THE EFFECTS OF SHORT-TERM STORAGE AND ELEVATED TEMPERATURES ON THE FLOCCULATION ACTIVITY OF AQUEOUS POLYMER SOLUTIONS

by

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ABSTRACT

Flocculation studies with polystyrene latex suspensions proved to be an effective method for determination of low concentrations of aqueous solutions of cationic polyelectrolytes in the parts per billion range with reasonable accuracy. The reproducibility of results has been attributed mainly to the fact that an ideal suspension with very narrow particle size distribution was obtained using polystyrene latices.

The effect of short-term storage of polymer solutions varied with respect to the concentration of the polymer and the effect was noticed mainly in the first two days of storage.

The effect of elevated temperatures on polymer solutions resulted in the partial breakdown of the polymer chains. The degradation rate was found to be greater in the first hour than subsequently.

Experiments showed that there was a decrease in the effectiveness of the polymer in promoting the flocculation of the latex suspension in the case of both stored and preheated polymer solutions. Morever, for these polymers, higher polymer dosage was found to be required for optimum flocculation to occur and also to bring the electrophoretic mobility to zero.

RESUME

Les études de floculation à l'aide de suspensions de latex de polystyrène se sont montrées une méthode efficace pour la détermination de faibles concentrations de solutions aqueuses de polyelectrolytes cationiques (parts par billion) avec une précision acceptable. La reproductibilité des résultats a été attribuée en grande partie au fait qu'une suspension idéale, ayant une distribution étroite des dimensions des particules, était obtenue à l'aide des latices de polystyrène.

Le storage à court-terme des solutions de polymer varié en rapport avec la concentration de celui-ci, et cet effet a été surtout remarqué lors des deux premiers jours de storage.

L'effet des températures élêvées sur les solutions de polymer avaient pour résultat de briser partiellement les chaines du polymer. Le taux de dégradation observé fut plus élevé durant les premières heures que plus tard.

Les expériences ont montré qu'il y avait une baisse d'efficacité du polymer lors de la floculation de la suspension de latex que ce soit durant le storage ou lorsque les solutions de polymer sont préréchauffées. Par consequent, pour ces polymers, on a constâté qu'un dosage élevé de polymer était necessaire pour réaliser une floculation optimale, et necessaire aussi pour ramener la mobilité éléctrophoretique à zéro.

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GLOSSARY

°C	degrees Celsius
COD	chemical oxygen demand
DMDAAC	dimethyldiallylammonium chloride
EM	electrophoretic mobility
GC	gas chromatrography
g/L	grams per liter
LC	liquid chromatography
min	minutes
mL	milliliters
mm	millimeters
mg/L	milligram per liter
MW	molecular weight
PEI	polyethylenimine
ppm	parts per million
ppb	parts per billion
PVSAK	polyvinylsulfuric acid
t_o	efflux time of solvent
t	efflux time of sample
TBO	toluidine blue O
TC	total carbon
TIC	total inorganic carbon
TKN	total kjeldahl nitrogen
TOC	total organic carbon
ZP	zeta potential
η_r	viscosity ratio
NTU	nephelometric turbidity unit

CHAPTER 1

Background

1.1 Introduction:

Synthetic organic polymers in water and wastewater treatment has gained wider application as the technology has been applied to the needs of meeting more stringent discharge limits and improving efficiencies of new and existing systems (2,23,55,56). Some of the applications reported in the literature include primary and secondary clarifier loading and performance, improving water treatment operation, treating industrial waste non-biologically, phosphorus removal, heavy metal and color removal, improving the removal and dewatering of waste solids, etc. (10,13,25,32,55).

These polymers have been found to be more efficient than the traditional inorganic flocculants and are non-corrosive towards metals, such as steel, used in processing equipment. Polyelectrolytes tend to produce sewage sludges with low ash content and to reduce the overall cost of water pollution control (32). Current usage trends from the water treatment industry lead to a projected worldwide market of $120 million for these polymers by 1990 (12).

1.2 Brief History:

Polyelectrolytes have long been used in water treatment as flocculants and flocculation aids, although it is only comparatively recently that the term "polyelectrolyte" has come into normal water treatment parlance. The crushed nuts of the Nirmali tree "STRYCHNOS POTATORUM" have been used in India for centuries to clarify muddy water. Their action almost certainly depends on the presence of a water soluble organic polymer (51). Activated silica, soluble starches, gelatins and sodium alginates are further examples of polyelectrolytes that are powerful flocculating agents used in olden days.

1.3 Meaning of the word "Polyelectrolyte":

In this thesis, the terms "Polymers" and "Polyelectrolytes" will be used interchangeably. Strictly, however, polyelectrolytes combine the properties of polymers and electrolytes. Essentially they are water soluble polymers with ionizable groups (51). The term is often restricted to synthetic organic polymers of this type, but this usage is incorrect. Polyelectrolytes may be natural or synthetic or either inorganic or organic (9).

The word "polyelectrolyte" is used te mean an organic polymer in this thesis and is defined as one which contains sufficient charged functional groups or neutral functional groups capable of becoming charged in aqueous solution, to impart water solubility to the polymer and to allow it behave as an electrolyte (42).

1.4 Classification of Polyelectrolytes:

Polyelectrolytes can be classified into four classes depending upon the residual charge of the polymer in an aqueous solution (23,42). They are a) Nonionic b) Anionic c) Cationic and d) Amphoteric.

1.4.1 Nonionic: These polymers have no formal charge. However, they are capable of developing a transient charge in aqueous solution, via protonation for example. As a result, they are water soluble and behave like weak electrolytes.

Examples: Polyalcohols, polyethers, polyamides, poly-N-vinyl hetercyclics.

The most obvious weakness of non-ionic polyelectrolytes is that the floc formed is both small and easily redispersed and broken. The small weak floc is generally attributable to the fact that flocculation is based on weak, hydrogen bond-type bridging (42).

1.4.2 Anionic: These polymers contain sulfonic, phosphonic or carboxylic acid (salt) functional groups.

Examples: acrylamide/acrylic acid, copolymers or hydrolyzed polyacrylamides, polystyrene sulfonate, polyvinylphosphate, etc.

Anionic polymers are often used in an acidic, alum-containing system. A multivalent positively charged ion (provided by the alum) is necessary to provide bridging between high molecular weight (MW) anionic polymers and the anionic fine suspended solids which are to be flocculated (42).

1.4.3 Cationic: These polymers are positively charged. They frequently contain the ammonium group, especially those used in water and waste treatment.

Examples: Poly(ethylenimine hydrochloride), Dimethyldialyl ammonium chloride, etc.

Many commercially available cationic polymers are copolymers of a cationic monomer and acrylamide. This is largely attributable to

a) The convenient, high MW building characteristic of acrylamide, and

b) the relatively high cost of manufacturing or purchasing a cationic homopolymer.

The balance of cationic/nonionic ratio in the polymer is also important in optimizing performance of the polymer (42).

A high MW cationic polymer (copolymer of acylamide) was used in this research but the exact composition is not known because of trade secrecy. Figure 1.1 shows the structure of a different polymer which is also a copolymer of acrylamide. The essential feature is that it is the copolymer which is responsible for the charge.

1.4.4 Amphoteric: These polymers contain both positive and negative functional groups on the same polymer chain. They are seldom used in water and wastewater treatment as flocculating agents because of their poor flocculating characteristics.

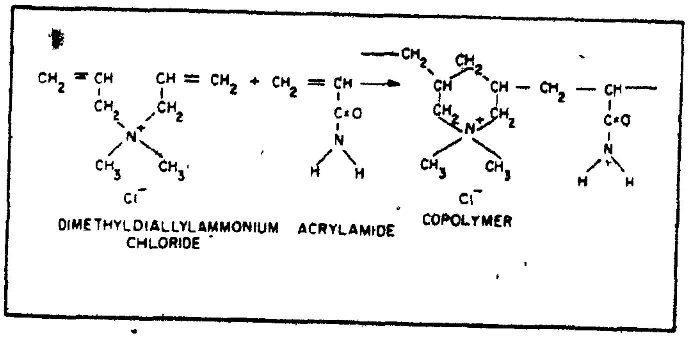


Figure 1.1. Structure of a Copolymer of Acrylamide

1.5 Objective of this Thesis:

The basic objective of this study may be summarized as:

i) To examine the flocculation characteristics of a high molecular weight cationic polymer, using a standard suspension such as polystyrene latex.

ii) Based upon the consideration of destabilization of latices by polymers, to develop a conceptual relationship regarding optimum flocculation with pertinent solution variables, and to use this relationship as a tool for the detection of unknown polymer concentration in a sample.

iii) To develop a "reliable" method for the detection of polymer concentrations, if possible in the parts per billion range (ppb). Upto now there is no satisfactory method for determining these low polymer concentrations. Also they were found to be highly toxic to fish even in the ppb range.

iv) To evaluate the effects of short term storage (1-5 days) and elevated temperatures on dilute and concentrated polymer solutions. This type of evaluation is important as polymer solutions in some water and waste water treatment plants are prepared in advance of application in order to reduce viscosity and allow more convenient application.

v) To relate the observed (diminished) concentrations of stored and preheated polymers to the flocculation activity of these polymers on a standard suspension (polystyrene latex suspension).

The results of the study are presented in five chapters as follows:

In chapter 4, flocculation of polystyrene latex suspensions over a range of polymer doses is described. Chapter 5 describes the various methods used in determining low polymer concentrations. In addition, this chapter also describes how very low concentrations (less than 1 mg/L) of cationic polymers can be measured by use of flocculation studies. Chapter 6 deals with the effects of storage on the observed (effective) concentrations of various polymer dilutions and also explains the probable reasons of aggregation or degradation that occurs during storage. In chapter 7, the effect of temperature on polymer breakdown is discussed. Finally, chapter 8 presents results which relate the storage and temperature effects of dilute polymer solutions to the loss of flocculation activity.

CHAPTER 2

Literature Review

2.1 Theory of the Action of Polyelectrolytes:

This section will cover briefly a review of the reaction mechanisms involved in polymer-colloid interactions, and the coagulation flocculation processes, stressing adsorption, interparticle bridging theories, and restabilization. This review will make extensive use of a review article "State of the Art of Coagulation", a committee report of the AWWA (16), and a later review in the 1980 Ph.D Thesis "The Role of Polymers in Dissolved Air Flotation" (26).

2.1.1 Reaction Mechanisms:

The aggregation of colloidal particles can be considered as involving some of the following mechanisms (56,65,73).

i) particle transport to effect particle contacts
ii) electrostatic charge reduction or charge neutralization by adsorption of counterions depending upon the charge of the polymer and the colloid
iii) adsorption, followed by interparticle bridging.

Particle transport in aqueous systems is essentially a physical process and is accomplished by fluid motion, Brownian motion and sedimentation (65). Ruehrwein and Ward (61) propose that in a system of negatively charged colloids, the positively charged polymer is adsorbed on the surface of the particle. The particle surface charge is reduced or neutralized sufficiently to permit cohesion and aggregation on collision, through residual valence forces. In coagulation with cationic polymers, charge neutralization is usually accomplished. The polymer may, if long enough, adsorb on more than one particle and thus be responsible, by a bridging action, for interparticle bonding (16,65). At this point, La Mer's distinction between the destabilization mechanisms involved is relevant (44):

i) The processes that effect a reduction of the total potential energy of interaction between the electrical double layers of two similar particles is designated as "coagulation",

ii) the processes that aggregate colloidal particles into a three dimensional floc network by the formation of chemical bridges is termed as "flocculation".

La Mer's definitions of the terms coagulation and flocculation are not universally accepted (73); however, and in this thesis they will be used interchangeably.

2.1.2 Adsorption:

The extended-segment theory of polymer adsorption was first proposed by Jenckel and Rumbach (7) to explain the adsorption of larger quantities of polymer onto a surface than could be accounted for by simple monolayer coverage. Later, investigations by Koral et al (43) provided additional evidence to support this theory. Simha, Frisch and Eirich (63) developed a theoretical model of polymer adsorption, (leading to the S.F.E. isotherm) in which the polymer is attached to the adsorbent surface by a fraction of the total number of segments comprising the polymer chain, while pendent loops extend into the solution. As the fraction of attached segments is reduced, the S.F.E adsorption isotherm approaches the well-known Langmuir isotherm. Consequently, Langmuirian adsorption behavior has been observed for many polymer-solvent adsorbent systems (6,45,76).

The attachment of the polymer molecule to the adsorbent surface may occur by chemical or physical interactions, depending upon the characteristics of the polymer chain and the adsorbent surface. For cationic polymers, Ruehrwein and Ward (61) have suggested that the polymer molecule is adsorbed on to the faces of a clay particle via a cation exchange mechanism. With the adsorption of anionic polymers by clay particles, the adsorption mechanism is considered to be either hydrogen bonding, anion exchange or chemical reaction with cations on the clay surface (48). Mortensen (49) has shown that anions in the solution compete with polymeric anions for adsorption sites on the clay particle. Mortensen also reports that there is an increase in adsorption of anionic polymers with an increase in sodium chloride concentration or with a decrease in pH, perhaps because of a reduction in the negative potentials of both polymer and clay, thereby permitting closer packing of the polymer molecules on the clay particles. Black et al (6) showed that the adsorption of cationic polymers onto negative colloids is rapid (30 seconds after being added).

2.1.3 Interparticle Bridging:

Ruehrwein and Ward (61) were the first to propose a polymer bridging mechanism. Later, LaMer and coworkers (45) developed a mathematical model for polymer bridging, which provides an improved model for understanding the ability of polymers to destabilize colloidal suspensions. In its simplest form, the chemical bridging theory proposes that a polymer molecule can attach itself to the surface of a colloidal particle to one or more adsorption sites, with the remainder of the molecule extending into the solution. These extended segments can then interact with vacant sites on another colloidal particle. Failing to find a suitable adsorption site on another particle, the extended segments can eventually adsorb at other sites on the original surface (65).

The phenomenon of physical bridging is predominant in the case of anionic polymers on negative surfaces (6,11,48). Michaels (48) has shown that anionic polymers possess a sufficient number of charged sites to extend the polymer chain, thus allowing interparticle bridging. Chemical bridging between particles is also possible in the case of cationic polymers (65). Black et al (6) have reported that long chain anionic polymers can better remove turbidity than can short chain polymers of the same degree of hydrolysis.

They also showed that increasing the suspension concentration improved interparticle bridging for both cationic and anionic polymers, presumably because of a decrease in the interparticle distance. Lastly, interparticle bridging of the polymer will depend upon many parameters such as polymer size (16,20,45,46), structure (45), flexibility (16), charge density (16,34,46), mixing and degree of shear (44,69) and interaction energy between molecule and the adsorbent surface (16).

2.1.4 Restabilization:

Restabilization of negative particles, which were originally negatively charged, by an excessive amount of polymer addition was observed by many researchers (8,20,31,76). This phenomenon might be because of steric and electrostatic interactions between polymer molecules adsorbed on the colloidal particles, which in turn inhibit the formation of polymer bridges (16,31). Pugh and Heller (58) observed restabilization of gold sols at very low polycation doses, which they attributed to steric repulsion. Yeh and Ghosh (76) claim that restabilization caused by overdosing was simply a result of charge reversal. Birkner and Morgan (4), and Healy and La Mer (34) relate this restabilization phenomenon to the effect of intensity of solution agitation. Kragh and Langston (44) suggest that intense solution agitation disrupts polymer bridges and causes polymer rearrangement on the adsorbent surface.

2.2 Zeta Potential:

2.2.1 Introduction:

When a colloidal particle is immersed in a solution, electrical charges will develop at the particle-water interface (16). The charge of these particles is mostly electronegative for raw colloids (59). The origin of these charges is due to the dissociation of the ionizable groups of the colloid itself (16). By electrostatic attraction, these negatively charged colloids attract to their surface a stationary surrounding layer of positive ions, referred to as the Stern layer (56). Surrounding this fixed layer is a moveable, diffuse layer wherein the concentration of positive ions falls off as it extends to the area of electroneutrality in the bulk of the suspending medium. This charged system - the surface of the colloid and the neutralizing counterions - is called a "double layer" (59). The overall potential drop is known as the Nernst potential (56). The potential drop in that part of the diffuse layer outside the plane of shear (i.e., the boundary between the water bound to the particle and the free water in the bulk of the solution) is called the "Zeta Potential" (ZP) (16,56). ZP measurement is usually performed using a technique based on the electrokinetic phenomenon of electrophoresis (16). The electrophoretic mobility (EM) under an imposed D.C. voltage can be observed directly by microscrope. To convert this measured electrophoretic mobility value to ZP in mV, the equations of

Helmholtz-Smoluchowski, Henry and Debye-Huckel can be applied. These are also conveniently graphed in the Zeta-Meter manual (77). In the subsequent discussion the words ZP and EM will be frequently used and it should be noted that there is a definite relationship between these two parameters.

2.2.2 Application of Zeta Potential to Coagulation Studies:

Thomas Riddick (59) claims that ZP is one of the important factors affecting coagulation. Treweek and Morgan (69), however, indicate that ZP has little validity when using anionic or nonionic flocculants where bridging theory is operative. There is still a lot of controversy at what ZP optimum flocculation occurs. This review will cover cases of varying ZP values at optimum flocculation with different types of suspensions.

Many researchers reported that cationic polymers are mainly responsible for large changes in ZP (6,8,31,40,59). Riddick (59) has emphasized the need for charge neutralization to obtain good flocculation. Black et al (6) showed that the ZP of the particles was reduced considerably by small additions of cationic polymer. The authors also reported that the changes in ZP with respect to polymer addition were extremely rapid. Work of Gregory (31) on polystyrene particles has indicated that with cationic polymers, optimum flocculation occurred when the ZP of the particles was reduced to zero. The same conclusion has been reached by

Teot (68) for suspensions of polystyrene latex and by Dixon (21) for bacteria. Zero ZP values also closely coincided with optimum polymer dose for flocculation of soy bean oil coated with emulsifiers of sodium salts of alkyl sulfates (27). Black and Vilaret (8), however, have reported that optimum flocculation of a polystyrene suspension with a fairly low molecular weight cationic polymer occurred when the ZP of the particles was still highly negative. With sufficient polymer to give zero mobility the particles were completely restabilized. No explanation of this anomaly has been given.

Changes in flocculation characteristics with respect to ZP were also observed in the case of inorganic colloids such as silica, kaolinite, bentonite, montmorillonite clay, etc. Yeh and Ghosh (76) reported that for bentonite, optimum flocculation occurred at close to zero ZP. Black et al (6) indicated that the maximum destabilization of kaolinite and montmorillonite clay suspensions occurred when the EM's of the clay particles were reduced to values within the range of -0.7 to 0.0 and -0.3 to +0.7 microns/sec per volt/cm respectively. These authors were the first to report that maximum destabilization occurred even at positive EM but no reasons were given for this behavior. Ockershausen and Peterman (50) noted that the optimum flocculation of suspensions of kaolinite and montmorillonite clays with a cationic polyelectrolyte at pH 7.6 occurs at ZP's of -31 to -7mV. In the case of silica suspensions, Kane et al (40) have indicated that the optimum flocculation at pH 6.8 with a cationic polyelectrolyte occurred when the EM of the suspended solids were reduced to -0.65 microns/sec per volt/cm.

Considering all of the above authors' views, the conclusion must be drawn that the reduction in ZP or EM for optimum flocculation or maximum destabilization depends upon many factors such as the type of suspension, concentration of suspension, impurities, pH, type of polymer, etc. Zero ZP values do not always point to optimum flocculation conditions.

2.3 Suspensions used in Flocculation Studies:

This section will briefly review the different types of suspensions as used by many researchers for flocculation studies.

2.3.1 Silica:

Lindquist and Stratton (46) studied the flocculation of negatively charged colloidal silica with polyethylenimine. They found that the extent of adsorption was not influenced by changes in MW, pH, or ionic strength at the concentration required for flocculation. At higher doses, all of these factors were significant. LaMer and coworkers (45) investigated the destabilization of silica with polymers and introduced mathematical relationships to describe the observed destabilization phenomenon for the silica suspensions. Dixon et al (20) studied the effect of MW of cationic polymers on the flocculation and the ZP of crystalline silica. Iler (37) used colloidal silica for flocculation studies and concluded that the amount of polymer required for optimum flocculation depends upon the particle size.

