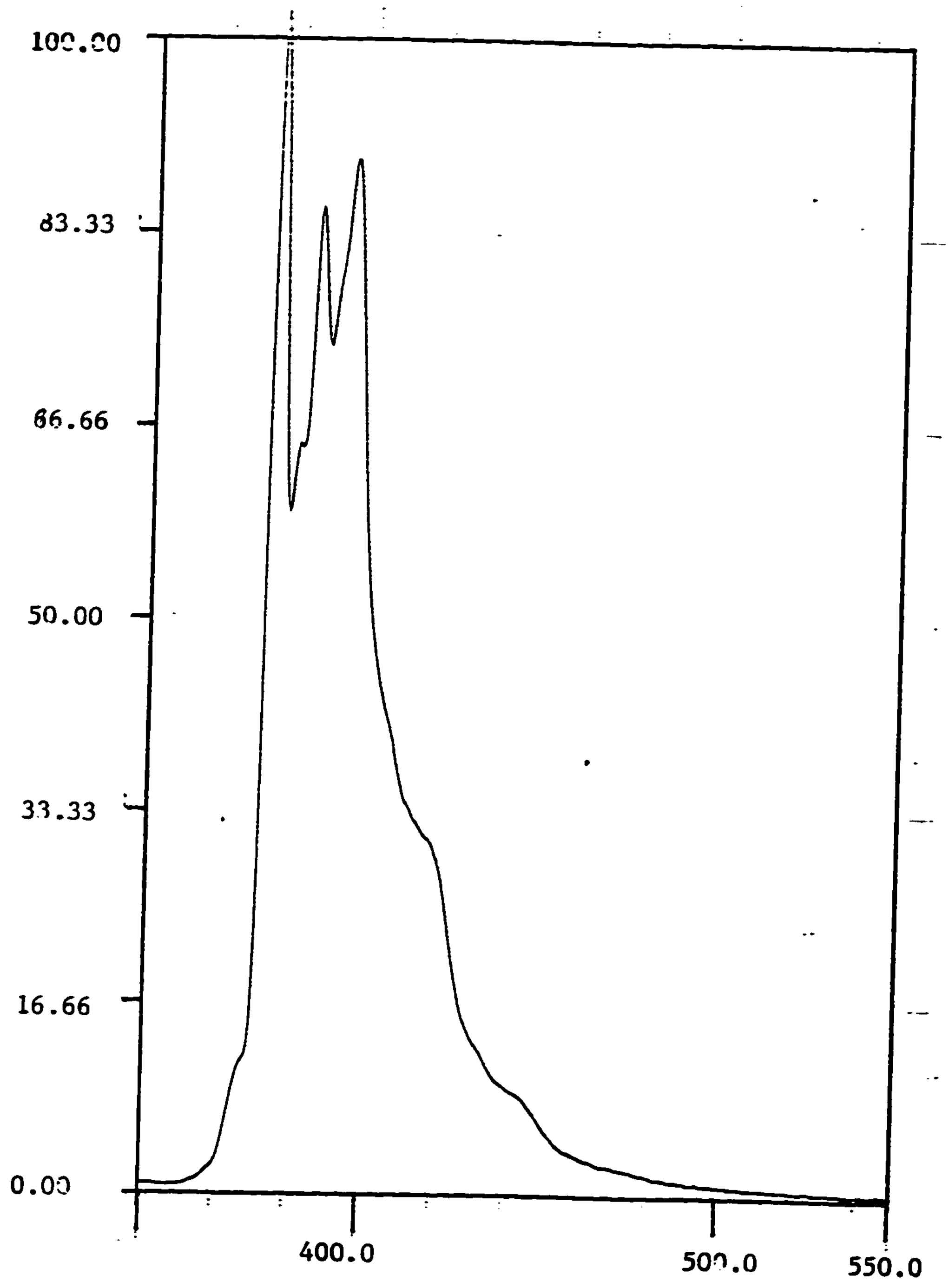


Figure B.7: Florescence Spectrum for P(AS)86 at 5% NaCl and a polymer concentration of 0.15%