2.3.2 Latices:

The use of polystyrene latices in fundamental colloidal studies is receiving considerable attention (8,31) owing to the highly spherical shape and uniform size of their particles. Habibian and O'Melia (33) studied the coagulation of latex particles with cationic polymers and concluded that the optimum polymer dose was independent of MW above a minimum MW. The same conclusion was reached by Gregory (31) in his study of the effect of cationic polymers on latex particles. The author explained that optimum flocculation occurs when a certain positive charge has been adsorbed by the particles, irrespective of the length of the polymer chains carrying the charge. Latex spheres were also used by Birkner (4), and Swift (66) with sodium chloride as coagulant to study the collision efficiency factor depending upon the type of flocculation used (perikinetic or orthokinetic). Perikinetic is a process where interparticle contacts are produced by Brownian motion, whereas in orthokinetic, contacts between particles are caused by fluid motion (mechanical).

2.3.3 Clay:

Michaels (47) and Mortensen (49) have studied the chemical interactions and destabilization of kaolinite clays with sodium polyacrylate, partially hydrolyzed polyacrylamide and polyacrylonitrile. Pacter (52) studied the interaction of montmorillonite clays with carboxymethylcellulose. Ockershausen and Peterman (50) used cationic polymer for the destabilization of a montmorillonite clay supension. Black et al (6) have evaluated the effectiveness and mode of action of very dilute aqueous solutions of a cationic polymer for the destabilization of dilute kaolinite and bentonite clay suspensions under controlled conditions of pH, ionic strength, initial colloid concentration and intensity and duration of solution agitation. Ruehrwein and Ward (61) have also studied the aggregation of kaolonite and montmorillonite clays with cationic polymers.

2.3.4 Bacteria:

The sedimentation of E.coli assisted by alum and polyacrylamides was studied by Roberts et al (60). Treweek and Morgan (69) reported the successful flocculation of E.coli by polyethylenimine polymer. Dixon et al (20) used E.coli bacteria and Chlorella ellipsoidia algae to study the measurement of the adsorption of labelled cationic polymers. Busch and Stumm (11) obtained flocculation curves for polyelectrolytes added to E.coli and A.aerogenes similar to those for silica or latex suspensions. Cohen et al (15) observed good flocculation of Chlorella cells with cationic polyelectrolytes and no flocculation was obtained with an anionic polymer. No reasons for this of type of phenomenon were reported by the authors. Tenney et al (67) were able to flocculate Chlorophyta with anionic and nonionic polymers.

2.4 Toxicity of Polyelectrolytes:

It has been assumed that all the added polymer in water and wastewater treatment was entirely adsorbed in the process of flocculation. However, it was found by Gehr (26) that under normal plant operations significant amounts of polymer appear in the effluent. Toxicity studies revealed that very low polymer concentrations were toxic to fish (<1 mg/L). In this section, some of the conclusions of different researchers regarding the toxicity of polymers and their constituent monomers will be reviewed.

The U.S. Environmental Protection Agency (E.P.A.) emphasizes that the use of some polyelectrolytes may present health hazards if used in drinking water treatment (30). According to studies by the World Health Organization (W.H.O.), Gopper and Straub (29) state that toxicity risk was associated with monomers rather than with polyelectrolytes. Croll and Simkins (18) even stated that the polymers of acrylamides themself were non-toxic but that the monomer, acrylamide, has a high chronic toxicity to rats even at very low levels. In contrast, in the studies of Spraggs et al (64) using fish, it was found that the monomer was always less toxic than its equivalent polymer. However, they concluded that the acrylamide monomer was more toxic than the monomer of dimethyldiallyl ammonium chloride.

Biesinger et al (3) reviewed studies of many researchers on the toxicity of polyelectrolytes and concluded that many cationic polymers were acutely toxic to fish in concentrations of about 2 to 3 mg/L whereas the anionic polymers were relatively non-toxic. In their own studies they found out that cationic polymers were toxic even at concentrations less than 1 mg/L. The same conclusion was reached in the Spraggs et al, fish avoidance studies (64). Packham (51) reports that the high MW polymers consisting of copolymer of 90% acrylamide were not toxic when fed to rats and dogs. On the other hand, acrylamide monomers were highly toxic!

2.5 Measurement of Polyelectrolyte Residuals:

As discussed in section 2.4, polymer residuals, especially from cationic polymers, may be acutely toxic at low concentrations and therefore their detection is very important. A number of methods have been developed to detect these residual polymers but unfortunately there is no satisfactory method for determining low residual concentrations of polyelectrolytes in treated water or sewage effluents. In an attempt to find a method of determination that would be applicable for research and field purposes, the author surveyed the currently available methods. This survey will explain briefly these different methods.

Michaels and Morelos (48) developed a method to determine polyacrylamide by measuring the light absorbed by the colloidally suspended complex formed by the reactions between diisobutylphenoxyethoxyethyl dimethylbenzylammonium chloride (Hyamine 1622) and hydrolyzed polyacrylamide, in order to follow the concentration of polyacrylamide in solution during flocculation. This technique was refined by Crummett and Hummel (19) by keeping the pH of the solution at 8.0, specifying the reaction time, hydrolyzing the sample with sodium hydroxide in polyethylene in a steam bath and removing interferences by ion-exchange. They claim that reproducible results were obtained by this method and were able to measure 0.1 mg/L of polymer by concentrating the sample by distillation. Later, Wimberley and Jordan (75) automated and extended this method for all anionic polyelectrolytes and were able to detect down to 5 mg/L. They commented that the accuracy of the method depends largely upon the molecular weight of the polymer. Crummett and Hummel (19) also presented another tedious Distillation-Nesslerization method for determination of polyacrylamides and were able to detect concentrations as low as 0.5 mg/L. Birkner and Edzwald (5) modified Burttshell's spectrophotometric method for the detection of non-ionic polymer residuals. This method involves the complexation of ethylene oxide with phosphotungstic acid and the extraction of the complex into methlyethyl ketone. After drying, the tungsten polymer is reduced with $TiCl_3$, complexed with dithiol, and extracted into CCl_4. The colored polymer-tungsten-dithiol complex exhibits a maximum absorbance at 625 nM. Croll (17) determined the acrylamide in polyelectrolytes by brominating the sample; the dibromopropionamide obtained is extracted with diethylether and the extract analyzed by electron capture gas chromotagraphy. Gopper (29) developed a semi-quantitative method to detect less than 0.01 microgram of cationic polyelectrolytes by concentrating the sample by activated carbon, extracting by using chloroform as solvent, and again concentrating in a flash evaporator. The concentrated sample was analyzed by using Thin Layer Chromatography. Furusawa et al (24) detected anionic polyacrylamide using Gel Permeation Chromatography with the addition of a salt (0.005M KCl) to the elutant. This gave rise to the elution behavior on accordance with the hydrodynamic volume concept of GPC separation. Tenney et al (67) were able to detect anionic and nonionic polymers in the range of 25 - 50 mg/L by using Chemical Oxygen Demand.

In the turbidimetric method of Joseph and Feitelson (39) the interaction of polyelectrolytes of opposite charge yields strong association complexes which form precipitates in all but the most dilute solutions. A plot of optical density against micro-equivalents of anionic polyelectrolyte added (i.e., the polyelectrolyte to be quantatively determined) per known amount of protamine solution (i.e., a cationic polyelectrolyte used as a reagent) yields a straight line. Using a prepared calibration curve, the concentration of an anionic polyelectrolyte solution can then be determined. The turbidimetric method is usable over a wide pH range but is sensitive to the added salt or buffer solution. Modifying this charge neutralization technique, Kawamura and Tanaka (41) developed a method where an unknown concentration of negative colloids is made to react with a known excess amount of positive colloid, methyl glycol chitosan (MGC); the oppositely charged colloids react very nearly stoichiometrically and are neutralized. The remaining excess MGC is then back titrated by potassium polyvinyl alcohol sulfate (PVSAK) using toluidine blue as an indicator. If the structure of a colloidal electrolyte is known, the equivalent weight of the molecule may be determined according to the number of charge-bearing functional groups. Wang and Shuster (72) modified this indirect titration method by using PVSAK as a standard anionic titrant for detecting the cationic polymers, and 1,5-dimethyl-1,5 diazaundecamethylene polymethobromide (DDPM) as a standard cationic titrant for detecting anionic polymers. In general, the above titration methods measure the net charge of the colloidal matter. Tsubouchi et al (70) developed a two phase titration method for detection of cationic surfactants in the concentration range of 10^{-4} to 10^{-5}M. This method involves mixing cationic sufactant, buffer solution, indicator, and 1,2 dichloroethane, and titrating with tetraphenylborate. The ion pair formed between the cationic surfactant and titrant is extracted from an aqueous phase (20 mL) into the organic solvent (0.5 - 1.5 mL). Color change of the dichloroethane phase indicates the end point of titration.

Black et al (6) used liquid scintillation counting techniques and a liquid scintillation spectrometer for determining the residuals of C^{14} labelled cationic polymers, down to concentrations of 0.003 mg/L. Cationic polymer of concentrations greater than 5 mg/L were detected by Tenney et al (67) using the Total Kjeldahl Nitrogen (TKN) method, but they reported that there may be leakage of nitrogeneous compounds from the algal suspension which they were using.

Packham (51) states that polymer concentrations greater than 5.0 mg/L can be detected by flocculation of standard silver bromide sol, assuming that the polymer has a critical coagulation concentration. He also states that polymer concentrations as low as 0.05 mg/L can be detected by relating the polymer quantity to the effect of settling rate or filtration rate of a standard 3% kaolin suspension. The disadvantage of the above methods is that the reproducibility of results is poor.

Cationic polymer residuals were measured by Gehr and Henry (78) by measuring the ZP. They concluded that only when polymer residual was detected, was the ZP reversed, and a positive value measured. Concentrations as low as 0.8 mg/L of high MW cationic polymer were detected by this method.

For convenience, this section dealing with methods of detecting polyelectrolytes in aqueous solutions has been summarized and tabulated in table 2.1. The sensitivity and applicability of each method are also tabulated.

Table 2.1. Summary of Methods for the Determination of Polyelectrolytes in Water

METHOD	SENSITIVITY/ ACCURACY	APPLICABILITY AND LIMITATIONS	REFERENCE
Colorimetric:			
Auto-analyzer: (Polyelectrolyte sample + citrate+air + Hyamine 1622) mixed and turbidity determined at 420 nM in a 8 mm flowing cell.	Depends on the MW of the polymer sometimes as low as 5 mg/L (±2.7%)	Anionic Polymers only. Response is not uniform for all types of polymers.	Wimberley (1971)
Spectrophotometric: Complexation of PEO with phosphotungstic acid; extraction of the complex into methyl ketone; dried; Reduced with TiCl$_3$; complexed with dithiol and extracted into CCl$_4$; maximum absorbance at 625 nM.	30 - 1300 mg/L	Nonionic polymer - Specific to PEO only	Birkner (1968)
Distillation - Nesslerization; Buffer + concentrate by boiling; cool + sulfuric acid + heat; cool + 400 mL distilled water + NaOH pellets; distill; Nessler's reagent; absorbance at 425 mµ in a 10 cm cell.	0.5 mg/L	Specific for polyacrylamides. Tedious	Crummett (1963)
Nephelometric: Sample hydrolyzed with NaOH in polyethylene in a steam bath and interferences removed by ion-exchange.	0.1 mg/L (±5.0 µg)	Specific to polyacrylamides; effected by interferences. (NaCl, KCl etc)	Crummett (1963)
Titrimetric:			
Polymer Sample + Toluidine Blue (indicator) + PVSAK (titrant) for cationic or DDPM (titrant) for anionic.	1.0 mg/L	Nearly all	Wang (1975)
Sample + known amount of MGC (for anionic) or PVSAK (for cationic); excess titrated with MGC (for anionic) or PVSAK (for cationic) using Toluidine Blue as indicator	1.0 mg/L	Nearly all	Kawamura (1966)
Sample + buffer solution + tetrabromophenol pthalein ethylester indicator + 1,2 dichloroethane + tetraphylborate (titrant)	10^{-4} to 10^{-5}M	Cationic surfactants only; subjected to interferences like clay	Tsubcuchi (1981)
Chromatographic:			
Thin Layer Chromatography: Polymer adsorbed on to activated carbon; dried; extracted with chloroform; concentrated in a rotating evaporator; detected by TLC.	less than 0.01 microgram	Laborious; subjected to many interferences.	Coppers (1976)
Gas Chromatography: Bromination of the sample; extraction with an oranic solvent and the extract analyzed by electron capture GC.	0.1 µg/L (±10%)	For acrylamides only; quantitative; laborious	Croll (1972)
Extraction of acrylamide from polymers by shaking them with methanol-water for 24 hours and flame ionization GC used for analysis	0.4 mg/L	For acrylamides only; quantitative; laborious	Croll (1972)
GPC using controlled porosity glass; salt added to the eluent to increase the elution time.	0.5 mg/L	Specific to polyacrylamides only.	Furusawa (1978)
Miscellaneous:			
TKN	5 -10 mg/L	Cationic polymers; leakage of nitrogeneous constituents	Tenney (1965)
COD	25-50 mg/L	Anionic and nonionic polymers	Tenney (1965)
C_{14} labelled + liquid scintillation counter.	1-3 µg/L (±3%)	Sensitivity depends upon the specific activity of the polymers; must have tagged polymer	Black (1965)
Settling rate of standard 3% kaolin suspension.	0.05 mg/L	Universal; subjected to interferences from coagulating species	Packham (1967)
Filtration rate of standard 3% kaolin suspension	0.05 mg/L	Universal; subjected to interferences from coagulating species	Packham (1967)
Determination of quantity of sample to flocculate standard silver bromide sol.	greater than 5.0 mg/L	Poor reproducibility; subjected to interferences from other coagulating species	Packham (1967)

CHAPTER 3

Materials and Methods

3.1 pH: The pH was determined by means of a Corning Portable Digital pH/Temp Meter#4, Corning Science Products, Medfield, MA 02052, USA.

3.2 TKN: Total Kjeldahl Nitrogen (TKN) was determined according to Standard Methods (1).

3.3 COD: Chemical Oxygen Demand (COD) was determined according to Standard Methods (1).

3.4 TOC: Total Organic Carbon (TOC) was determined using a Beckman model 915-A Total Organic Carbon Analyzer.

3.4.1 Principle: The principle involved is as follows:

Total Inorganic Carbon (TIC): The sample is passed through a glass tube at 150°C containing quartz chips wetted with 85% phosphoric acid, and the liberated carbon dioxide is measured by an Infrared Analyzer.

Total Carbon (TC): The sample is oxidized at 950°C in a ceramic combustion tube containing cobalt oxide deposited on an inert igneous substrate and the carbon dioxide released is measured by an Infrared Analyzer.

Total Organic Carbon (TOC): TC - TIC

3.5 Polymer Detection:

The synthetic polymer detection method used was that proposed by Wang and Shuster (72), with refinements. The technique is based on the direct neutralization reaction between cationic and anionic forms. It should be noted that this method basically measures the charge on the colloid. This method seems to be the most suitable and reliable method of all available methods. It is applicable to both cationic and anionic polymers. In the present study, as only cationic polymers were used, only the method used for the detection of cationic polymers will be described.

3.5.1 Reagents:

Toluidine Blue O (TBO) -	1 gm in 1.0 liter. Obtainable from Eastman Cat. No. C1756
Polyvinylsulfuric acid - (PVSAK)	Stock solution 1.6221 gm in 1.0 liter. Obtainable from Eastman Cat. No.8587

3.5.2 Procedure:

i) Measure 50 mL of sample into a 250 mL Erlenmeyer flask or 300 mL beaker.

ii) Add approximately 3 drops TBO solution and mix it by means of a magnetic stirrer. If the color is blue, the sample contains cationic or no polyelectrolytes.

iii) Titrate the blue colored sample with standard PVSAK solution by adding small amounts from a micro-buret until the color of the sample turns light blue to bluish purple. A dip-in-probe colorimeter(*) with 620 nM filter was used to precisely detect the color change.

iv) A blank sample is tested using the same procedure and sample readings are reduced by a blank correction to account for

a) background interferences in the solvent used and

b) possible trace amounts of sample within the chemical reagents.

v) A series of standards consisting of known dilutions of the polymer being tested provides the calibration curve.

vi) Determine the unknown concentration of the cationic polyelectrolyte in the sample from the calibration curve.

(*) Brinkman Probe Colorimeter - Model PC/800
Conditions used: 620 nM filter,
2 cm probe tip
7.8v lamp voltage

3.6 Zeta Potential:

The Zeta Potential (ZP) was measured using a Zeta-Meter manufactured by Zeta-Meter Inc., New York.

3.6.1 Components:

Stereo microscope with two illuminators
Electrophoresis cell
Electrodes
Control box

3.6.2 Principle and Procedure:

Zeta Potential measurements were made using a procedure called "microelectrophoresis". The sample is placed in an electrophoresis cell and observed under a microscope. As a D.C. voltage is appplied, if the particles are electrically charged, they move toward the opposite electrode. Their velocity is relative to the ZP. Velocity is measured by timing individual particles on a microscrope grid. Twenty colloids are tracked and the average time determined. Electophoretic Mobility (EM) is calculated from the conversion charts provided by the manufacturer (77).

EM values were used instead of ZP because the viscosity and dielectric constant were not known for the sample.

3.7 Turbidity: Turbidity measurements were performed by means of a Turbidimeter, Model 2100-A manufactured by HACH (71). This instrument utilizes the "light scattering" or nephelometric principle.

3.8 Jar Tests:

Jar Tests were performed using a commercially available six-position stirrer (Phipps and Bird, Inc., Richmond, Va). The jars used were based on those developed by Hudson and Wagner (36). These are square jars fabricated of acrylic plastic, with dimensions as shown in figure 3.1. These jars can operate with a maximum of 2.0 liters sample.

3.8.1 Rapid Mix and Flocculation:

After the addition of predetermined quantities of polymer to the latex bead suspension samples, the samples were mixed at 100 rpm for 20 min followed by a slow mixing at 15 rpm for 20 min. A 20 min sedimentation period was employed to allow the particle aggregates which were formed during the coagulation-flocculation reaction to settle from the suspension. After this, sample aliquots were removed from the jars at a level 100mm below the surface of the liquid for further analysis such as residual turbidity, ZP, particle size distribution, etc.

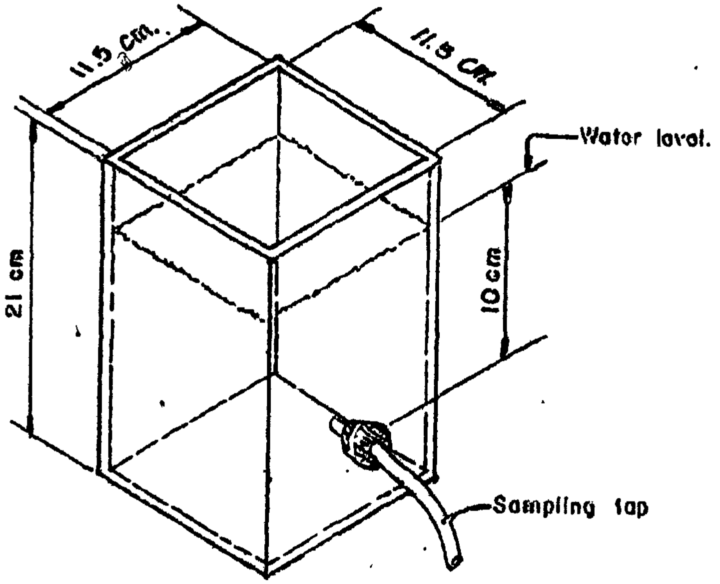


Figure 3.1 Two Liter Jar Fabricated from Acrylic Plastic (after Hudson & Wagner, 1981)

3.9 Coating of Glassware:

A Prosil-28 coating was applied to the surfaces of all glassware and equipment which came into contact with pure polymer solutions or polymer-latex bead systems. This was necessary to prevent loss of polymer due to adsorption on the surfaces of the equipment. Prosil-28 is a product of PCR Research Chemicals, Inc., Gainesville, Florida 32602.

3.10 Preparation of Polymer Stock Solutions in the Case of Dry Polymers:

The first step in the use of a dry polymer is the preparation of a polymer stock solution. The practical maximum concentration for this solution is limited to about 1% because of high viscosity, stirring capabilities etc. The equipment required for dissolving dry polymer usually consists of a wet-out device (coating individual particles with solvents like ethanol, methanol or isopropanol). The key to dissolution of a dry polymer is achieving an uniform wet-out of each polymer particle followed by subsequent rapid dispersion. If uniform wet-out is not achieved, large gelled lumps of polymer will be formed, and these lumps are extremely difficult to dissolve. To wet-out the polymer, ethanol was used in this research.

3.10.1 Procedure:

i) 1 g of dry polymer powder was placed in a dry bottle and 5 mL of ethanol were added. It was ensured that all particles were wet-out and dispersed.

ii) 95 mL of distilled water was added and shaken well and allowed to rest for at least 6-8 hours to ensure that all the particles were dissolved and a homogeneous 1% stock solution resulted.

iii) Further dilutions were made from the stock solution.

3.11 Particle Size Distribution:

Particle size distributions were measured using a Microtrac, 7991 Particle Size Analyzer manufactured by Leeds and Northup, Largo, Fla, USA. This instrument can analyze the size of suspended particles over the range of 1.9 to 176 microns.

3.11.1 Components:

Laser light source
Sample cell
Lenses
Spatial Filter
Solid state detector
Microcomputer digital data processing system

3.11.2 Principle:

The analyzer utilizes the phenomenon of low angle forward scattering of light. In the analyzer the sample is transported across a continuous laser beam; particles in the sample scatter light; the scattered light is collected by a lens, and focused on a solid state detector. The resulting detector output is proportional to selected functions of the particle diameter. These sequential signals are then processed by the microprocessor to provide measured and calculated values (53).

3.12 Preparation of Polystyrene Latex Suspensions:

The method proposed by Goodwin et al (28) was used for the preparation of monodisperse polystyrene latices. The procedure involved is described below in detail.

3.12.1 Reagents:

Potassium persulfate crystals	- Obtainable from Anachemia Chemicals Ltd.
Styrene	- Obtainable from Fisher Scientific Company Cat No 0-4507

3.12.2 Procedure:

All the polymerization reactions were carried out in a 1.0 liter round bottomed three-necked flask. A typical preparation was carried out in the following manner.

a) 670 mL of distilled water was added to the flask and a glass stirrer with a T-shaped blade was fitted to one inlet.

b) A water-cooled reflux condenser was added to the second inlet and the flask was then immersed in a thermostat bath initially set at 70°C.

c) The third inlet was connected to a nitrogen bubbler through which nitrogen was bubbled through the water in the reaction vessel to remove oxygen from the system.

d) The stirrer was adjusted to 350 rpm and stirred for 10 min with nitrogen passing through the system.

e) 73.0 g of styrene was added through the inlet connected to the condenser. The system was then left for 15.0 min to attain temperature equilibrium and to saturate the aqueous phase with styrene.

f) The initiator, potassium persulfate, dissolved in 30 mL of distilled water, was added and washed in with a further 20 mL of distilled water. The reaction was allowed to continue for 24 hours.

g) At the end of the reaction time, the latex was decanted through a funnel packed with glass wool to remove the unreacted monomer and any coagulum formed.

h) The suspension was then dialyzed against distilled water, using well boiled Dialyzer Tubing (Fisher Scientific Company, Cat No 8-667E), in order to remove sodium chloride, unreacted monomer, potassium sulfate and sulfuric acid formed in the reaction. The dialysate was changed every 24 hours and the dialysis was considered to be complete when the conductance of the dialysate became close to that of distilled water. The particle size distribution was examined in a Carl Zeiss TGX-3 Particle Size Analyzer. The mean particle diameter obtained was 556 nM with a coefficient of variation on mean diameter of 0.77%. Figure 5.1 shows the particle size distribution obtained by this method.

3.13 Flocculation Studies with Latex Suspensions:

In this section, the procedure developed by the author for the detection of low polymer concentrations by flocculation studies with polystyrene latex suspension will be explained.

3.13.1 Preparation of Calibration Curves:

i) Choose various latex concentrations polymer concentrations for a series of experiments.

ii) Follow the procedure for jar tests as described before in section 3.8.

iii) Measure the residual turbidity, and the EM of the samples taken at 100 mm from the top of free water level.

iv) Prepare the necessary graphs (for example, figures 4.1 & 4.2)

Note: When the initial latex concentration is less than 100 mg/L the pH has to be depressed to 3.0. The reason for this is explained later in Chapter 4.

3.13.2 Detection of unknown concentration of polymer in a sample:

i) Add the appropriate volume of samples into different jars, depending upon the latex concentration.

ii) Make up different latex concentrations using a stock latex suspension. (Recommended stock solution 1%).

iii) Follow the same procedure used previously for the Jar Tests.

iv) Measure residual turbidity and EM.

v) Take the results of the jar whose % turbidity removal is the maximum.

vi) Use the calibration curves to determine the concentration of the unknown polymer in the sample.

The advantage of this method is that there are two measurable appropriate parameters - residual turbidity and EM. The results obtained based on these two parameters are very similar (% difference was not greater than ±10%). Having two parameters yielding the same results allows for conclusions to be drawn with greater confidence.

3.13.3 Alternative Method for the Detection of Unknown Polymer Concentrations:

If the sample volume available is small (less than 3000 mL) or if there is a need to detect the unknown polymer concentration rapidly, the following procedure may be used:

i) Take 500 or 250 mL samples in six different flasks.

ii) Pipet different volumes of latex stock solution to make-up different initial solids concentrations.

iii) Shake the samples vigorously for 60-120 seconds.

iv) Measure the EM.

v) Choose the sample whose EM is close to zero.

vi) Prepare the calibration curves as shown in figure 4.2 by using different latex concentrations and different known polymer concentrations.

vii) From the calibration curves, obtain the unknown polymer concentration in the sample.

The reproducibility of results by the above methods is good (±10%) and the accuracy is about ±10%. This method is especially suitable for polymer concentrations less than 2.0 mg/L.

3.14 Acid/Bleach Precipitation Method:

Polymers, especially polyacrylamide copolymers present in a sample, can be detected by the Acid/Bleach Precipitation Method (54).

3.14.1 Reagents:

i) Acid Solution - Glacial Acetic Acid (26.3mL)
+ Deionized water (73.7mL)
+ Concentrated Hydrochloric acid (4.2mL)

ii)Bleach Solution - Sodium Hypochlorite, 1.3% available chlorine

3.14.2 Procedure:

i) Add 2.5 mL (i.e., 5% of polymer sample volume) of acid solution to 50 mL of polymer solution.

ii) Mix well and leave standing for one minute.

iii) Mix in 2.5 mL (i.e., 5% of polymer sample volume) of bleach solution over a two minute period.

iv) After 10 minutes, turbidity of the solution is measured.

v) A calibration curve is prepared with known polymer solutions, from which unknown polymer concentrations are extrapolated.

3.14.3 Principle:

The sodium hypochlorite (bleach solution) ionizes in water as shown in equation(1). Since hypochlorous acids are weak acids, the equilibrium of this equation is mainly towards the right. As a result there is a predominant amount of hypochlorous acid in the salt solution. Chlorides are produced by decomposition of the hypochlorous acid as shown in equation(2). At low pH hypochlorous acid combines with halides, generating halogens as shown in equation(3). The chlorine evolved precipitates polyacrylamide copolymers quantitatively, causing turbidity.

$$NaOCl + H_2O \rightleftharpoons HOCl + OH^- + Na^+ \qquad (1)$$

$$2HOCl \longrightarrow 2H^+ + 2Cl^- + O_2 \qquad (2)$$

$$HOCl + Cl^- + H^+ \longrightarrow Cl_2 + H_2O \qquad (3)$$

7

3.15 Preparation of Ion Exchange Column:

The ion exchange column was prepared as described below:

i) Place a plug of glass wool just above the stop-cock of a 50 mL buret.

ii) Stir 10 mL resin (cation exchanger, Rexyn 101(H), manufactured by Fisher Scientific Company, Cat No. R-231) in 10 mL water in a beaker.

iii) Transfer the wet resin to the buret and place plug of glass wool on top of the resin.

iv) Withdraw the water from the column until the water level is just above the top of the resin.

CHAPTER 4

Flocculation Studies

4.1 Introduction:

In this section, the effect of polymer dosage on the flocculation of a very narrow particle size distribution latex suspension will be discussed. The polymer used was a commercially available high MW cationic polymer herein designated as polymer A. This polymer was a co-polymer of acrylamide but the exact composition is not known because of trade secrecy.

Initially, a short set of experiments was done with various polymers and polymer A was found to be more efficient in terms of flocculation characteristics (i.e. maximum turbidity removal). Hence, further research has been conducted with polymer A. The commonly used "Jar Test" laboratory procedure was used for all the flocculation studies.

4.2 Results and Discussion:

It can be seen from figures 4.1 and 4.2, that dilute latex suspensions such as 10 mg/L can be successfully destabilized by bringing down the pH to 3.0 by the addition of 6N HCl. Application of polymer A to the latex suspension formed flocs that were robust during the mixing stage of the flocculation tests. However, these flocs were not strong enough for adequate particle size distribution measurement with a Microtrac instrument.

Figure 4.1 shows the results of flocculation tests with polymer A at different latex suspension concentrations. As expected, the EM behavior of the polystyrene particles was markedly affected by the addition of small quantities of polymer A. Typical mobility results are shown in figure 4.2. Comparing figures 4.1 and 4.2, it can be concluded that the correspondence between residual turbidity and EM was excellent. Minimum residual turbidity corresponded to zero EM at different optimum dosages for different latex suspension concentrations. This conclusion has been confirmed using a constant latex concentration but with various polymer dosages, as can be seen in figure 4.3. The same conclusion has been reached by Gregory (31) for polystyrene latices, Yeh and Ghosh (76) for bentonite and by many other researchers (31,68).

Optimum polymer dosage in this report is defined as that dosage which produces maximum destabilization of the latex suspension (i.e., minimum residual turbidity). This

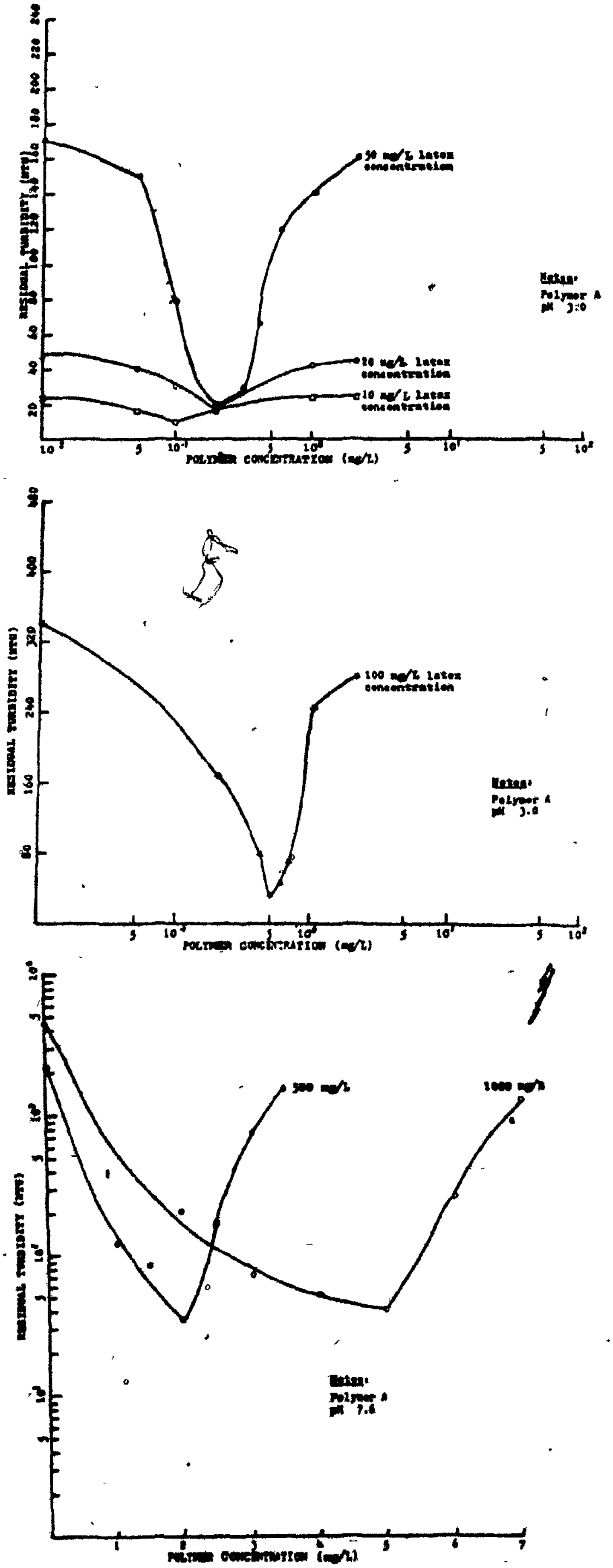


Figure 4.1 Relationship Between Polymer Concentration and Residual Turbidity for Different Latex Concentrations

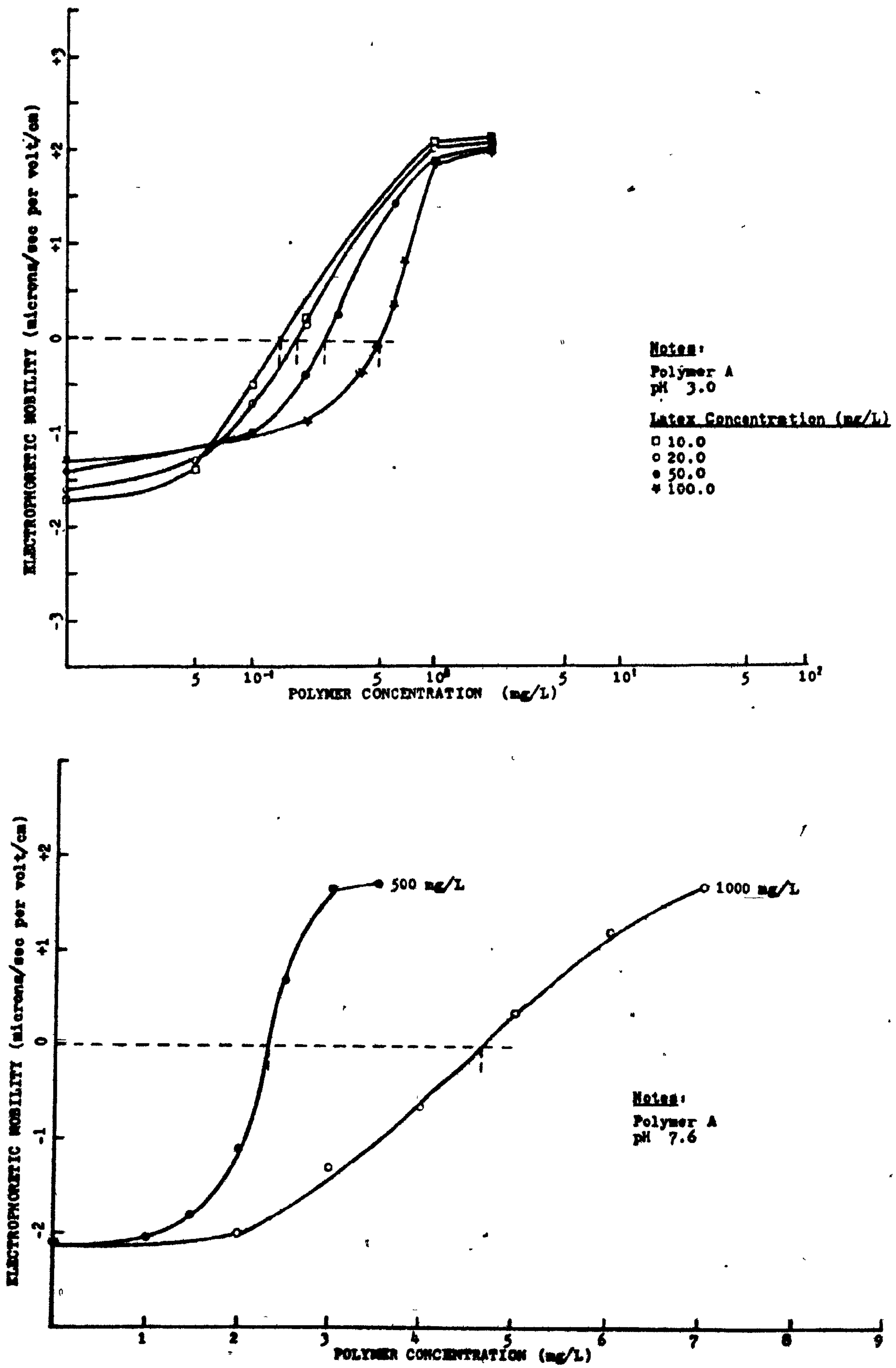
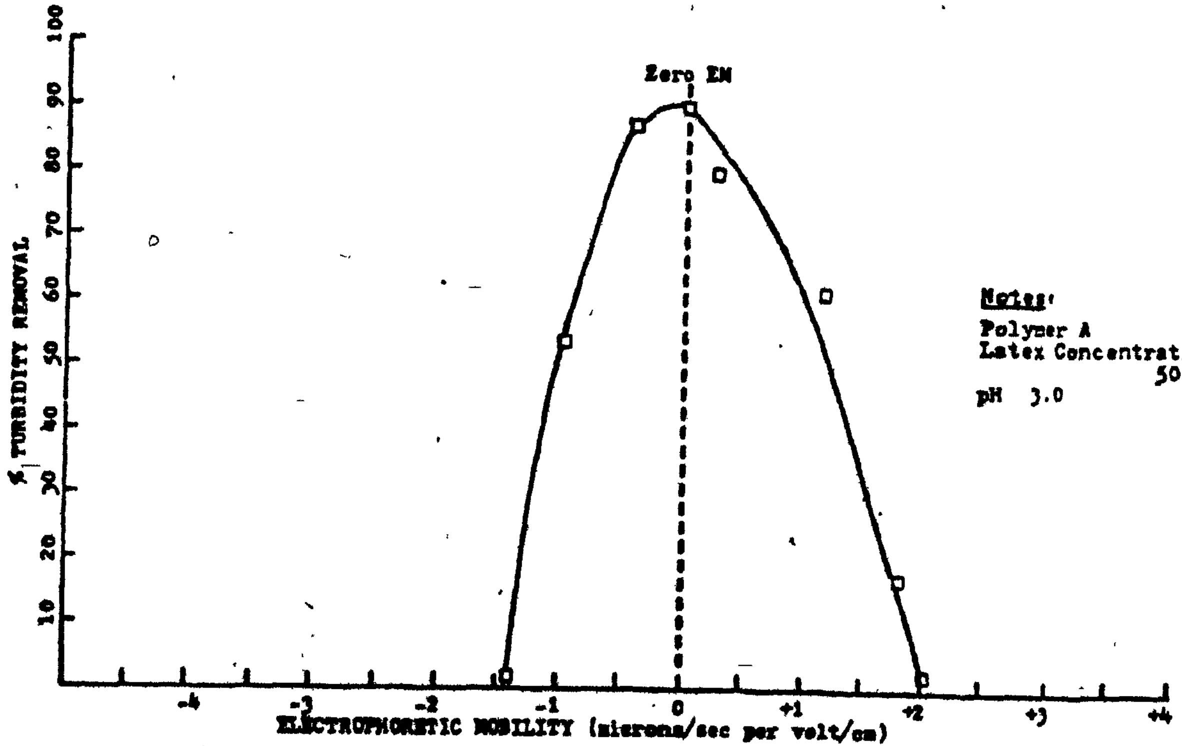


Figure 4.2 Relationship Between Polymer Concentration and Electrophoretic Mobility for Different Latex Concentrations

Table 4.1. Polymer Concentration at Zero EM for Different Latex Concentrations

Latex Conc. (mg/L)	Polymer Conc. (mg/L)
10	0.17
20	0.19
50	0.27
100	0.51
500	2.40
1000	4.80



Notes:
Polymer A
Latex Concentration: 50 mg/L
pH 3.0

Figure 4.3. Relationship Between %Turbidity Removal and Electrophoretic Mobility

phenomenon of minimum residual turbidity at zero EM has been explained by Black et al (6). They claim that the decrease in EM is caused by a reduction of the surface potential of the colloid, owing to the adsorption of polycation molecules, and an interaction of polymer molecules with the electrical double layer. As a result of these interactions, the gap between adjacent particles is reduced, and thus interparticle bridging by extended segments of the adsorbed polymer molecules is favored.