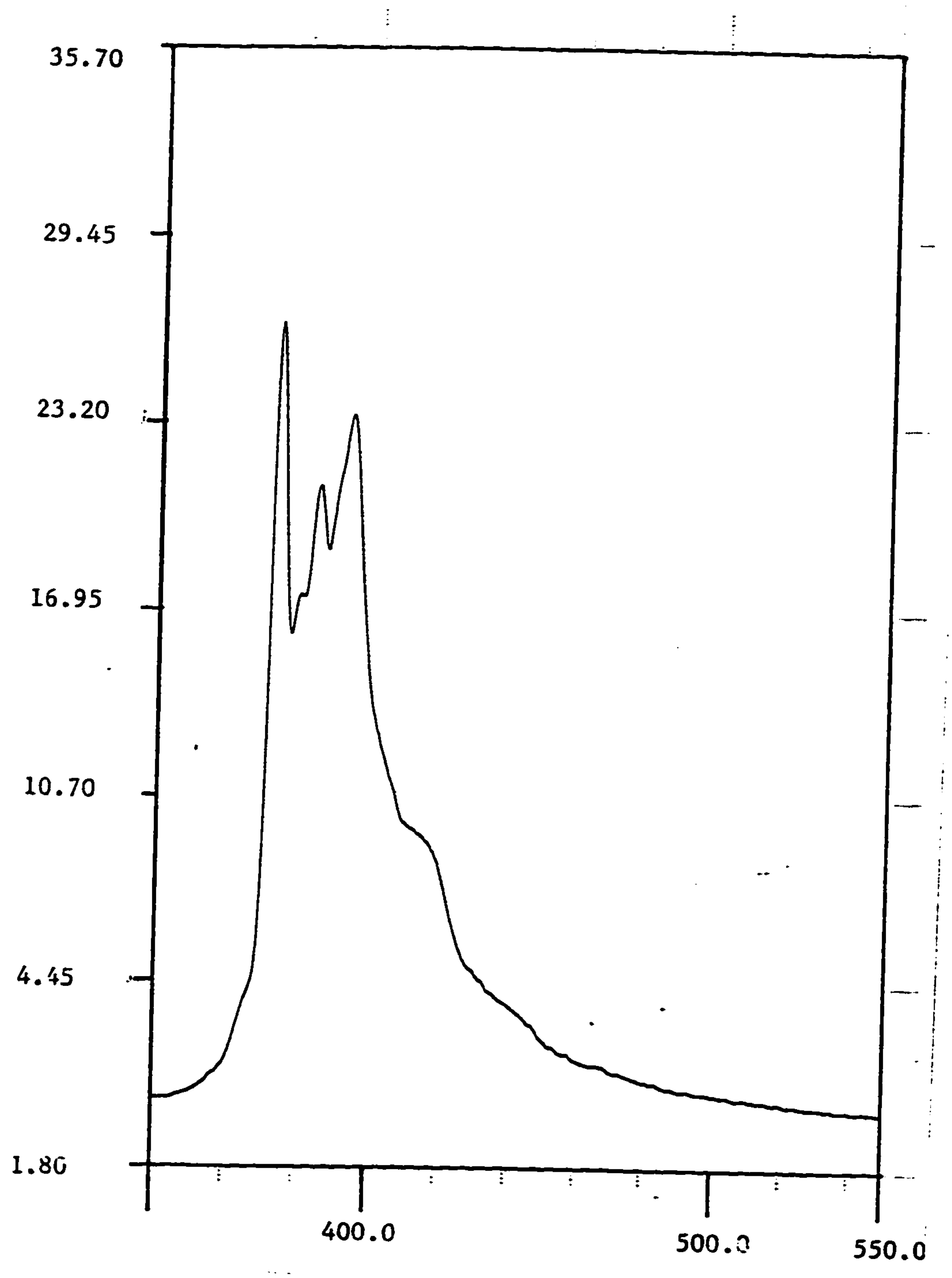


Figure B.8: Florescence Spectrum for PVA1 at 0% NaCl and a polymer concentration of 0.2%

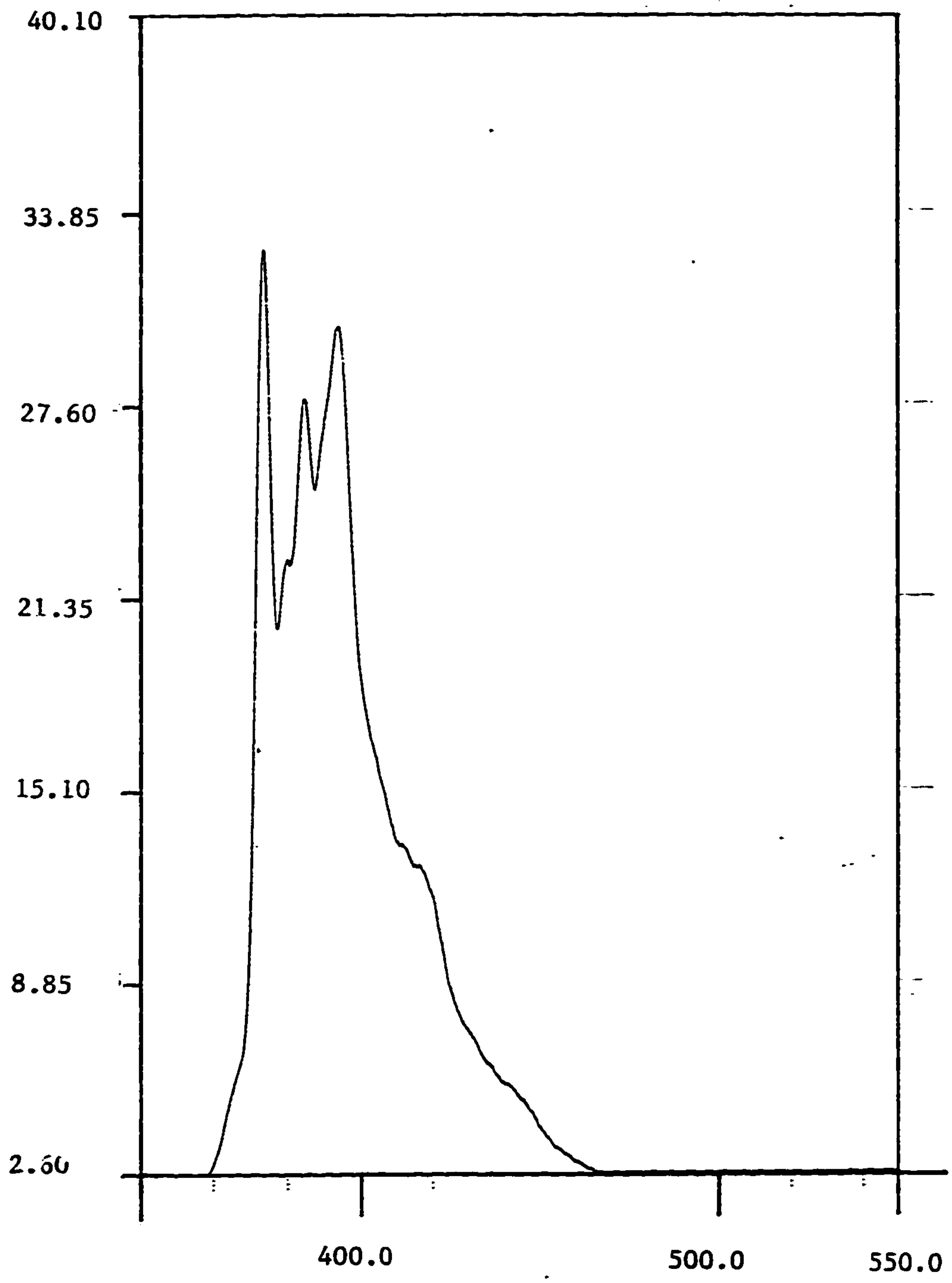


Figure B.9: Florescence Spectrum for PVA1 at 0% NaCl and a polymer concentration of 0.4%