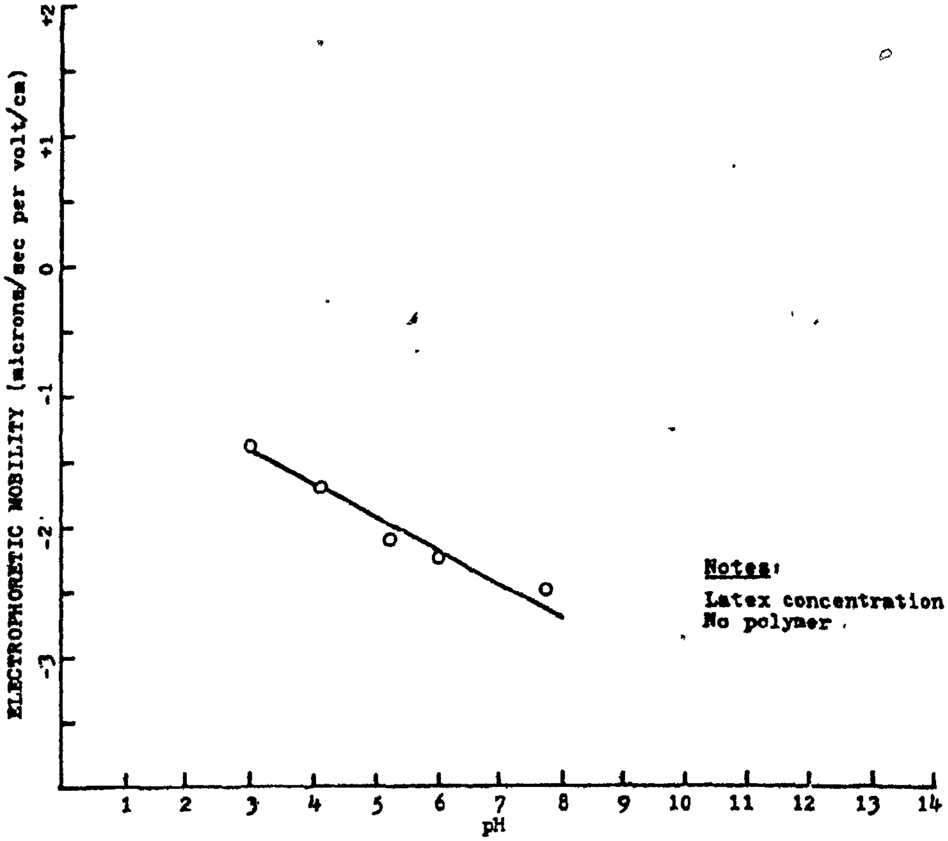
Figure 4.2 also show that there was a clear relationship between polymer dosage and EM. It shows that the EM reaches a plateau value - the part of the curve where there was little change in the EM - with an increase in polymer concentration beyond a certain value. Welday and Baumann (74) explain that this is because there is no more interaction between the particle previously coated with polymer, and the additional polymer. At this stage, comparing figures 4.1 and 4.2, it can be seen that there was no appreciable decrease in the residual turbidity when the EM curve was at the plateau. This was because restabilization was caused by overdosing. It was observed by electrophoresis studies that the restabilization was because of charge reversal. Thus it can be concluded that these high residual turbidity values denote that the systems have undergone destabilization and the aggregates formed were small enough not to settle out completely. These small flocs or aggregates formed were probably covered with too many polymer molecules, thereby possibly resulting in :

i) a decrease in the number of available bridge sites, hence

decreasing the chances of interparticle bridging (45).
ii) steric hinderance and electrostatic interactions between adsorbed polymer molecules, as suggested by Heller and Pugh (35).

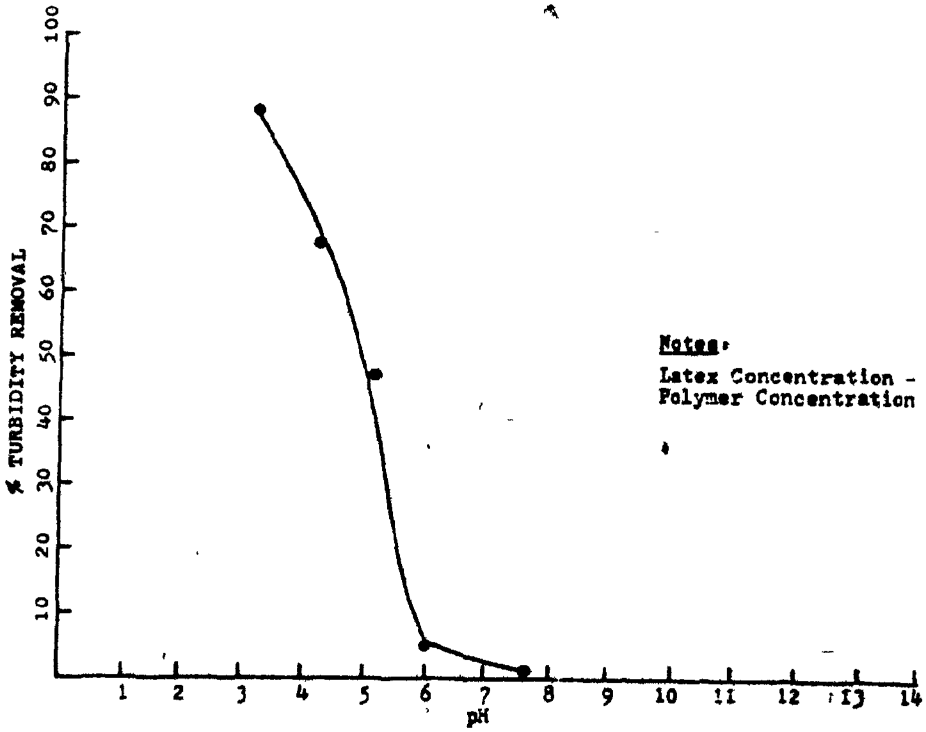
Figures 4.4 and 4.5 show the effect of pH on EM and turbidity removal. It was found that it is necessary to decrease the pH of the suspension for effective flocculation, especially for suspensions of concentration less than 100 mg/L. It should be noted that there was no change in the initial turbidity of the suspension with respect to change in pH. That is one of the advantages of the latex suspensions - it is stable over a wide range of pH and also has a high turbidity value in NTU even at very low concentrations (10 - 50 mg/L).

Figure 4.4 shows the effect of pH on EM. As the pH was decreased from 7.6 to 3.0, the EM was increased from -2.5 to -1.4 microns/sec per volt/cm. Figure 4.5 shows that the percentage turbidity removal at a pH of 3.2 was 88% whereas at a higher pH i.e., 7.6, the percentage turbidity removal was nearly zero. One of the reasons for this phenomenon may be that by decreasing the pH, the negative surface charge is reduced, as can be seen in figure 4.4. The EM becomes less negative as pH increases from pH 3.0 to pH 7.6 and the width of the optimum flocculation zone is increased. In other words, the same percentage turbidity removal may be obtained at a higher pH but at a very narrow optimum flocculation zone which is difficult to find and which has not been experimentally proven by the author. An alternative reason may be that the stable



Notes:
Latex concentration - 50 mg/L
No polymer

Figure 4.4. Relationship Between Electrophoretic Mobility and pH



Notes:
Latex Concentration - 50 mg/L
Polymer Concentration - 0.2 mg/L

Figure 4.5. Effect of pH on % Turbidity Removal

colloids might have been destabilized or rendered unstable without any change in the turbidity values of the sample by lowering the pH and thereby enabling flocculation of the suspended colloids. The effect of decrease in pH on the polymer itself is assumed to be minimum as the flocculation activity of the polymer at pH 7.6 for concentrated latex suspensions (say 500 mg/L) was as good as at pH 3.0.

Figure 4.6 shows that the kinetics of the polymer latex reaction were extremely rapid. The same conclusion has been reached by Black et al (6) for Kaolinite clays. An interesting point is that no appreciable change in percentage turbidity removal was observed with one minute rapid mixing time. But when the period of rapid mix was increased to 20 min, the percentage turbidity removal was increased to 90%. This implies that a certain amount of shear is required to allow bridging to occur. La Mer (45) has also pointed out that the initial attachment of the polymer to the surface of the particle by a few segments per molecule is very fast. Increasing the rapid mixing time favors rearrangement of the polymer molecules on the particle surface so that more segments per molecule are attached to the surface of the particle.

Figure 4.7 shows the relationship between optimum polymer dosage (mg/g) and initial latex concentration. It can be observed from figure 4.7 that, for optimum flocculation:

i) When the initial latex concentration was less than 50.0 mg/L, the optimum polymer/latex weight ratio increased continuously for lower latex concentrations.

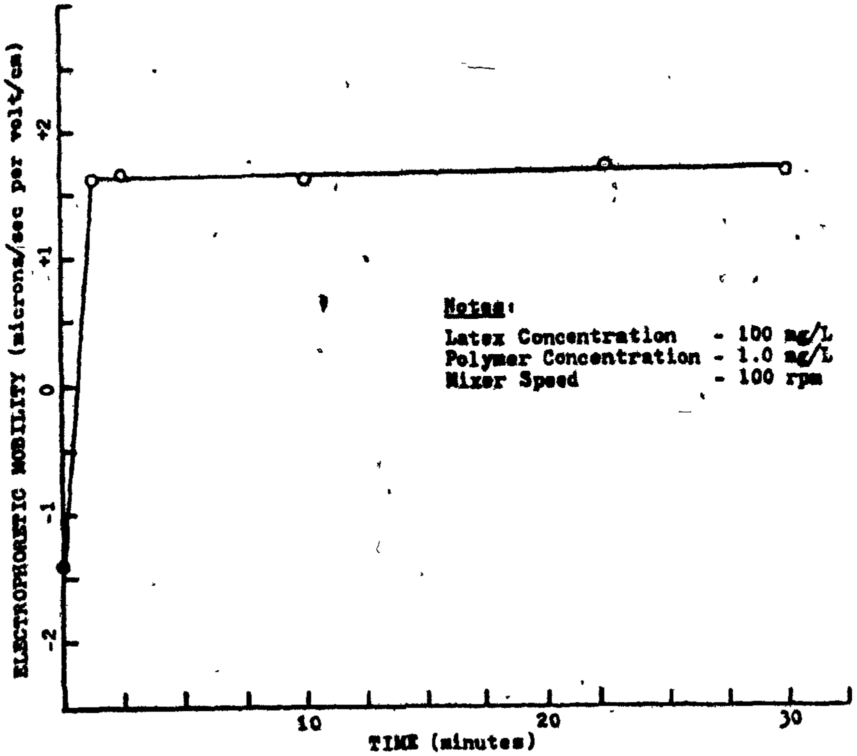


Figure 4.6. Adsorption Kinetics

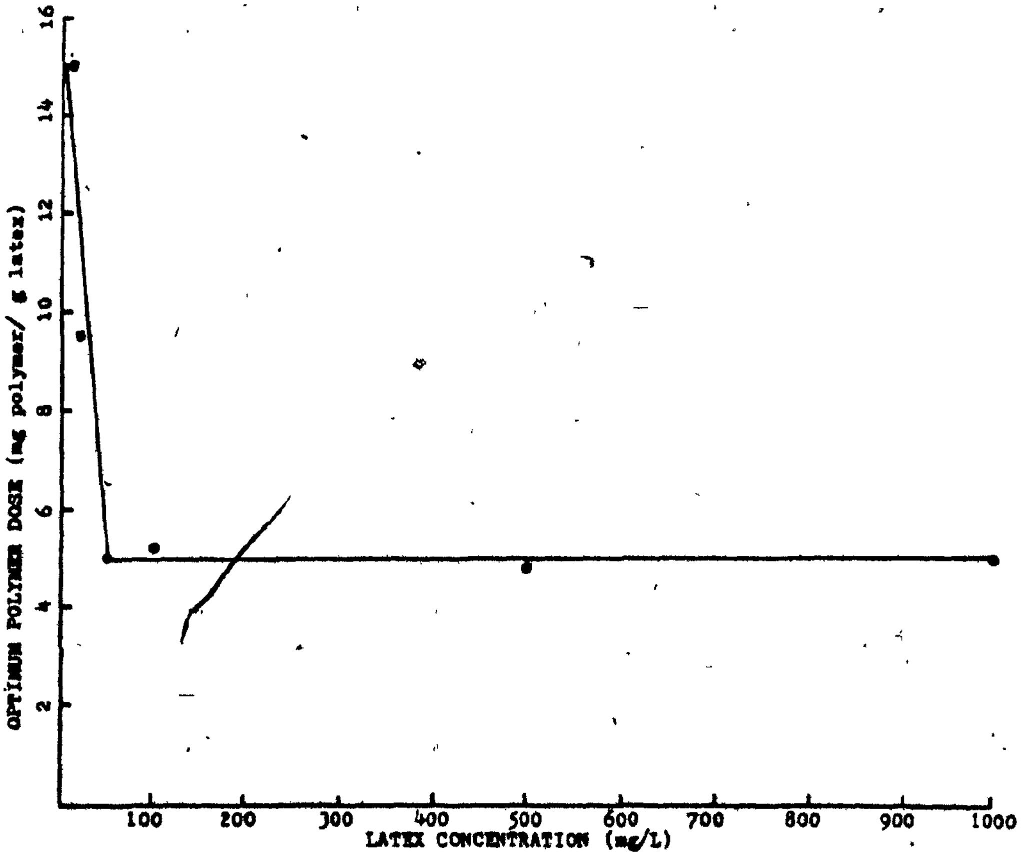


Figure 4.7. Relationship Between Latex Concentration and Optimum Polymer Dose (mg/g)

ii) When the initial latex concentration was greater than or equal to 50.0 mg/L, the polymer/latex weight ratio remained constant at 5 mg/g.

The phenomenon of having different polymer/latex weight ratios is thought to be purely kinetic. Supposing if interparticle bridging is the mechanism involved in the flocculation of latex suspension, then logically one would expect concentrated latex suspensions to adsorb less polymer per unit weight of latex than when compared with dilute latex suspensions. This is simply because larger frequency of interparticle collisions occur in concentrated latex suspension and consequently there is a greater probability of interparticle bridging. When interparticle bridging occurs, one polymer molecule must occupy at least one adsorption site on each particle surface that is being bridged (6). In dilute suspensions, where the probability of interparticle collisions is low, perhaps one polymer molecule is attached to each adsorption site on the latex particle surface, (each particle likely has more than one adsorption site) giving rise to a larger weight ratio of polymer to latex as can be seen in figure 4.7.

However in dilute suspensions, if the speed of the rapid mix is increased, it would probably give the same polymer/latex ratio (5mg/g). The maximum speed of the jar test apparatus used in the laboratory is 100 rpm. No further experiments could be done at higher speeds to check if the above assumed phenomenon occurs or not.

It can be seen from figure 4.8 that the lower the initial latex concentration, the smaller the maximum degree of destabilization or the smaller the percentage turbidity removed at optimum polymer dose.

4.4 Conclusions:

i) At all latex concentrations, the EM of the particle was reversed by the polymer and approached a limiting positive value for excessive polymer.

ii) The amount of polymer in mg/L required to reverse the sign of the EM was dependent upon the initial latex concentration.

iii) The polymer/latex weight ratio was 5.0 mg/g when the initial latex concentration was greater than or equal to 50 mg/L. But when the initial latex concentration was less than 50 mg/L, the polymer/latex weight ratio increased continuously.

iv) For all the latex concentrations investigated, optimum destabilization occurred when the EM was around zero.

v) Polymer/latex reactions were extremely rapid and a certain amount of shear is required for bridging to occur.

vi) A decrease in pH increased the width of the optimum flocculation zone, and decreased the negative surface charge density.

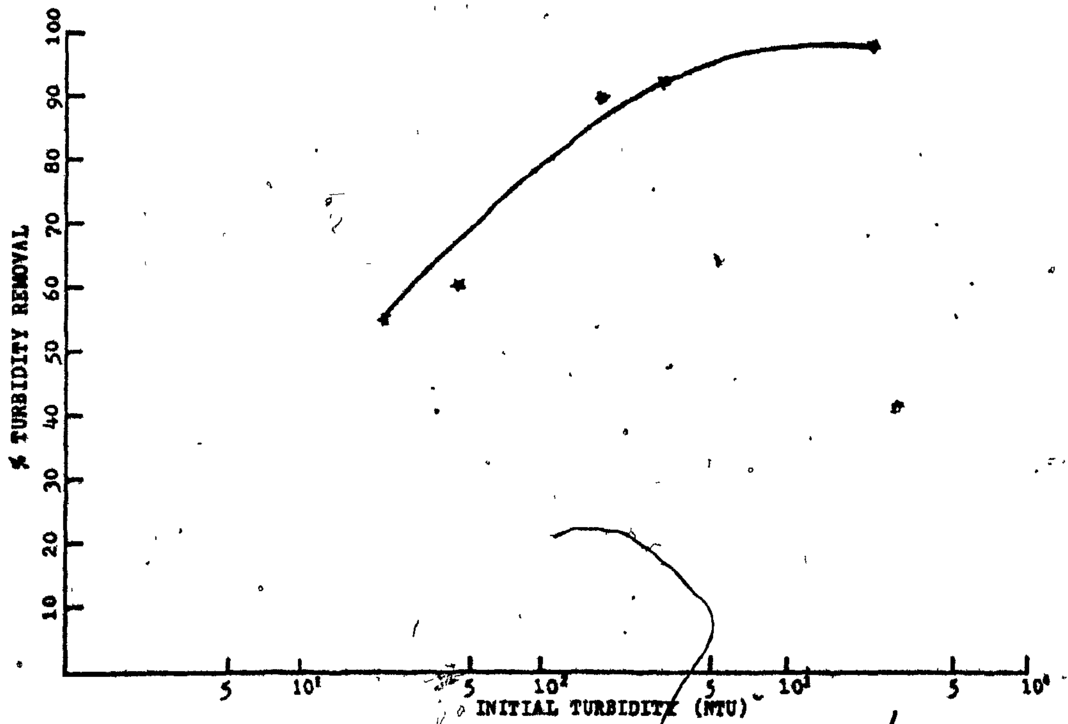


Figure 4.8. Relationship Between Turbidity Removal and Initial Turbidity at Optimum Polymer Dosages

CHAPTER 5

Detection of Low Concentrations of Polymers

5.1 Introduction:

In general, there is no satisfactory method in determining very low residual concentrations of polyelectrolytes in treated waters except the one proposed by Wang and Shuster (72). In this chapter, the various methods tried by the author in determining low polyelectrolyte concentrations will be discussed. In addition, the author's experiments to determine low concentrations of cationic polymers by relating the polymer dosage to the flocculation activity of latex suspensions will be examined. A latex suspension has been used because it has following features:

i) It is highly spherical in shape and the particle size distribution can be accurately controlled within a a very narrow range as can be seen in figure 5.1

ii) It is stable over a wide range of pH.

iii) The suspension is available in both anionic and cationic forms.

iv) It has good aggregation properties and charge development.

v) Turbidity in NTU even at low suspension concentrations is sufficiently high to permit accurate measurements.