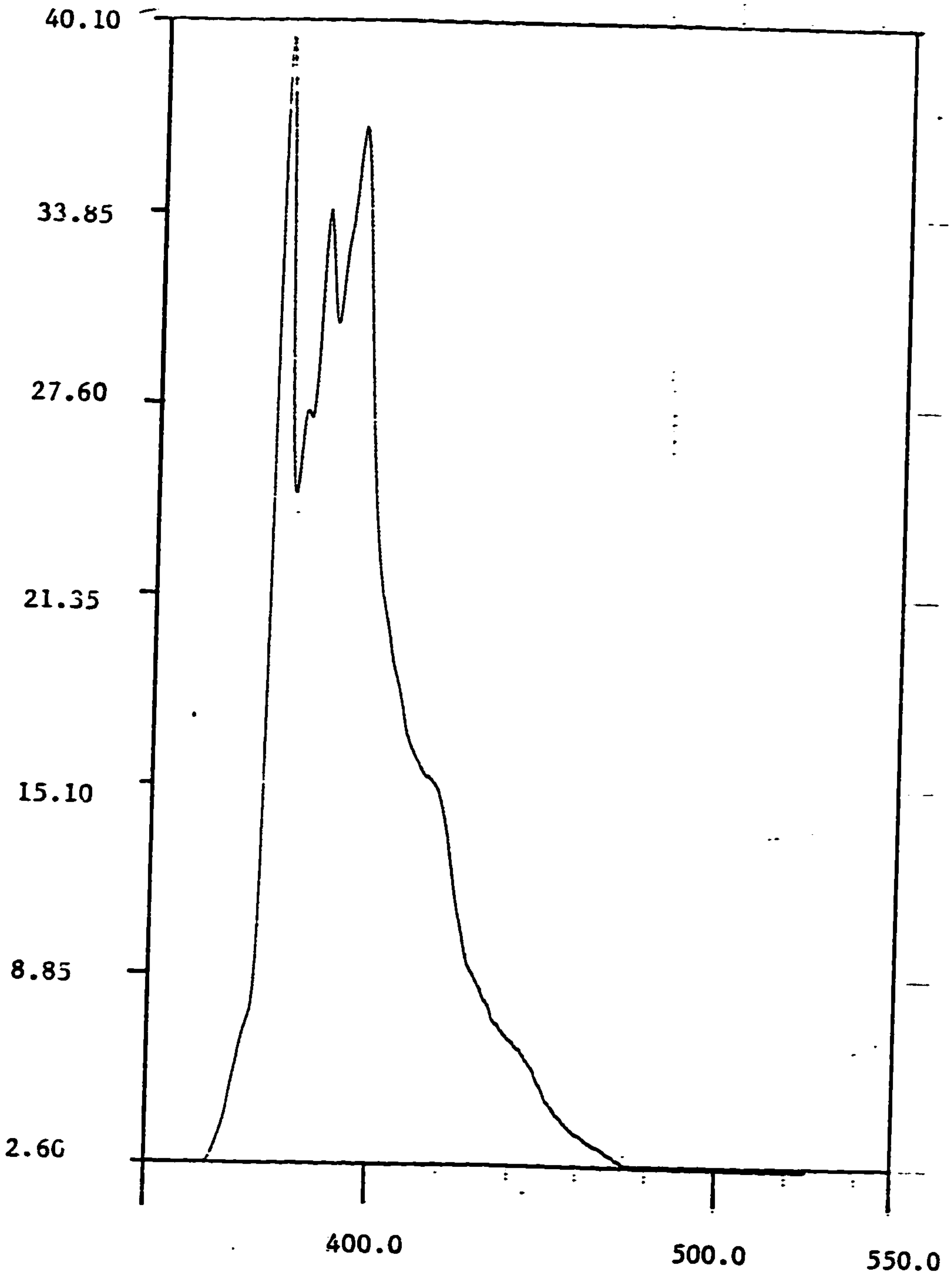


Figure B.10: Florescence Spectrum for PVA1 at 0% NaCl and a polymer concentration of 0.5%

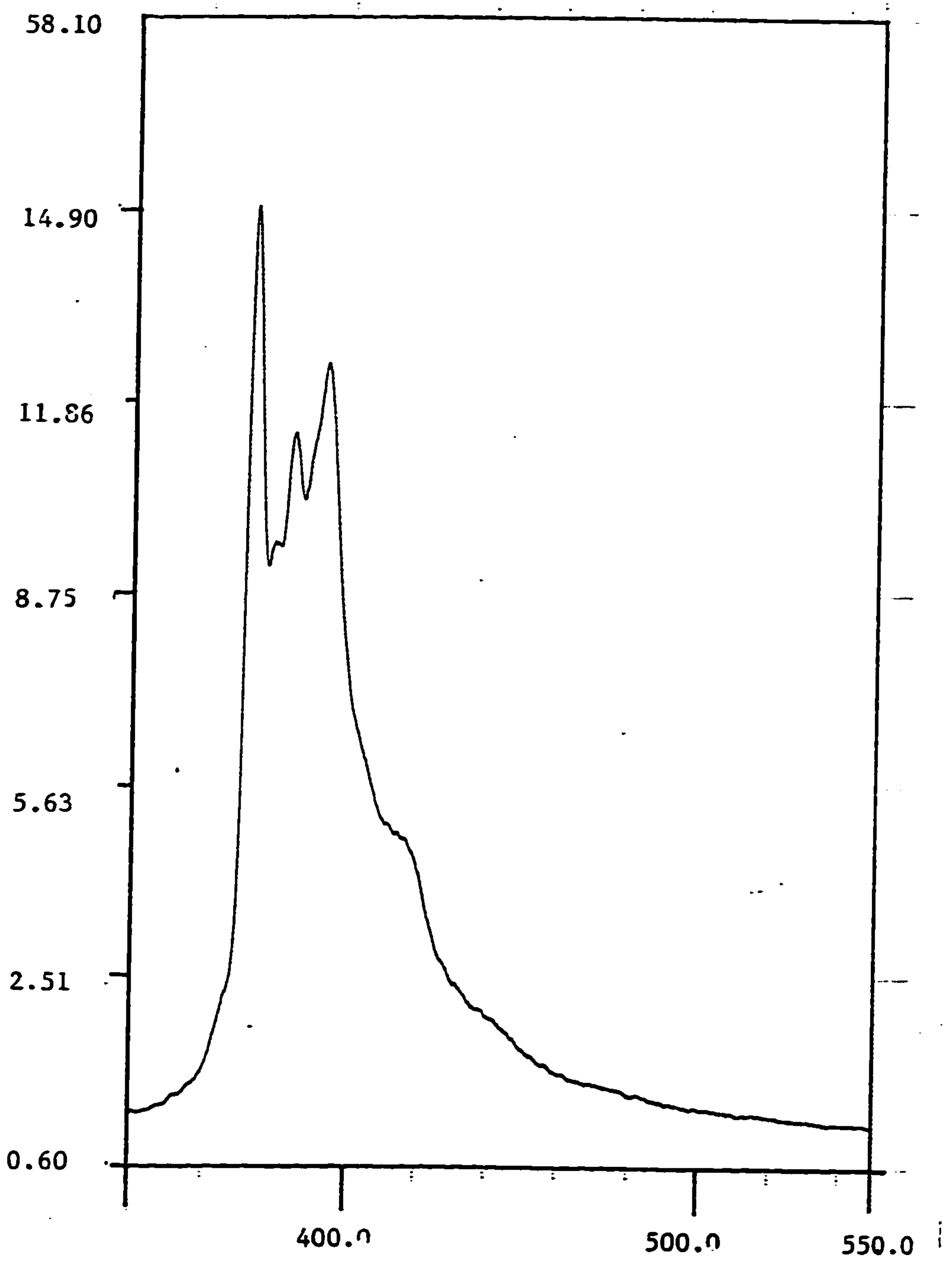


Figure B.11: Florescence Spectrum for PVA1 at 5% NaCl and a polymer concentration of 0.1%