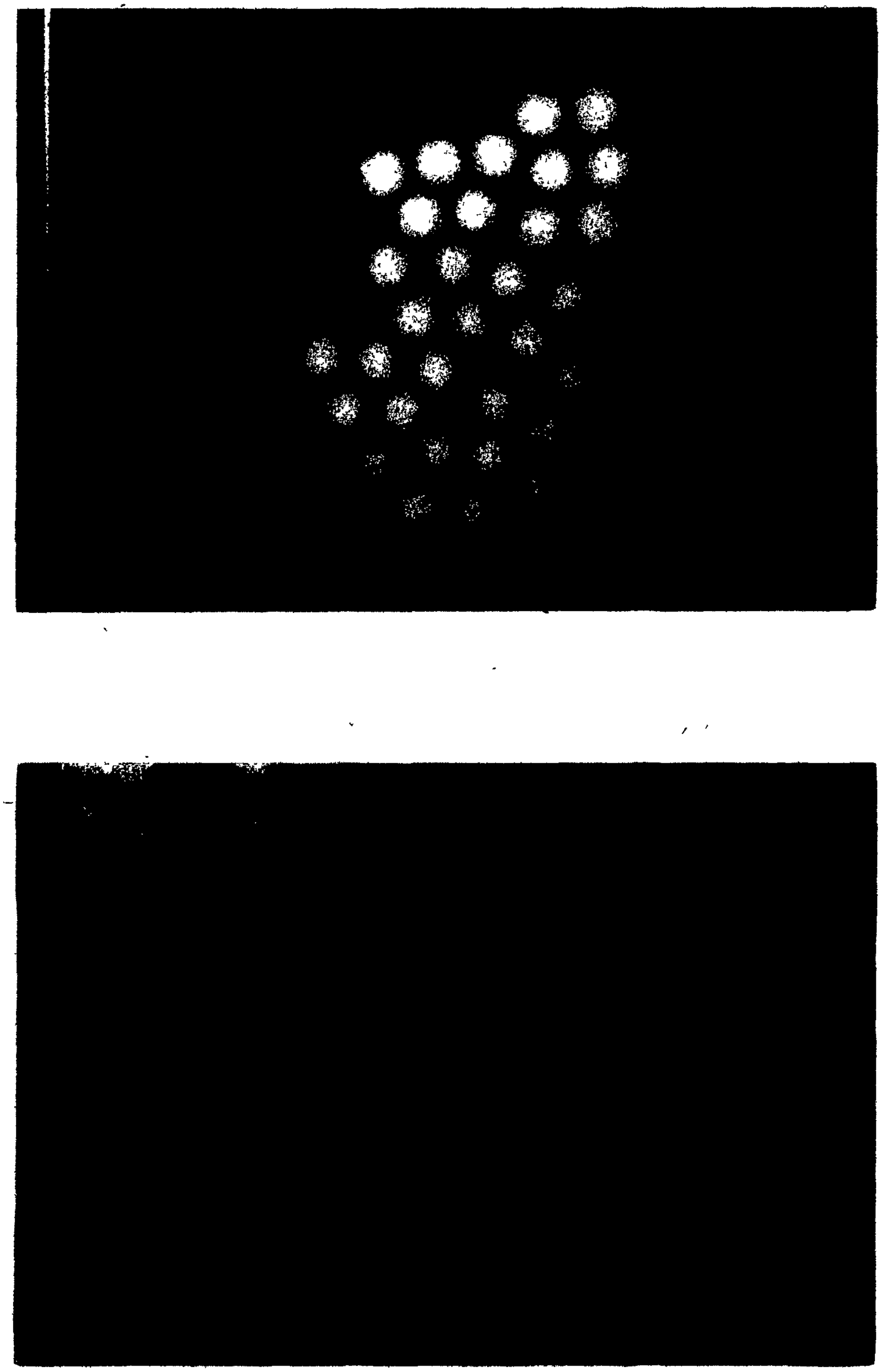


Figure 5.1. Particle Size Distribution of Unreacted Polystyrene Latex Suspension

5.2 Detection of Low Concentrations of Cationic Polymer by Various Methods:

5.2.1 Flocculation Studies with Latex Suspensions:

It was noticed in Chapter 4 that there existed a definite relationship between polymer concentration and various parameters such as initial latex concentration, EM, residual turbidity etc. Using these relationships, the author was able to detect polymer concentrations as low as 0.1 mg/L, which is tenfold less than the minimum detectable level possible by the colloid titration method. The procedure for preparation of calibration curves and detection of unknown polymer concentrations in a sample was explained in section 3.13.

The use of this method for determining polymer concentrations has the following important implications:

i) It is very sensitive relative to other methods particularly for polymer concentrations less than 2.0 mg/L.

ii) It provides insight into the behavior of the polymer with respect to its flocculation activity.

iii) It is applicable to unmodified polymers (for example by C^{14} labelling) and to treated and process waters.

iv) There are two measurable appropriate parameters:- residual turbidity and EM.

v) The results obtained by this method show good correlation with results obtained by the colloid titration method (above 1 mg/L).

explained in section 3.13.

On the other hand, the disadvantage of this type of test is that relatively large quantities of samples are required (12.0 L, typically), and the procedure is also time consuming. Therefore, if the available sample volume is smaller and/or if the unknown polymer concentration needs to be determined more rapidly, the author has devised an alternate method for detection of low polymer concentrations. As discussed before in section 4.2, the kinetics of polymer latex reactions are extremely rapid. Thus instead of performing the entire flocculation study, i.e., rapid mix, slow mix, settling etc., the polymer concentration can be determined more rapidly by obtaining the variations in EM with respect to latex concentration. The procedure for the alternate method was explained in section 3.13.4

The above methods are especially suitable for detection of polymer concentrations less than 2.0 mg/L. The reproducibility of the results is very good and the accuracy is about ±10% for concentrations up to 0.2 mg/L and ±25% for concentrations less than 0.2 mg/L.

5.2.2 COD and TOC:

Chemical Oxygen Demand (COD) is one of the methods that can be used for the detection of cationic polymers. Tenney (67) has used this method to detect anionic and nonionic polymers and was able to detect from 25 to 50 mg/L. The author has extended this method to high MW cationic polymers. The COD of the polymer was measured by the oxidation method with potassium dichromate, and the procedure was the same as described in Standard Methods (1). The sample used was Polymer A and dilutions were prepared from 1% stock solution with distilled water. The sample volume used was 50 mL.

The results obtained are shown in Figure 5.2. The reproducibility of the results was good and the accuracy was ±10%. As can be seen from the graph, the lowest cationic polymer that can be detected was 2.5 mg/L. The relationship between COD and polymer concentration was linear with a coefficient of regression of 0.98. (see figure 5.2). It should be noted that the disadvantage of this method with all solvents but distilled water is that the COD of the solvent is likely to mask the COD of any residual polymer.

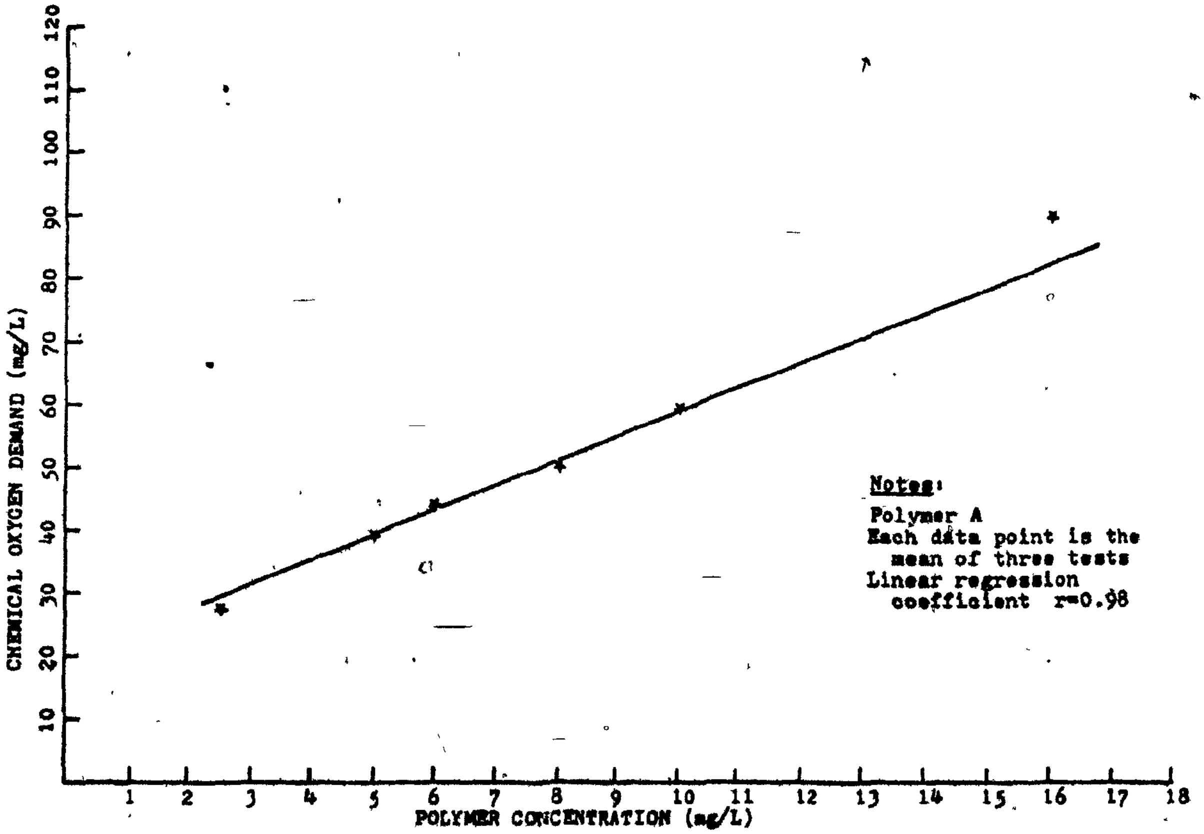
As discussed previously, the colloid titration method measures the overall charge on the polymer molecule. As the polymer breaks down, the charge on the polymer decreases. So instead of using the titration method COD or TOC can be used to detect the polymer concentration as these methods do not take charge into consideration. But the disadvantages of using COD or TOC are:

i) A blank is always needed.

ii) They cannot differentiate the charge on the polymers.

iii) These methods cannot distinguish between monomers and polymers.

iv) Interferences from other organics, can cause background values to be significantly higher than the polymer concentration to be measured.



Notes:
Polymer A
Each data point is the
mean of three tests
Linear regression
coefficient r=0.98

Figure 5.2. Relationship Between Polymer Concentration and C.O.D

Another method for measuring the organic matter present in water is the Total Organic Carbon (TOC) test, which is especially applicable to small concentrations of soluble organic matter. The test is performed by injecting a known quantity of sample into a high temperature furnace. The organic carbon is oxidized to carbon dioxide in the presence of a catalyst. The carbon dioxide that is produced is quantatively measured by means of an infrared analyzer. Figure 5.3 shows the results obtained by TOC for polymer A. As the polymer used was wetted with ethanol initially, the TOC of ethanol has to be determined and subtracted to calculate the real organic carbon content in the polymer sample. The minimum concentration that could be detected by this method was approximately 10.0 mg/L, using the particular TOC apparatus available.

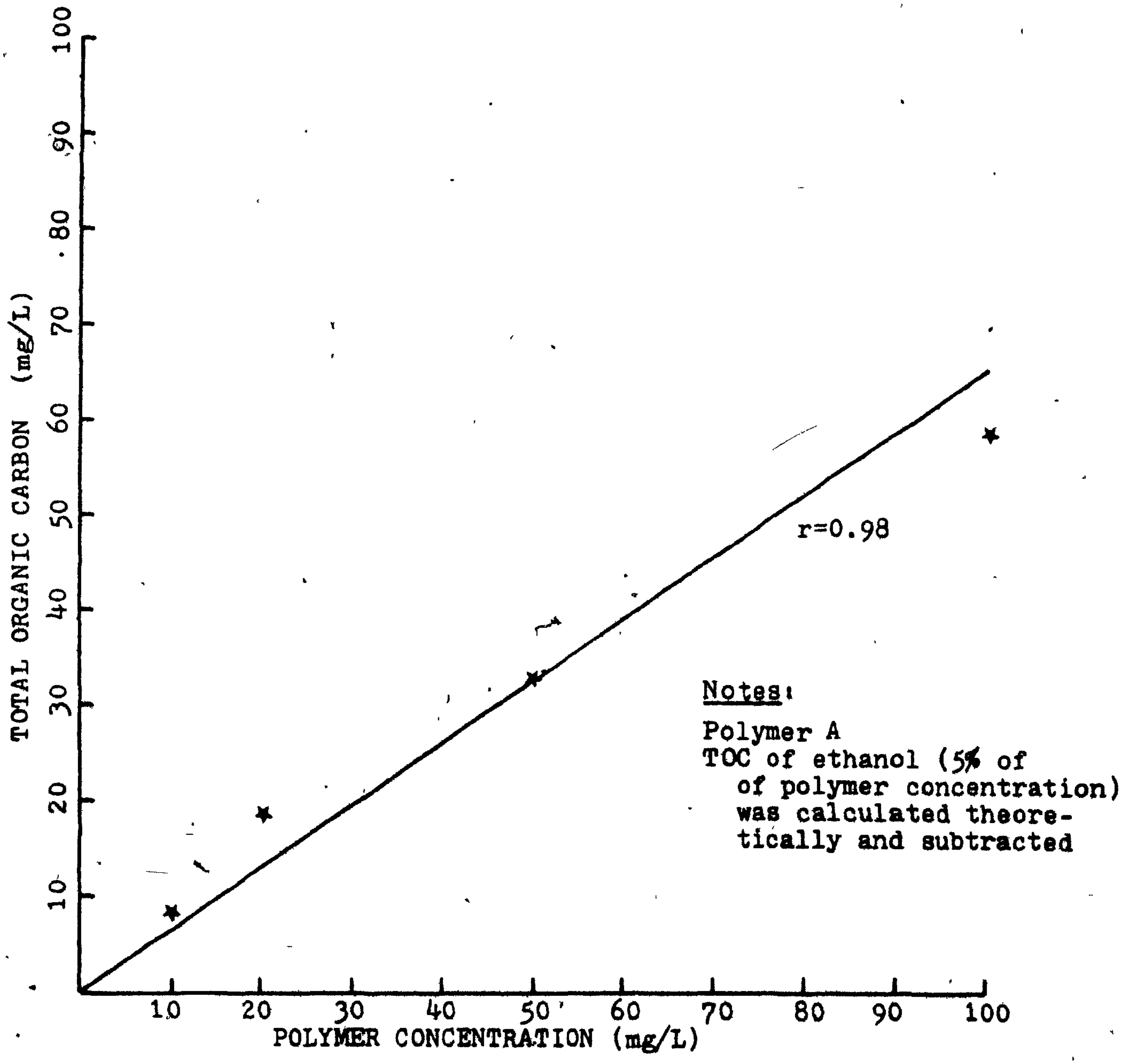


Figure 5.3. Relationship Between Polymer Concentration and T.O.C

5.2.3 Concentration:

For determining trace amounts of contaminants present in aqueous solutions, a typical first step is to concentrate the trace amounts up to a point where they can be determined by the reliable method available. Jolley (38) reports that concentration methods can be divided into two basic categories:

i) Concentration - those processes in which water is removed and the dissolved substances are left behind. For example, vacuum distillation.

ii) Isolation - those processes in which organic substances are removed from the water. For example, ion exchange.

5.2.3.1 Vacuum Distillation:

This is also called an evaporation process, in which the liquid sample is boiled at reduced pressure in a rotatory evaporator near ambient temperature. A set-up as described in the Manufacturer's Manual (79) was used and can be seen in Figure 5.4.

For all the experiments, 500 mL sample volumes of known polymer concentrations were evaporated to approximately 80 to 100 mL. The process used to concentrate the samples was a standard procedure. To determine the polymer concentration in the samples, the colloid titration method (72) was used.

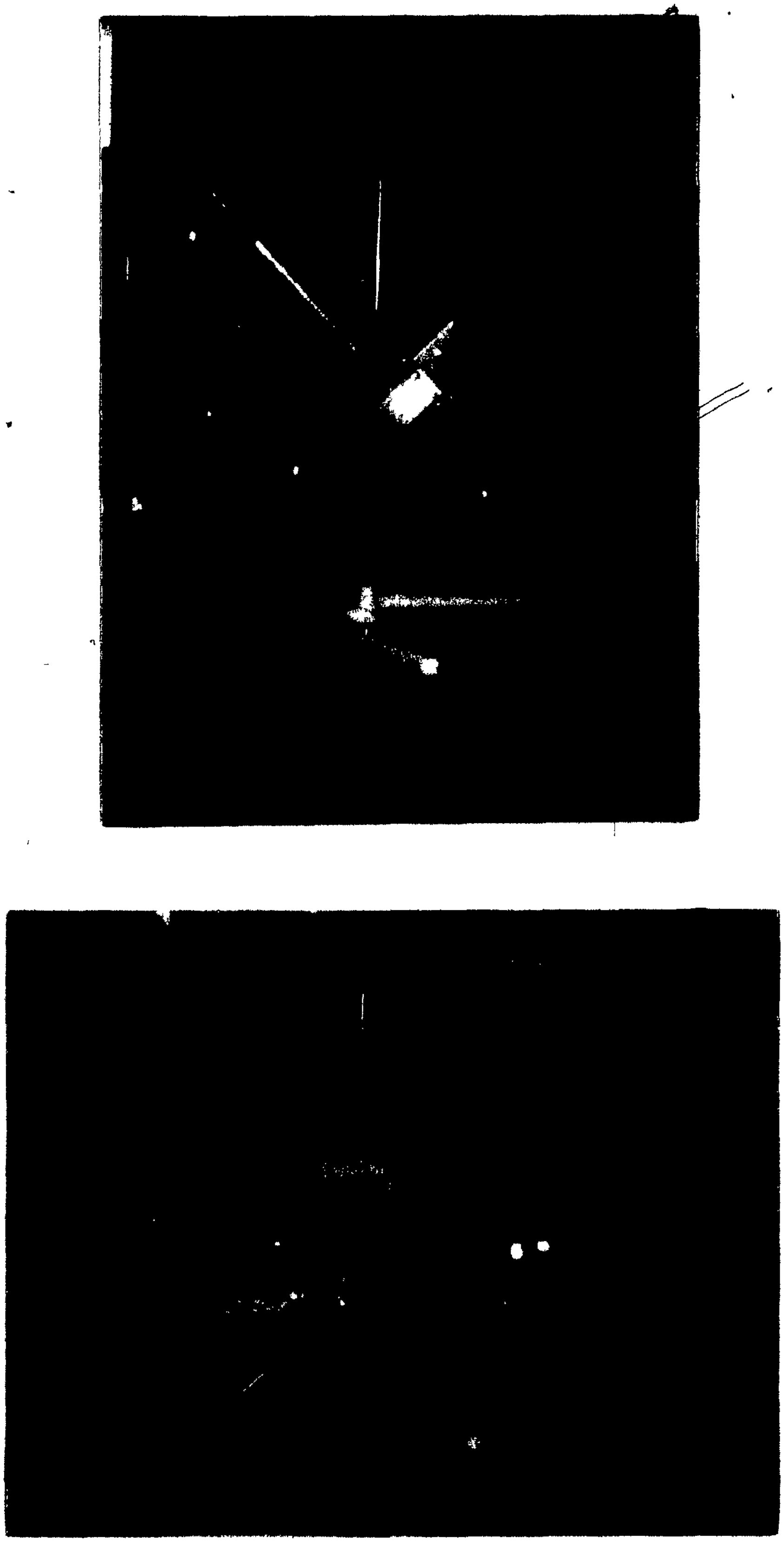


Figure 5.4. Set-up for Vacuum Distillation Apparatus

The results are shown in table 5.1.

It can be seen from the results that for the polymer samples of concentration greater than or equal to 5 mg/L, the samples can be successfully concentrated and the percentage recovery of polymer by evaporating the samples at 35°C was 91-95%, whereas for 2 mg/L the % recovery was 35-44%. When the initial polymer concentration of the samples was less than 2.0 mg/L, the % recovery was zero. The results also show that at elevated temperatures, the % recovery of polymer in the evaporating flask decreased. It should be noted that no polymer was found in the receiving flask indicating that all the dissolved substances were concentrated in the evaporating flask. This implies that something was happening to the polymer in the evaporating flask; it was possibly breaking down into monomers or losing its charge because of the elevated temperature. This prompted further experiments to determine the effect of temperature on dilute and concentrated polymer solutions. The effect of temperature on polymer solutions will be discussed later in Chapter 7.

Previous researchers (19,29) have used vacuum distillation for concentrating very dilute polymer samples, which indicates that their results do not take the state of the polymer into consideration, and all the monomers were probably also taken as polyelectrolytes.

Legend of Table 5.1

A = Temperature (°C)
B = Volume of polymer sample taken (mL)
C = Volume of sample left in evaporating flask (mL)
D = Volume of sample left is receiving flask (mL)
E = Initial Theoretical Polymer Concentration (mg/L)
F = Final measured polymer concentration in evaporating flask (mg/L)
G = Theoretical final polymer concentration (mg/L)
H = % recovery

Table 5.1: Concentrating Dilute Polymer Solutions by Vacuum Distillation

No.	A	B	C	D	E	F	G	H
1	60	500.0	160.0	330.0	5.0	10.8	15.6	69.0
2	60	500.0	110.0	385.0	5.0	14.1	22.7	62.0
3	50	500.0	80.0	413.0	5.0	21.5	31.1	69.0
4	50	500.0	105.0	390.0	5.0	17.9	23.8	75.0
5	35	500.0	150.0	345.0	5.0	15.1	16.6	91.0
6	35	500.0	160.0	332.0	5.0	14.8	15.6	95.0
7	60	500.0	140.0	353.0	2.0	0.0	7.1	0.0
8	60	500.0	135.0	361.0	2.0	0.0	7.4	0.0
9	50	500.0	80.0	410.0	2.0	0.0	12.5	0.0
10	50	500.0	100.0	391.0	2.0	0.0	10.0	0.0
11	35	500.0	67.0	430.0	2.0	5.2	14.9	35.0
12	35	500.0	82.0	410.0	2.0	5.4	12.2	44.0
13	60	500.0	100.0	385.0	1.0	0.0	5.0	0.0
14	60	500.0	160.0	330.0	1.0	0.0	3.1	0.0
15	50	500.0	80.0	316.0	1.0	0.0	6.3	0.0
16	50	500.0	120.0	375.0	1.0	0.0	4.2	0.0
17	35	500.0	150.0	340.0	1.0	0.0	3.3	0.0
18	35	500.0	160.0	330.0	1.0	0.0	3.1	0.0

5.2.3.2 Ion Exchange:

An attempt was made to concentrate polymer in solution by the ion exchange method. Ion exchange is a process in which ions in the solution are exchanged reversibly by ions contained in an insoluble resinous material.

1000 mL samples of 10 mg/L polymer concentration were poured into different ion-exchange columns and collected at a rate of 5 to 7 mL/min. The polymer concentration was detected by the colloid titration method. It was found that the cationic polymer was successfully exchanged onto the cationic exchanger resin, but the problem was then to extract the polymer back from the resin. Different solvents were used to elute the polymer from the resin but they were unsuccessful. As the resin does not have any nitrogeneous matter, TKN measurements was attempted for the entire sample (resin + exchanged polymer). However, as the concentration of organics in the resin were enormous, it was not possible to accurately find the nitrogen content by the TKN method.

5.2.4 Filtration:

An attempt was made to concentrate the polymer on 0.45 micron Millipore filters. Known concentrations of polymer solutions were vacuum filtered through 0.45 micron Millipore filter paper (Cat No HAWP 047 00). The non-filtrable matter on the filter paper, was extracted by immersing the filter paper in 0.1M NaCl and stirring it for half an hour. The polymer concentration was detected by using the colloid titration method. The results obtained are tabulated in table 5.2.

It can be seen from the results that when the initial polymer concentration of the solution was 5 mg/L or greater, the polymer was concentrated on the filter paper, even though it was in a dissolved state. However, for solutions whose polymer concentration was less than or equal to 2.0 mg/L, the polymer solution passed through the filter and appeared in the filtrate (the original polymer concentration was detected in the filtered solution). The reason for this type of behavior was probably that when the polymer concentration was equal to or greater than 5 mg/L, the polymer was retained on the filter paper because the aggregated polymer chains were larger than the pore size of the filter (0.45 microns). However, in the case of solutions with less than 2.0 mg/L polymer concentration, the polymer chains are dispersed. This decreased the chances of aggregation by entanglement during the filtration process. It is precisely this low range of polymer concentration which is not retained on the filter paper that is of greatest interest. Therefore, this method cannot be used to concentrate the polymer solution.

Legend of Table 5.2

A1 = Volume of polymer sample filtered (mL)

B1 = Initial theoretical polymer concentration filtered (mg/L)

C1 = Polymer concentration in filtrate (mg/L)

D1 = Final measured polymer concentration recovered from the filter paper in a 50.0 mL 0.1M NaCl solution (mg/L)

E1 = Theoretical final polymer concentration (mg/L)

F1 = % recovery

Table 5.2 Results of Filtration Tests

No.	A1	B1	C1	D1	E1	F1
1	200.0	10.0	0.0	15.8	20.0	79.0
2	200.0	10.0	0.0	16.6	20.0	83.0
3	200.0	5.0	0.0	18.4	20.0	92.0
4	200.0	5.0	0.0	17.6	20.0	88.0
5	200.0	2.0	2.0	0.0	8.0	0.0
6	200.0	2.0	2.0	0.0	8.0	0.0
7	200.0	1.0	1.0	0.0	4.0	0.0
8	200.0	1.0	1.0	0.0	4.0	0.0

5.2.4 Acid/Bleach Precipitation Method:

This method involves the quantitative precipitation from solution of polyacrylamide copolymers by chlorine evolved from the reaction of sodium hypochlorite with glacial acetic acid.

Figure 5.5 shows the results obtained for Polymer A by this method. It shows that the difference in turbidity caused over a wide range of polymer concentrations (0.1 to 100 mg/L) was very little (0.6 - 1.6 NTU). The interpretation of unknown polymer concentrations by this method would thus be very difficult because of the small change in turbidity with respect to polymer concentration.

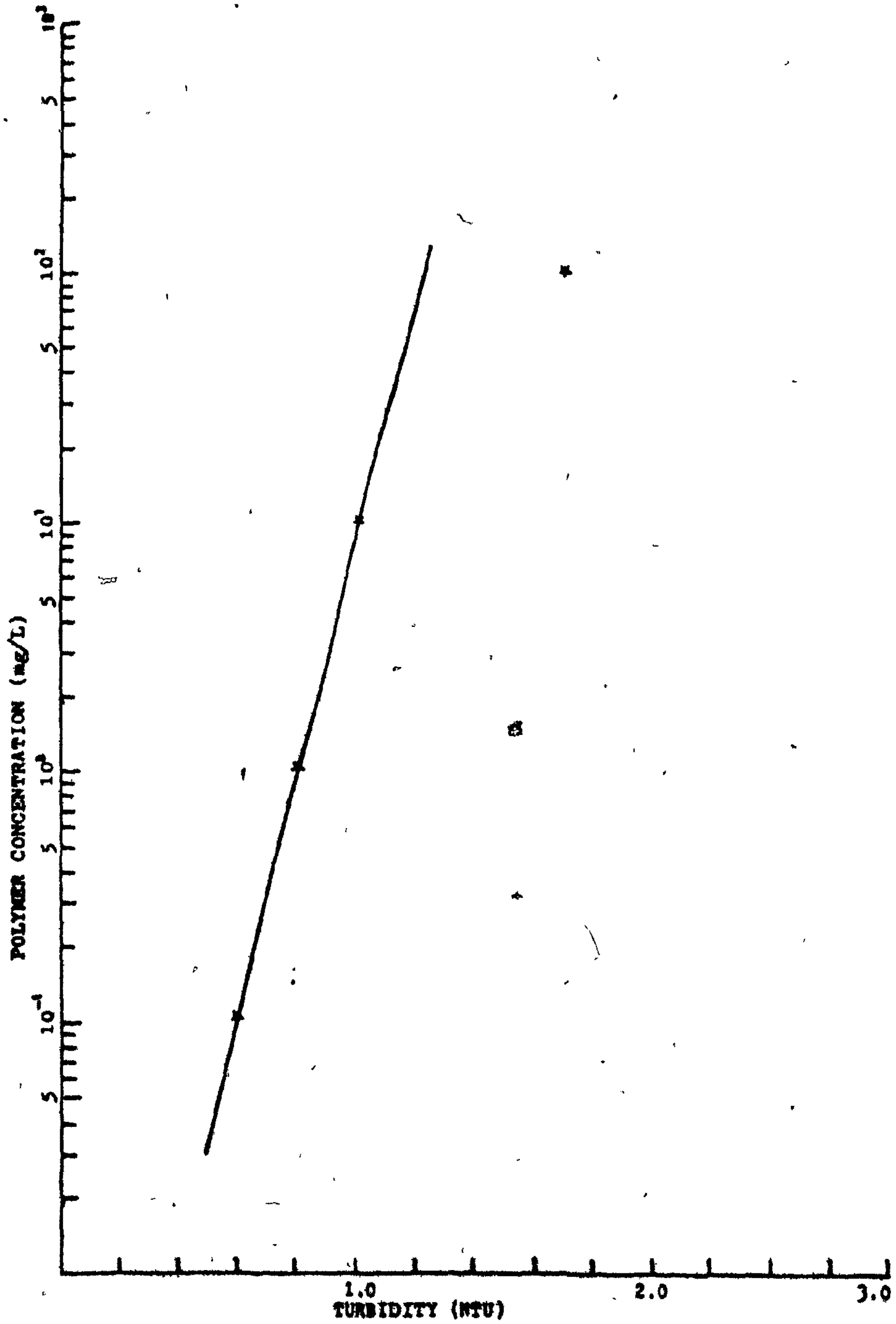


Figure 5.5. Calibration Curve for Polymer A using Acid/Bleach Precipitation Method

5.2.5 Conclusions:

The experiments show that flocculation studies with polystyrene latex suspensions is an effective method for determination of unknown polymer concentrations in the range of 0.1 to 2 mg/L with reasonable accuracy. The reproducibility of results has been attributed mainly to the fact that an ideal suspension with very narrow particle size distribution was obtained using polystyrene latices.

Regarding other methods for measurement of dilute polymer solutions:-

i) Concentrating dilute polymer solutions by vacuum distillation leads to the breakdown of the polymer.

ii) Filtration of high molecular weight polymers through 0.45 micron Millipore filter paper results in a high percentage loss of polymer at concentrations less than 2.0 mg/L due to passage of polymer through the filter.

iii) A turbidimetric method using acid/bleach precipitation was insensitive over the range of interest (less than 100 mg/L polymer concentration).

Thus only the method involving flocculation of a polystyrene suspension is a viable alternative to the colloid titration method for measuring low concentrations (i.e., less than 10 mg/L) of polyelectrolytes in process or treated waters.

CHAPTER 6

Effects of Short Term Storage on Polymer Solutions

6.1 Introduction:

In this chapter, the effects of storage on various dilutions of polymer A will be studied. Different dilutions of polymer A were prepared from the stock solution (which was prepared 8 hours before the dilutions) in a 1.0 liter calibrated flask. The samples were stored at a temperature of 5°C. At every 24 hours aliquots of these dilutions were taken and titrated after bringing the sample temperature to room temperature (28-32 °C). Another set of experiments was also conducted by storing or aging the polymer samples at 20°C. The colloid titration method developed by Wang and Shuster (72) was used as a basis for determining the polymer concentration to follow the effect of storage on the polymer solutions. In this thesis the words aging and storage will be used interchangeably.

6.2 Results and Discussion:

Figures 6.1 and 6.2 show graphs of storage versus remaining polymer concentration. Each curve represents a different dilution of Polymer A. It can be seen from figures 6.1 and 6.2 that as the solutions were stored, the effective polymer concentration decreased for diluted polymer solutions (5mg/L and 10mg/L) and increased for concentrated samples (100 mg/L and 1000 mg/L). The final effective concentration after 5 days of storage at 5°C decreased by about 10% for 10 mg/L original polymer dilution and 30% for 5 mg/L. On the other hand, there was a 15% increase in the polymer concentration after 5 days of storage for 100 and 1000 mg/L dilutions stored at 5°C. When the samples were stored at 20°C, there was a 14% and 36% decrease in polymer concentration for 5mg/L and 10 mg/L respectively. In the case of concentrated samples stored at 20°C, the results obtained were the same as that for concentrated samples stored at 5°C

It can also be seen that there was a rapid decrease or increase of polymer concentration in the first two days and that subsequently the polymer concentration remained virtually steady. The changes in effective concentration of polymer with respect to storage can possibly be explained by the mechanism of entanglement formation during original polymer growth. The notion of "entanglement" can be better understood from figure 7.4. According to Chinal and Schneider (14) the chain entanglements are a function of size and the number of molecules in a solution, hence the molecular weight and concentration of the dissolved polymer are important

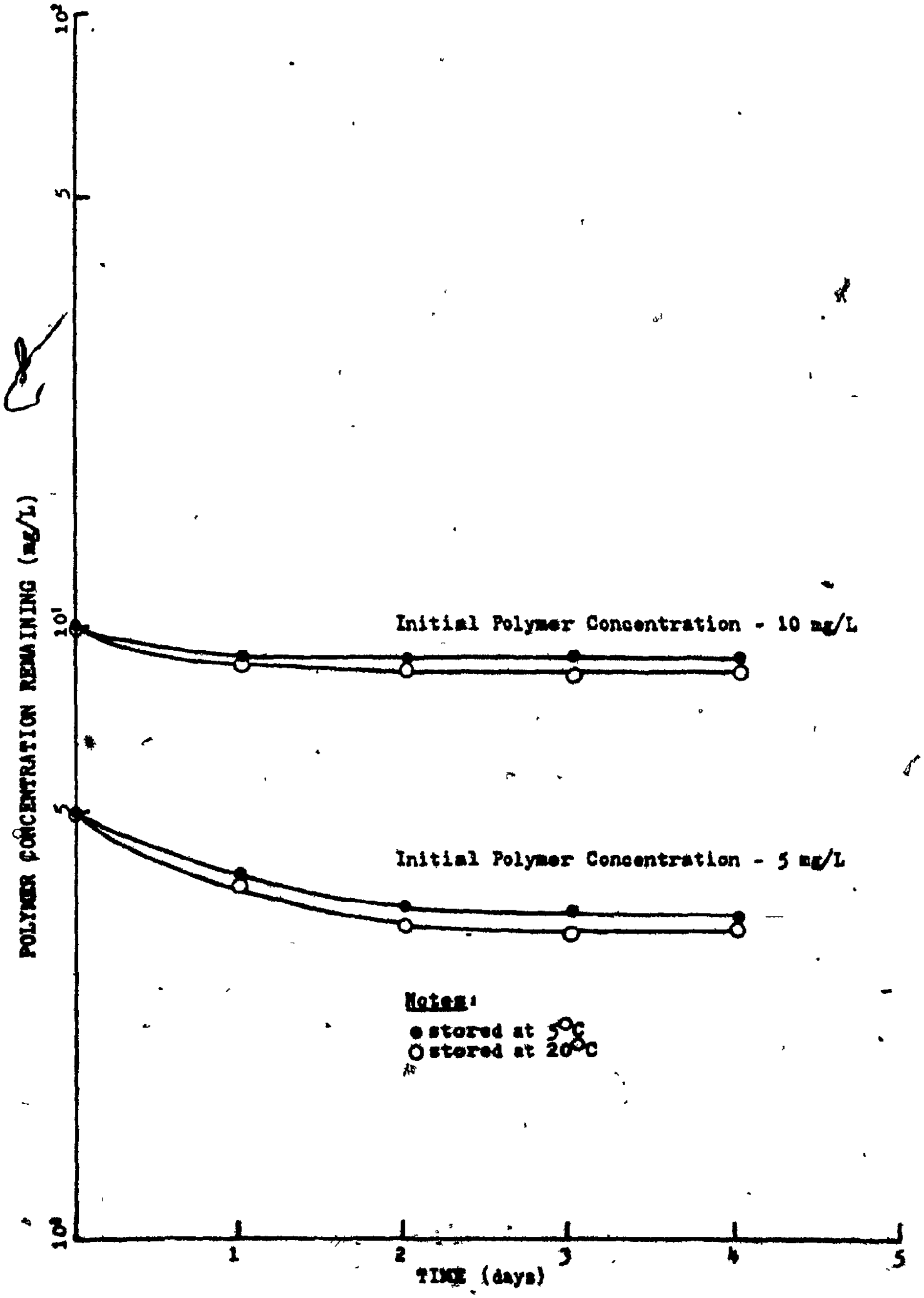
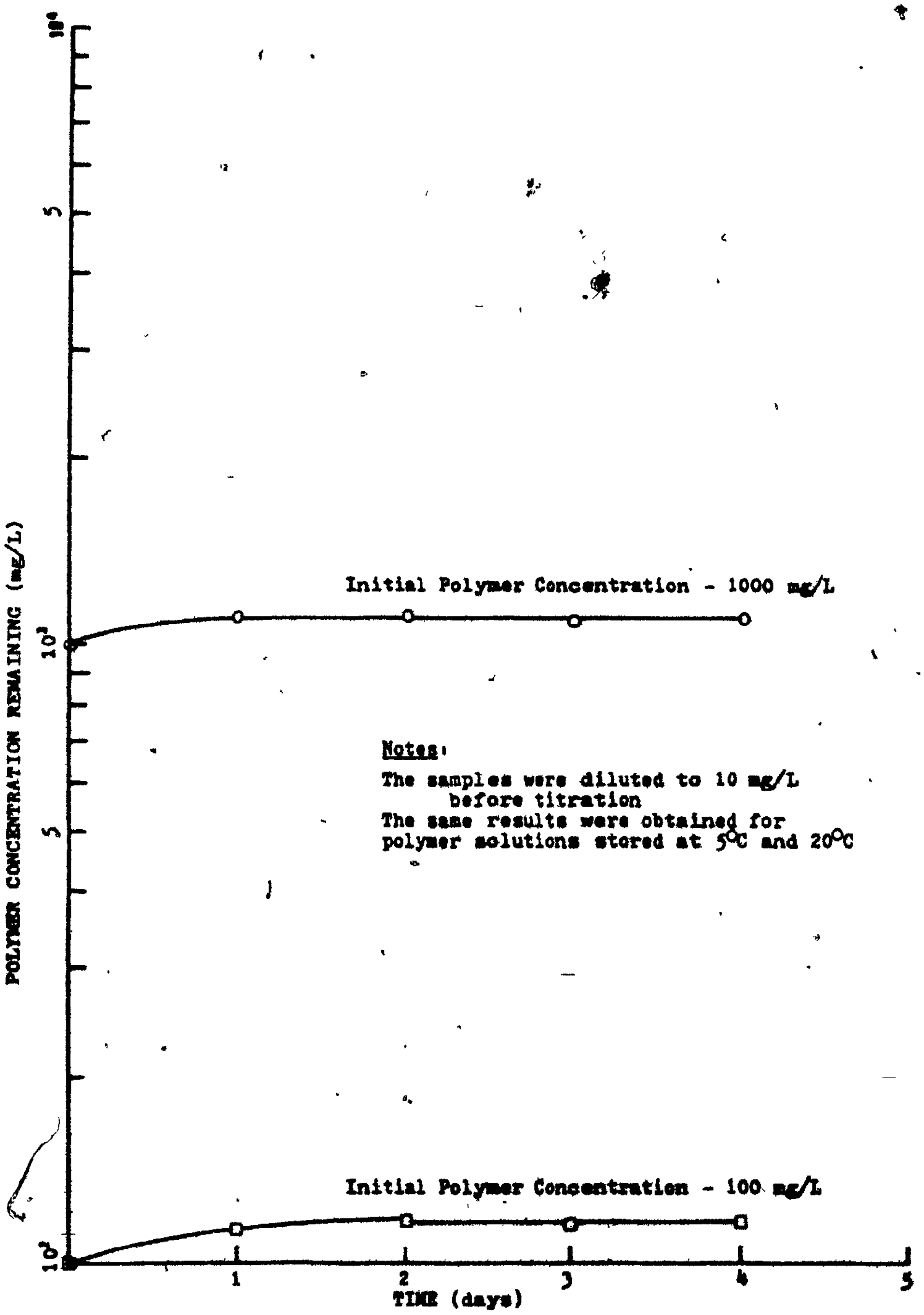


Figure 6.1. Effects of Storage on Dilute Polymer Solutions



<u>Notes</u>:
The samples were diluted to 10 mg/L before titration
The same results were obtained for polymer solutions stored at 5°C and 20°C

Figure 6.2. Effects of Storage on Concentrated Polymer Solutions

factors. They also stated that as the molecular weight increases, there is an increasing probability of a large number of entanglements for the length of the chain. In addition, as the concentration increases, the number of chains in a given volume increases and the chances become greater for molecules to become entangled in loops of other molecules. The degree of entanglement in the concentrated solution is larger than for dilute solutions. This statement has been demonstrated by passing different dilutions of polymer through 0.45 micron Millipore filter papers. As can be seen from the results in table 5.2, the polymer can be concentrated on the filter paper for polymer dilutions greater than or equal to 5 mg/L, whereas when the concentration was less than 2 mg/L, it passed through the filter paper. This was thought to be mainly because of the aggregation of loops as the degree of entanglement became larger in concentrated samples.