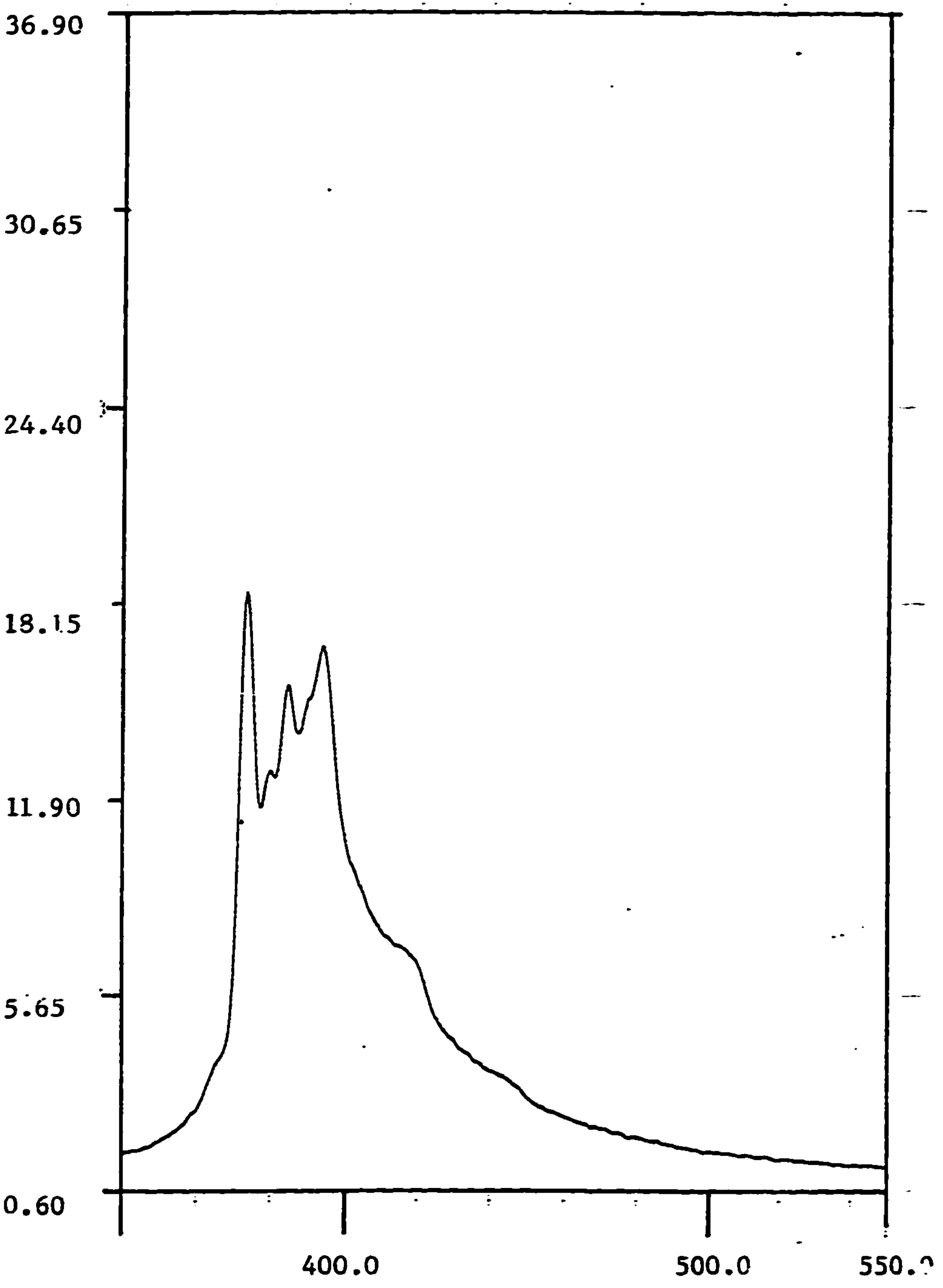


Figure B.12: Florescence Spectrum for PVA1 at 5% NaCl and a polymer concentration of 0.3%