Originally, during the preparation of dilutions of stock solution, water molecules diffuse into the polymer chains and separate them. One of the factors that may affect this separation is the degree of entanglement. (Other factors that may influence this separation may be bond energy, chemical forces etc. As the exact composition of the polymer sample is not known, these factors will not be discussed in this thesis). In the case of concentrated polymer solutions, as the number of polymer chains in a given volume are greater, the free end of the molecule can more easily undergo re-entanglement with a nearby molecule. However as the solvent (water) concentration is increased, the chances for re-entanglement are decreased and the chances for disentanglement increased. In the case of dilute solutions, the polymer chain that has succeeded in freeing itself from entanglement can move into the solvent without becoming entangled with another molecule. In addition, the chances for breakdown are increased. Thus for dilute solutions, the polymer concentration decreases. For example, considering figure 1.1, when the polymer is dissolved in water, a positive charge is localized at the nitrogen atoms along the chain. One of the possible mechanisms of losing this charge is by formation of a covalent bond between N and CH or by opening of the ring by breakdown of the molecule. The chances of this occurring in dilute solutions is greater as the polymer chains are more widely dispersed and also free from entanglements. (It should be noted that the colloid titration method measures the charge on the colloid). At this stage of research, it is not possible to draw any definite conclusions about the reasons for the increase or decrease in effective polymer concentration. Further investigation using nuclear magnetic resonance, liquid chromatography, etc., are needed to determine the structure, composition, etc. This type of investigation would enable one to draw conclusions such as whether the polymer loses its charge by breakdown of a molecule, by rearrangement of the atoms in a molecule, etc.

From figures 6.1 and 6.2, it can be concluded that time is the important factor in achieving an equilibrium between entanglement and disentanglement. Once the equilibrium is reached, i.e., after 2 days, the concentration remains virtually constant (for 3-5 days). No attempt has been made to extend this experiment over a long period such as 30 to 60 days. A prediction for long term storage is that the dilute polymer solutions would probably breakdown further if stored at room temperature, whereas in the case of concentrated samples no change would be observed.

6.3 Conclusion:

The effect of storage on polymer solutions varied with respect to concentration of polymer. In the case of dilute polymer solutions, the concentration decreased in the first two days and remained steady later. For concentrated polymer solutions the concentration increased in the first two days and remained steady later. This phenomenon has been attributed to the fact that time, in the order of a few days, is required to achieve an equilibrium between entanglement and disentanglement processes.

The effect of short-term storage is an important consideration, because polymer solutions are frequently prepared in advance of application. In addition, polymer solutions may be stored at an elevated temperature in order to reduce the viscosity for ease of application. The effect on polymer solutions of temperature alone is presented in the following chapter.

Flocculation studies with polymer solutions stored at elevated temperatures for 3 days were conducted and will be presented in Chapter 8.

CHAPTER 7

Effects of Temperature on Polymer Solutions

7.1 Introduction:

In this chapter, the effect of temperature on the polymer breakdown and its decrease in molecular charge will be discussed.

A series of experiments was conducted with temperature, initial concentration of polymer, and time as variables. The experimental set-up can be seen in Figure 7.1. For all experiments, 200mL of polymer samples were taken in 500 mL round bottomed flasks, connected to reflux condensers, and subjected to the required temperature for a required time by immersing them in a constant temperature water bath. Samples of polymer solutions were taken every hour and measured for polymer concentration by using the colloid titration method (72). All the samples were titrated at room temperature (28-32°C). All polymer dilutions were prepared from the stock polymer solution which was prepared 8-10 hours before the experiments.

Figure 7.1. Experimental Set-up for Heating Polymer Solutions

7.2 Results and Discussion:

Typical data for the polymer concentration changes that occurred with respect to temperature and time are given in figures 7.2 and 7.3. Each line represents a different temperature.

In this discussion, the decrease in the apparent charge density or effective polymer concentration as measured by the colloid titration method will be assumed to be proportional to the breakdown of the polymer. It is also assumed that the degradation during the first hour is linear. Two processes appear to be occurring, which give a rapid stage and a slow stage in the degradation of polymer A in water. It can also be seen from the figures, that the rate constant of degradation (K) decreased as the polymer concentration was increased, i.e., degradation is inversely proportional to its concentration. The effect of temperature was minimal when the polymer concentration was greater than 1000 mg/L.

One of the reasons postulated for the high degradation rate in the case of dilute polymer solutions is that the polymer chains are more dispersed when compared with concentrated polymer solutions. This facilitates the disentanglement of the molecules from the aggregate thereby increasing the degradation rate constant when the polymer concentration was decreased. In other words, in the case of dilute polymer solutions, the ends of the polymer chains were free because

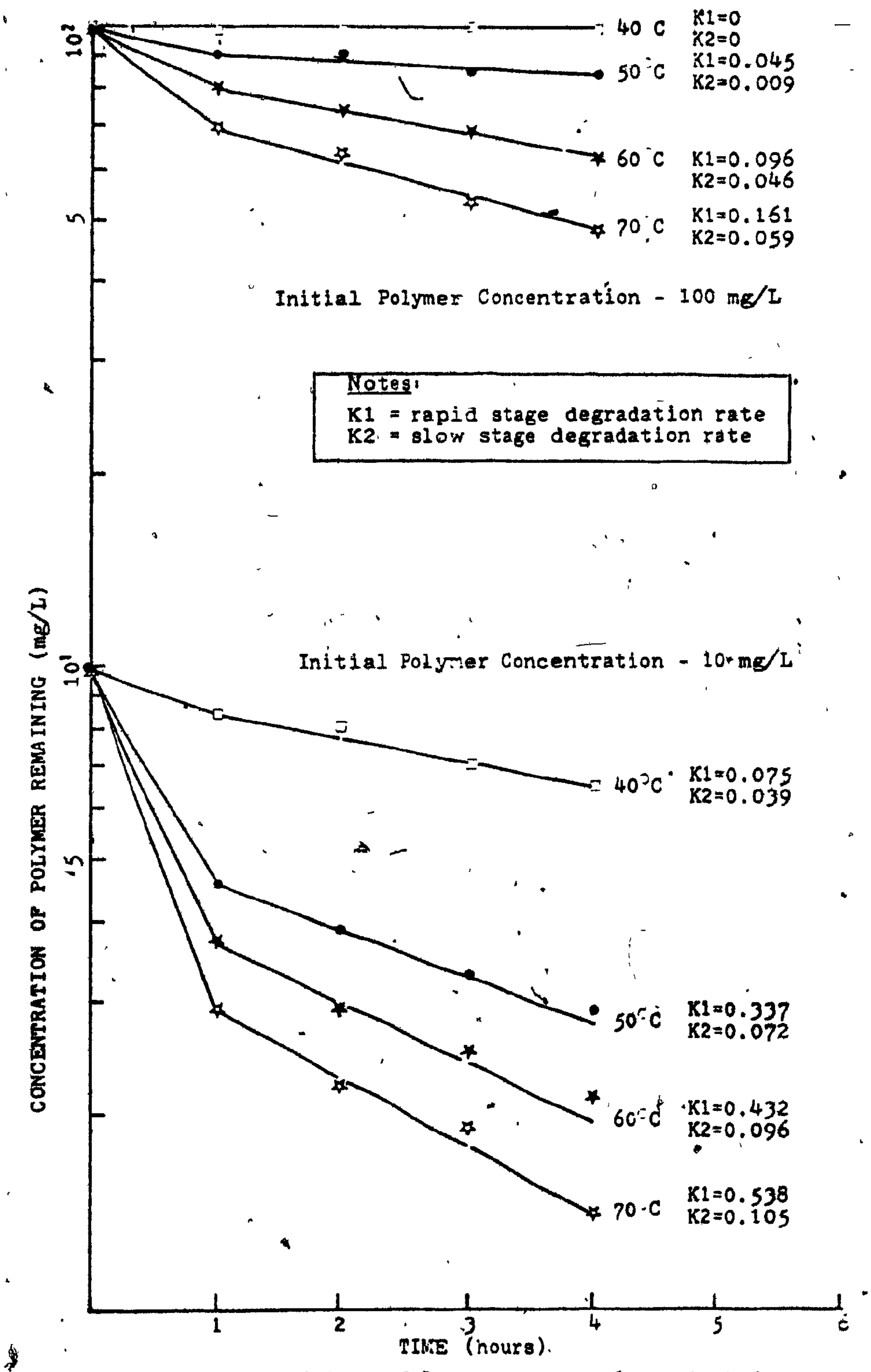


Figure 7.2. Effect of Temperature on Concentrated and Dilute Polymer Solutions

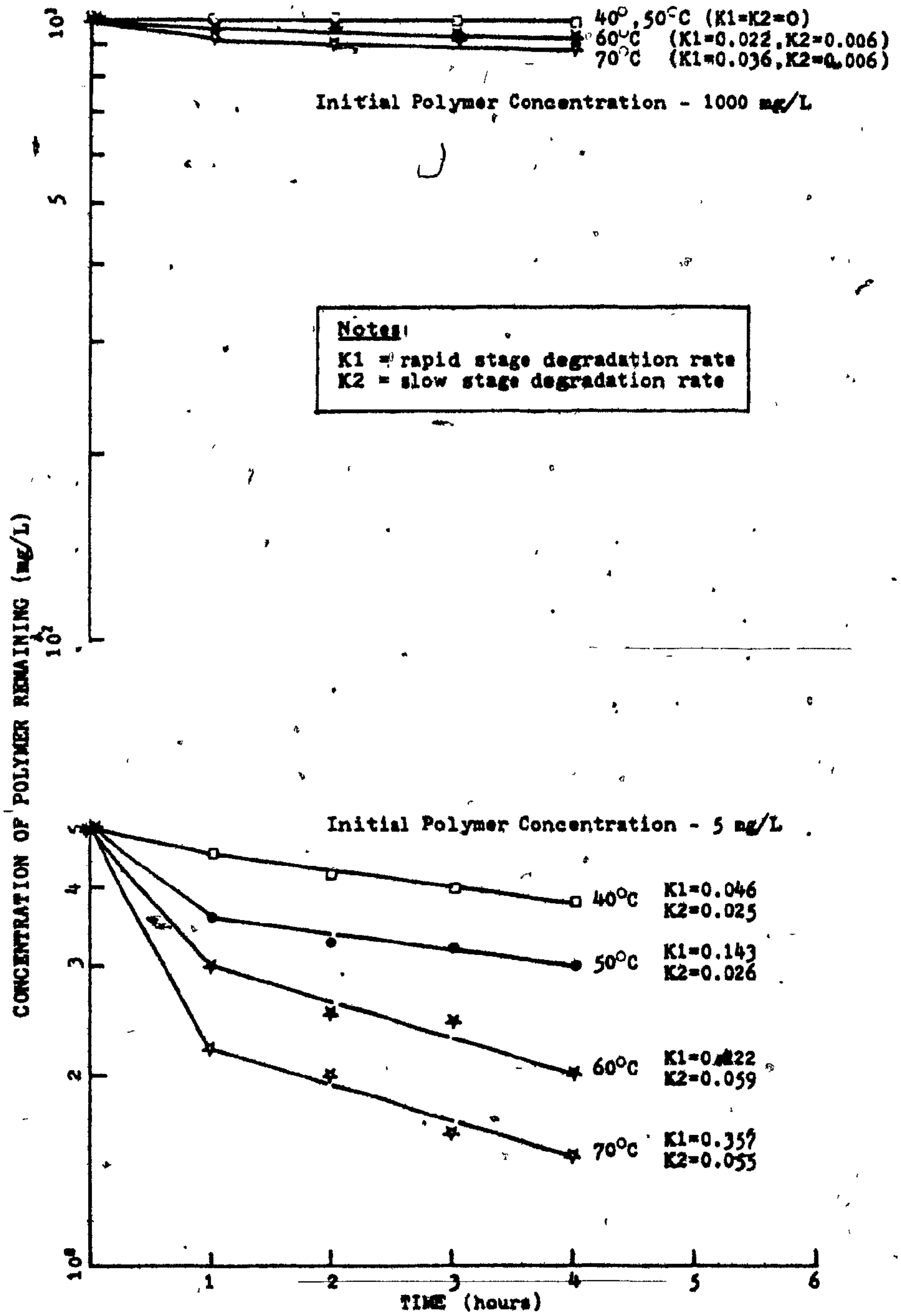
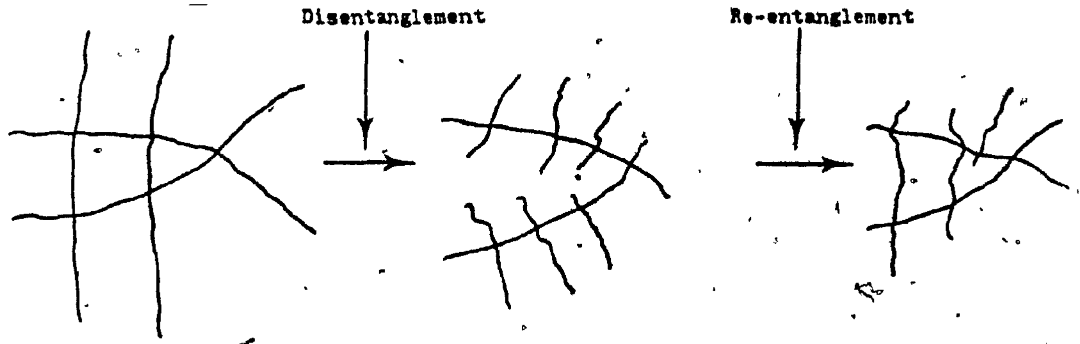


Figure 7.3. Effect of Temperature on Concentrated and Dilute Polymer Solutions

of reduced crowding, thereby facilitating the breakdown of the polymer chain with any change in the equilibrium caused by temperature increments. The reason for the occurrence of rapid and slow stages is thought to be as follows:

A certain amount of time is required for rearrangement of the polymer chains to reach an equilibrium which was disturbed by the temperature increments. As can be seen in figure 7.4, assuming the original arrangement of the chains at the room temperature is as shown in figure 7.4(a). When the temperature is increased (say to 40 °C) the arrangement might be as in figure 7.4(b) for the first hour, thereby exposing more ends of the polymer chains, in turn facilitating breakdown. The arrangement of chains is assumed to have reached an equilibrium after the first hour and may be as in figure 7.4(c). It then remains the same at that temperature. It should be noted that the degree of re-entanglement also depends upon the concentration of the solution. By comparing figures 7.4(b) and 7.4(c) the number of exposed ends decrease in figure 7.4(c) and therefore the breakdown (or degradation) rate decreases; this is called "the slow stage". The degradation rate constants depend upon the temperature. Silberberg et al (62) maintain that intermolecular hydrogen would be expected to provide a barrier against disaggregation. Their study in dilute polyacrylamide solutions suggests that hydrogen bonding decreases with an increase in temperature. This might be one of the reasons why the degradation rate is temperature dependent.



7.4(a)

7.4(b)

The total polymer chain <u>length</u> is less than in Figure 7.4(a) but the <u>number</u> of exposed chain ends is greater.

7.4(b)

The total polymer chain <u>length</u> is less than in Figure 7.4(b); furthermore, the <u>number</u> of exposed chain ends is less.

Figure 7.4. Possible Arrangement of Polymer Chains with Respect to Time in the Case of Preheated Polymers

It should be noted that the reproducibility of these results was relatively poor and that the degradation rate constants K1 and K2 always change (±20%) with repetition of experiment. This is mainly because of the uncertainity of the arrangement of the polymer chains.

Figures 7.5, 7.6 and 7.7 show a comparison of the effect of temperature on fresh and stored polymers. No definite conclusions can be drawn because of the poor reproducibility of the results.

Table 7.1 shows the results in figures 7.1 and 7.2 in equation form. Linear regression analysis was done using a SAS computer package. The equations obtained satisfy the results under a confidence interval of 95%.