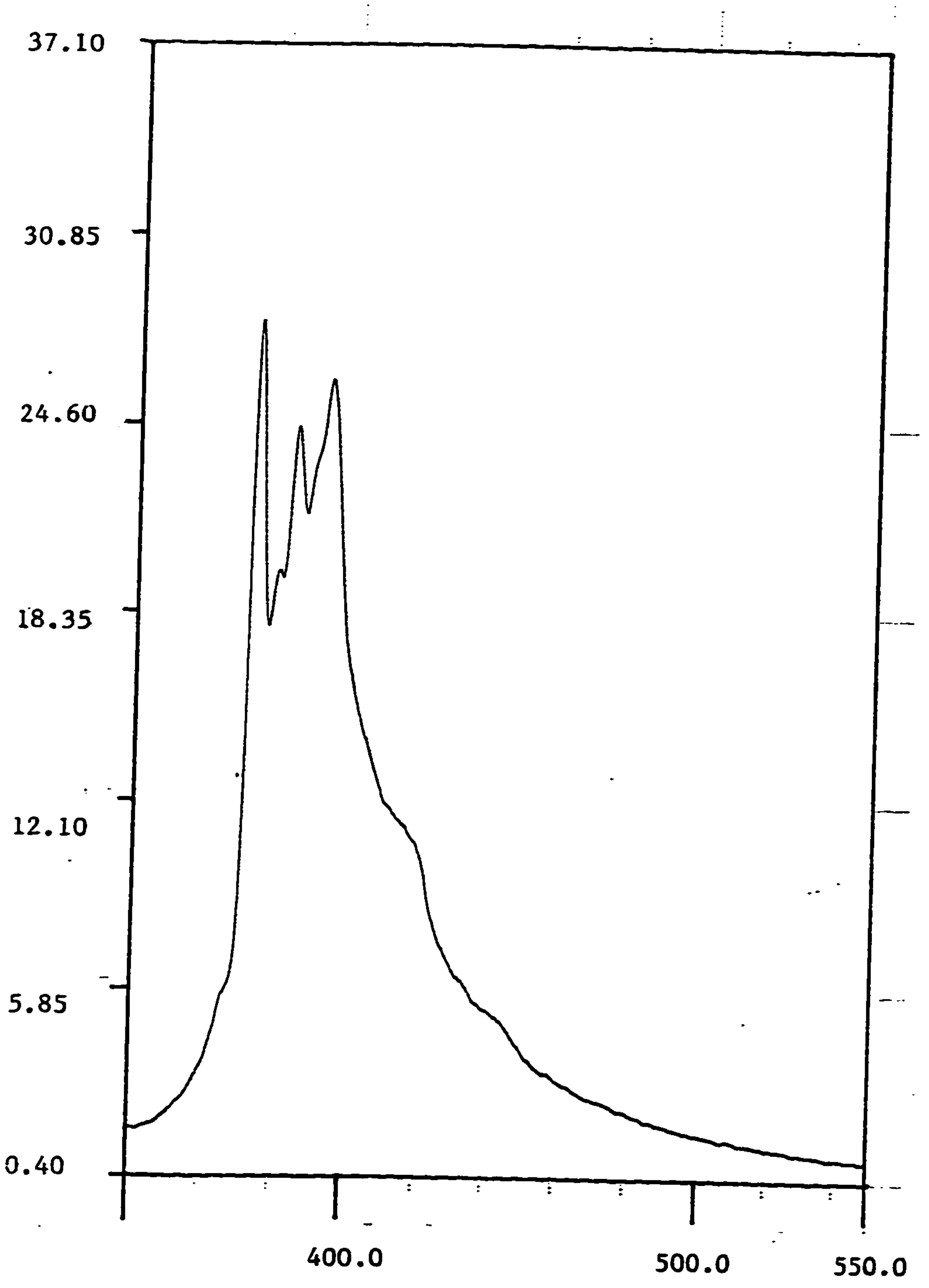


Figure B.13: Florescence Spectrum for PVA1 at 5% NaCl and a polymer concentration of 0.5%

Appendix C

Nuclear Magnetic Resonance Spectra

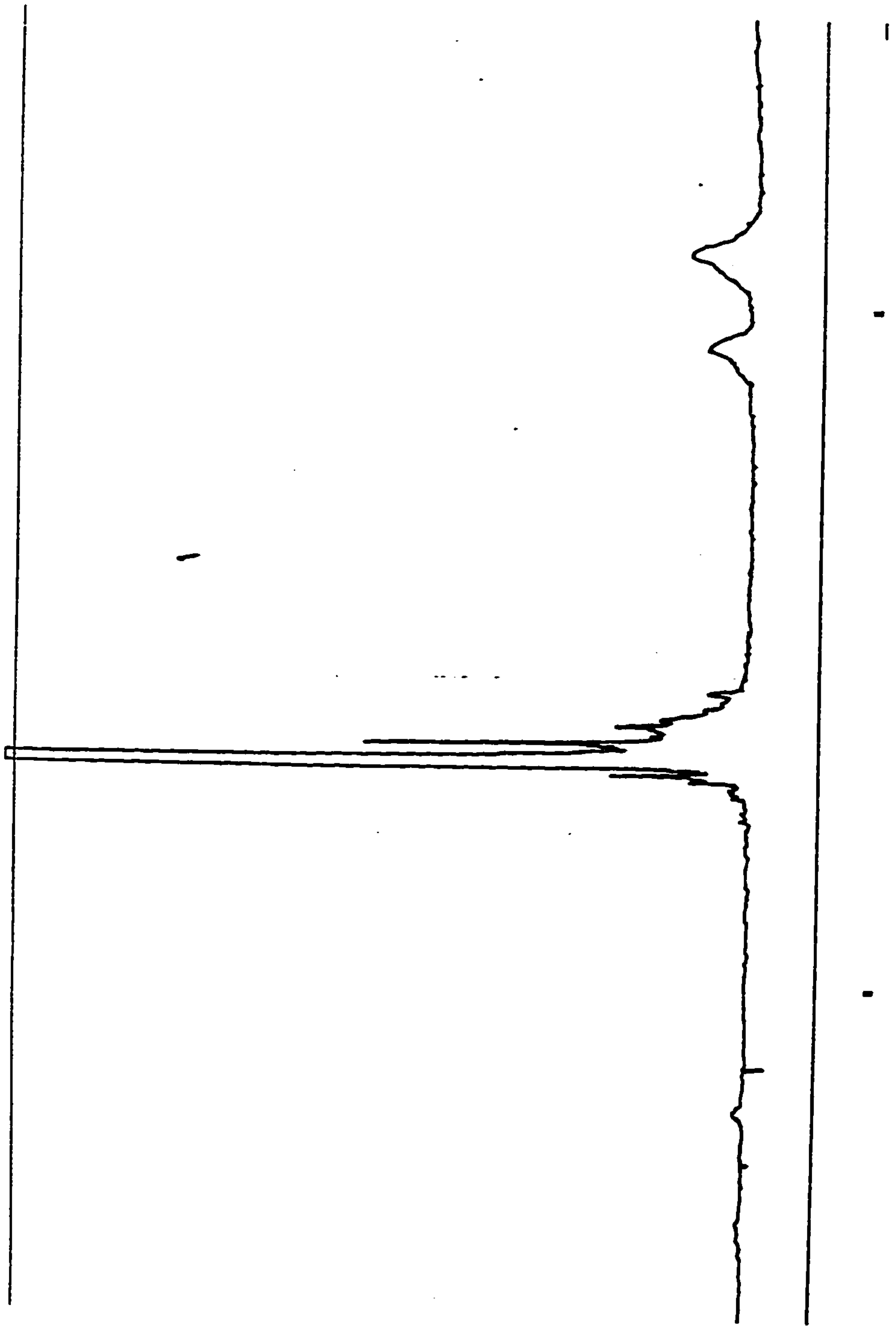


Figure C.1: NMR Spectrum for Homopolyacrylamide

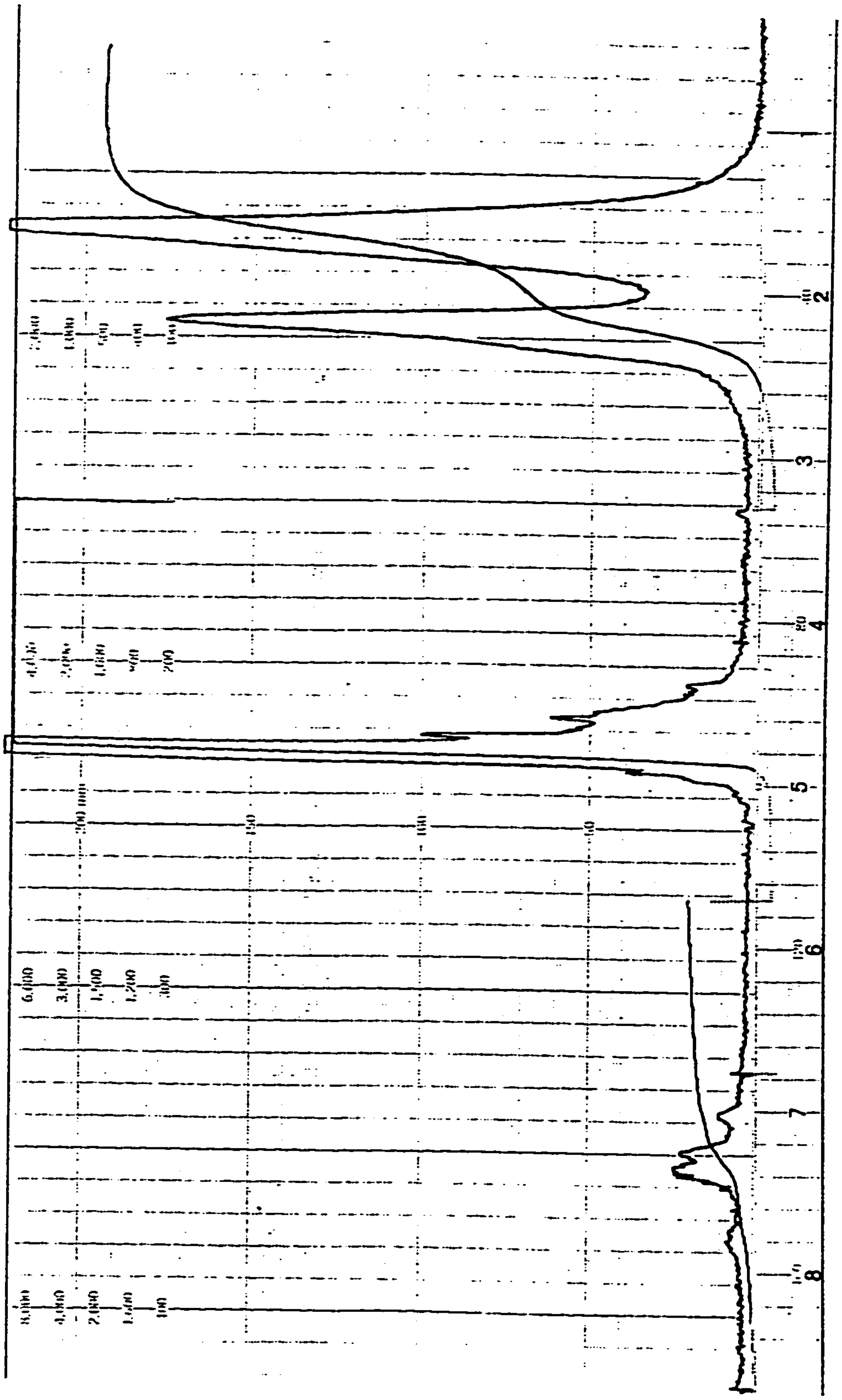


Figure C.2: NMR Spectrum for P(AS)86

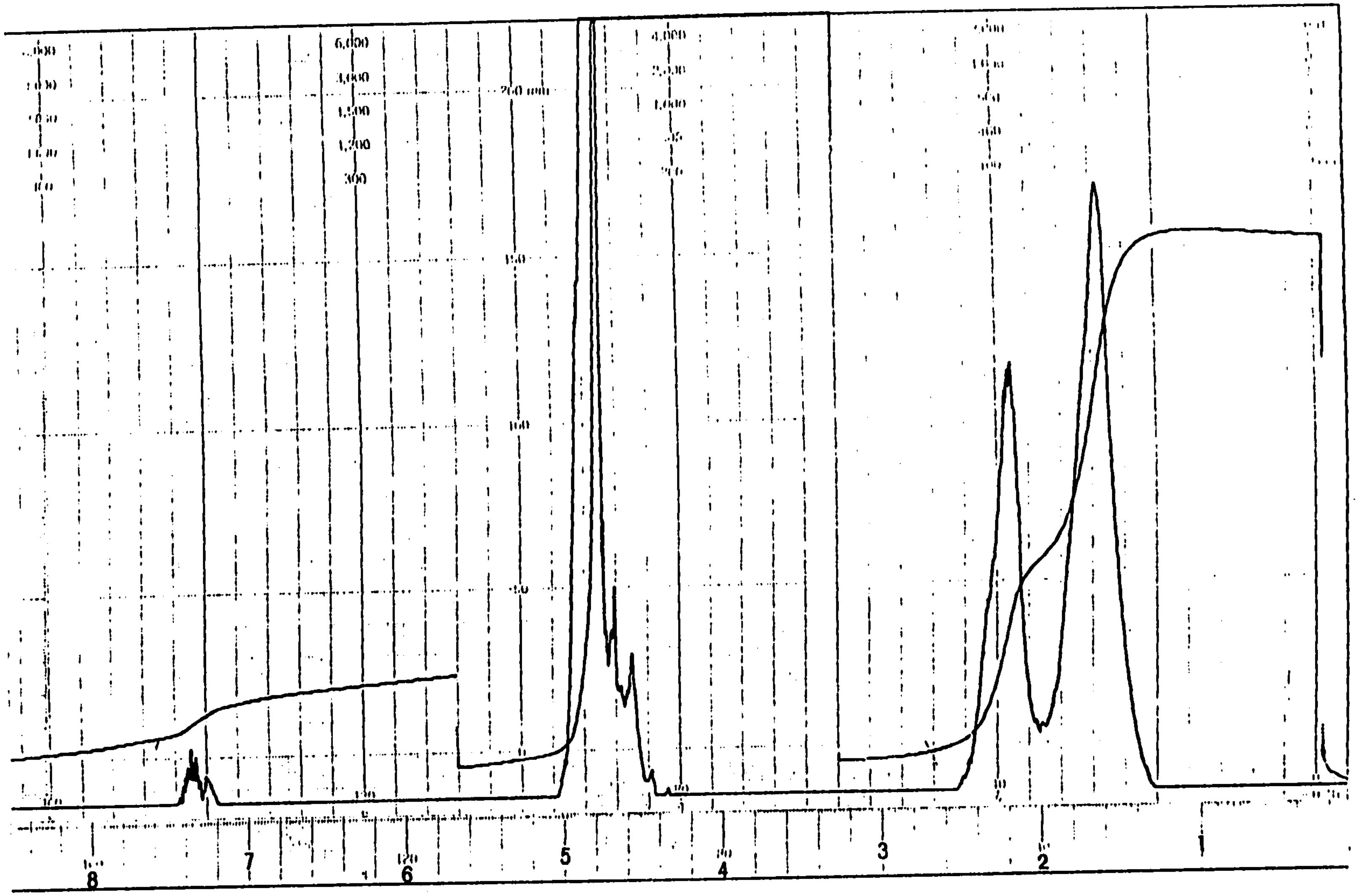


Figure C.3: NMR Spectrum for P(AS)87

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