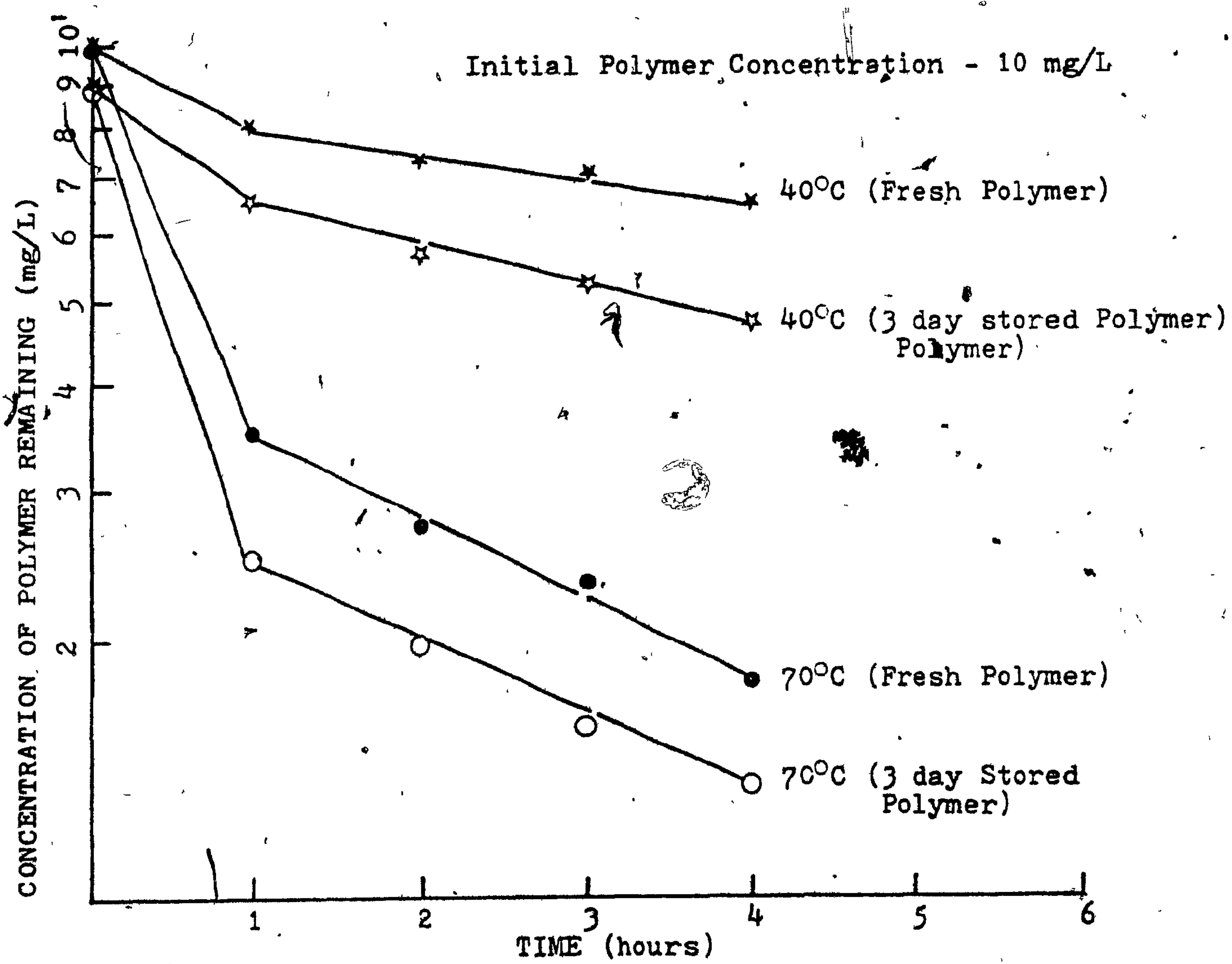


Figure 7.5. Effect of Temperature on Stored Polymer

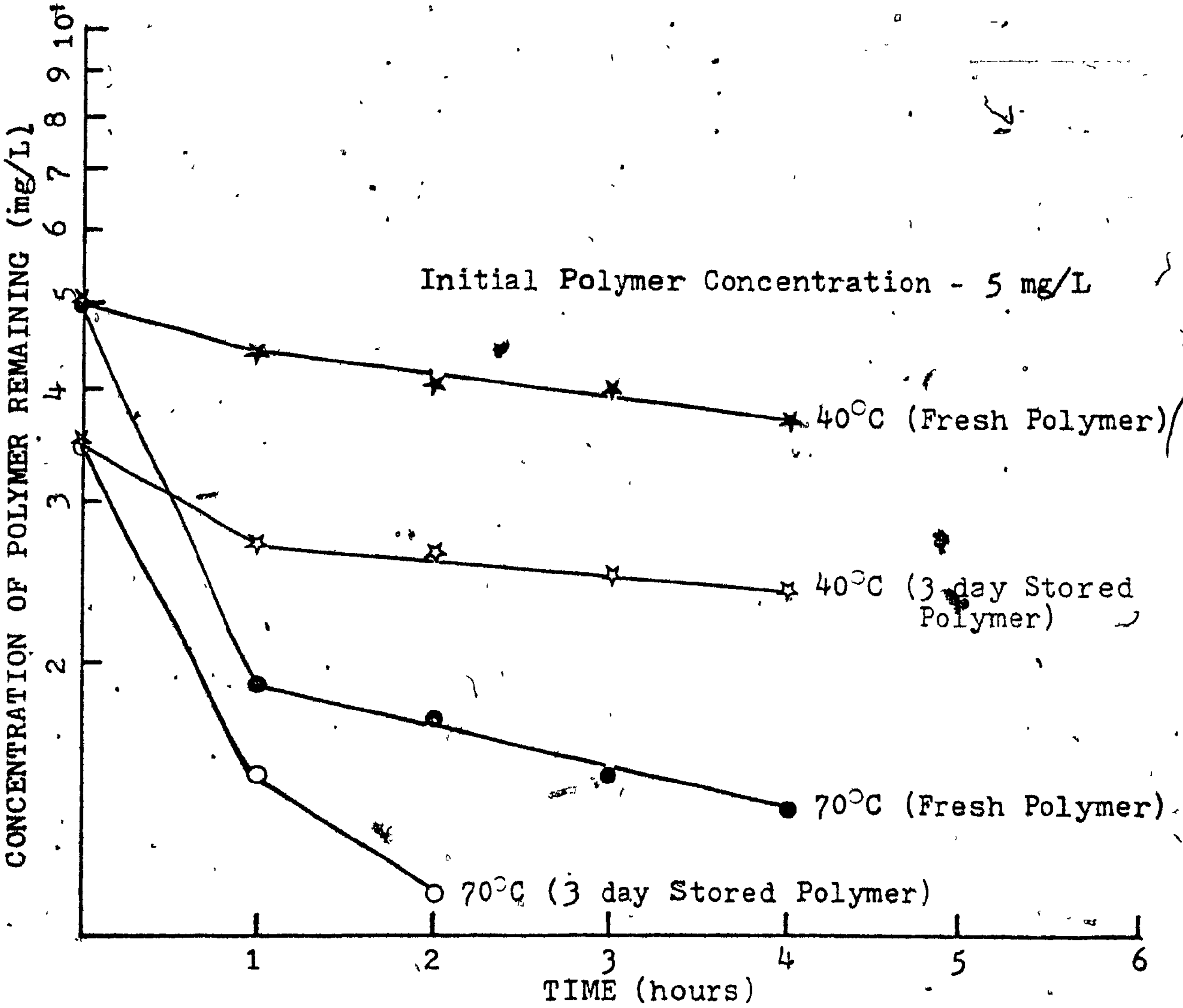


Figure 7.6. Effect of Temperature on Stored Polymer

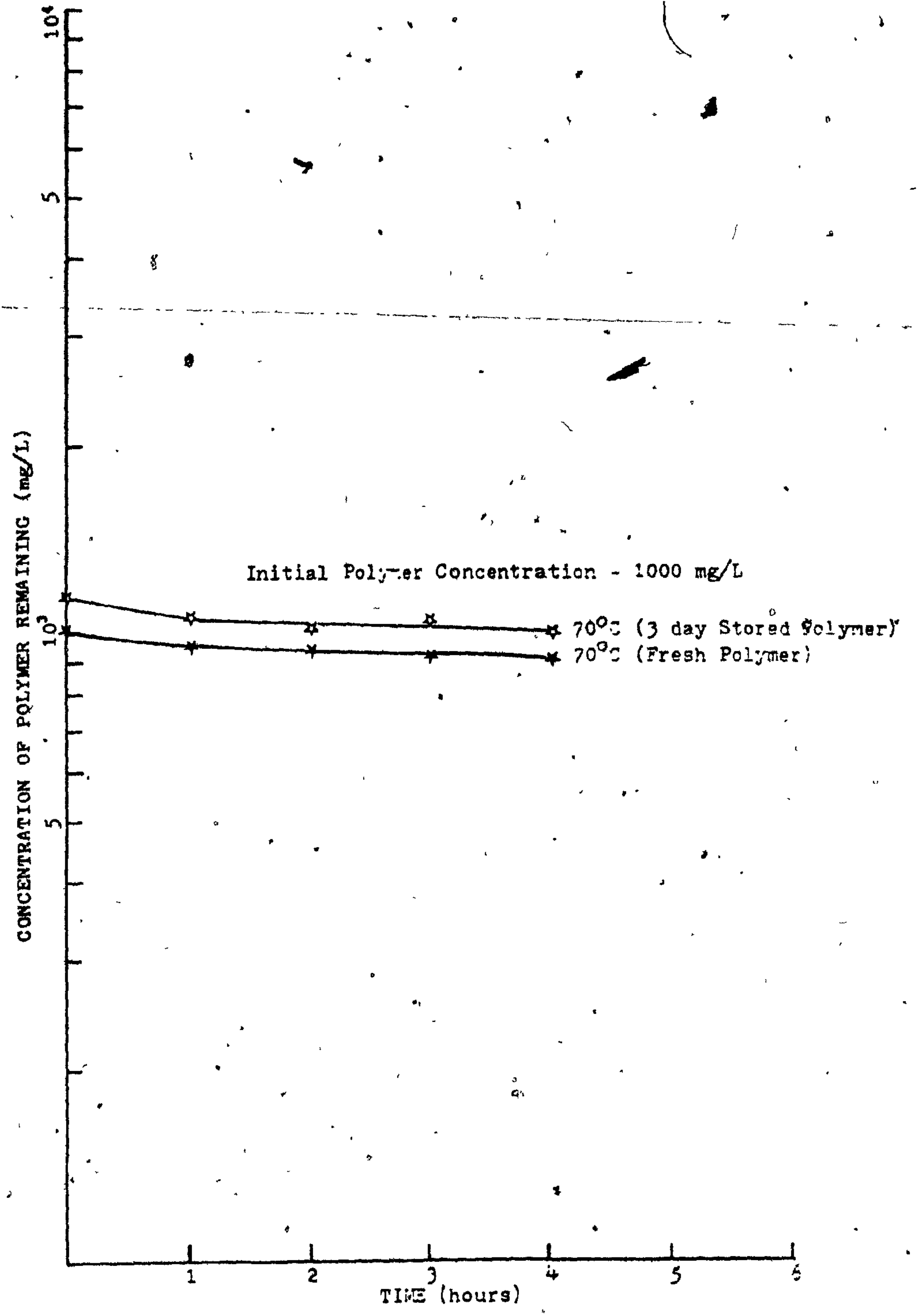


Figure 7.7. Effect of Temperature on Concentrated Stored Polymer

Table 7.1: Appropriate Equations for Preheated Polymers for the Calculation of Polymer Concentration Remaining in a Sample

Initial Polymer Concentration (mg/L)	Time (X2) (hours)	Appropriate Equation	R-Square
5.0	≤1.0	Y(5.0)=14.785-0.087(X1)-5.1(X2)	0.865
	>1.0	Y(5.0)=15.018-0.179(X1)-0.408(X2)	0.860
10.0	≤1.0	Y(10.0)=7.062-0.0375(X1)-1.675(X2)	0.831
	>1.0	Y(10.0)=7.733-0.0765(X1)-0.240(X2)	0.986
100.0	≤1.0	Y(100)=128.325-0.0515(X1)-15.25(X2)	0.733
	>1.0	Y(100)=169.40-1.455(X1)-4.30(X2)	0.950
1000.0	≤1.0	Y(1000)=1077.0-1.40(X1)-30.0(X2)	0.606
	>1.0	Y(1000)=1169.75-3.45(X1)-7.56(X2)	0.826

Notes:

These equations are applicable to Polymer A only.

X1 = Temperature to which polymer solution is subjected (°C)
X2 = Length of time the polymer solution is subjected to any temperature (hours)
Y(C) = Concentration of polymer remaining in a preheated sample of initial polymer concentration 'C' (mg/L)

7.3 Conclusion:

The effect of elevated temperatures (40-70 °C) on polymer solutions is a rapid, followed by a slow, stage of degradation. The effect is minimal for concentrated polymer solutions (>1000 mg/L), and degradation is inversely proportional to the concentration of the polymer. The occurrence of the rapid and slow stages is thought to be mainly because of the disturbance in the equilibrium of the polymer chain arrangements due to the temperature increases. The rate of degradation depends directly on the temperature.

The results of flocculation studies with polymers subjected to elevated temperatures are presented in the following chapter.

CHAPTER 8

EFFECT OF STORED AND PREHEATED POLYMERS ON THE FLOCCULATION ACTIVITY

8.1 Introduction:

This chapter describes the effectiveness of stored and preheated polymer solutions on the flocculation activity of polystyrene latex suspension. The purpose of this study is to demonstrate practically the effects of storage and preheating of polymers.

Jar Tests were used to check the effect of stored and preheated polymer solutions. In the case of stored polymers, the polymer was stored for three days at 5 °C. Preheated polymers were prepared in the same way as described in Chapter 7. The solutions were brought to room temperature (28-32°C) before being used in Jar Testing.

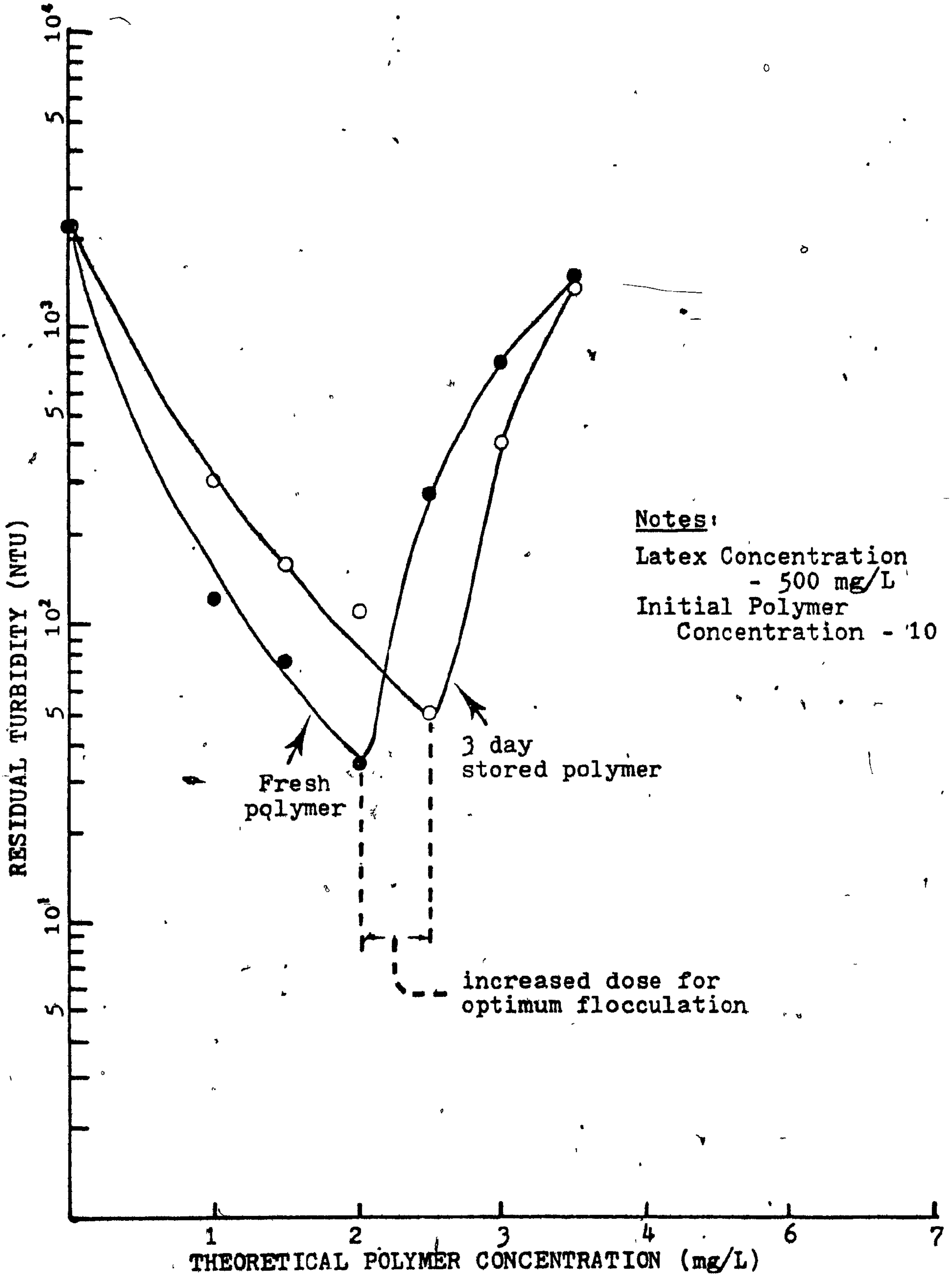
The procedure used for the Jar Tests is described in section.3.2.1. In order not to have to dilute the polymer sample many times, the concentration of the polystyrene latex suspension used was 500 mg/L for all experiments.

In all cases, "theoretical polymer concentration" will be the concentration of polymer initially prepared (as a known mass to volume ratio) and "actual polymer concentration" will be the concentration as measured (after heating or storage) by the colloid titration method.

8.2 Results and Discussion:

Figure 8.1 shows the effect of fresh and stored polymer solutions on the flocculation activity of the polystyrene latex suspension. For the fresh polymer, maximum destabilization (optimum flocculation) occurred at 2.0 mg/L polymer concentration, whereas in the case of stored polymer, the optimum flocculation dose increased to 2.5 mg/L. Figure 8.2 shows the relationship between polymer concentration and EM for fresh and stored polymer. More polymer was thus also required for attaining zero EM in the case of stored polymer (2.5 mg/L, compared with 2.2 mg/L).

Figures 8.3,8.4,8.5 & 8.6 show the effects of preheated polymers on the flocculation activity. Curve A in figure 8.3 was obtained by using a polymer solution which was not subjected to any temperature variations. Curves B & C were obtained by using polymer solutions which were subjected to a temperature of 40 °C for one hour and four hours respectively. It can be seen from the figure 8.3 that the optimum flocculation occurred at a theoretical polymer concentration of 2.0 mg/L for curve A. But in the case of curves B & C, it occurred at 2.5 and 3.5 mg/L theoretical polymer concentrations respectively. In all the cases restabilization occurred above the optimum polymer dosage.



Notes:

Latex Concentration - 500 mg/L

Initial Polymer Concentration - 10 mg/L

Figure 8.1. Effect of Stored Polymers on Flocculation Activity

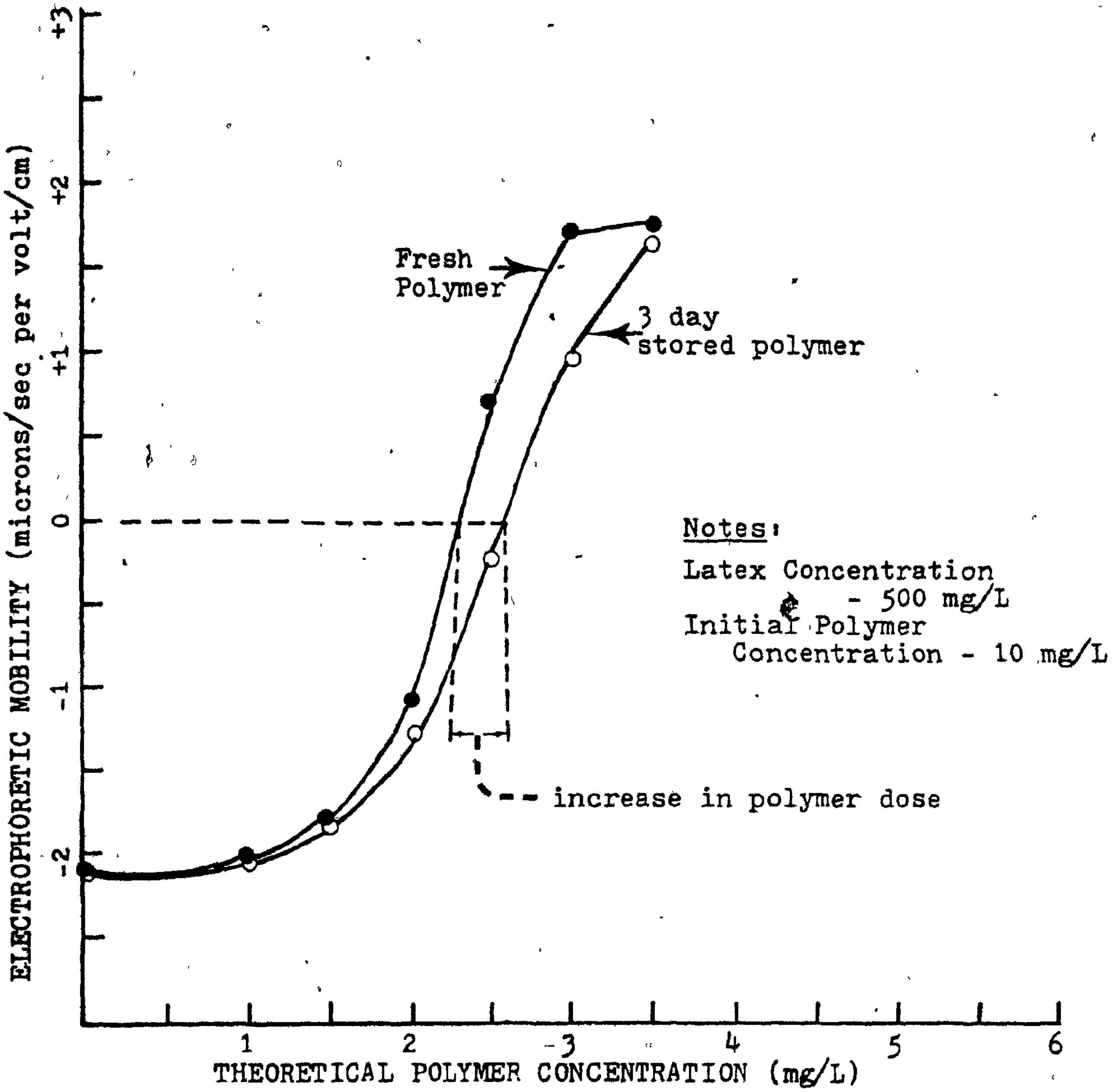


Figure 8.2. Effect of Polymer Storage on Electrophoretic Mobility

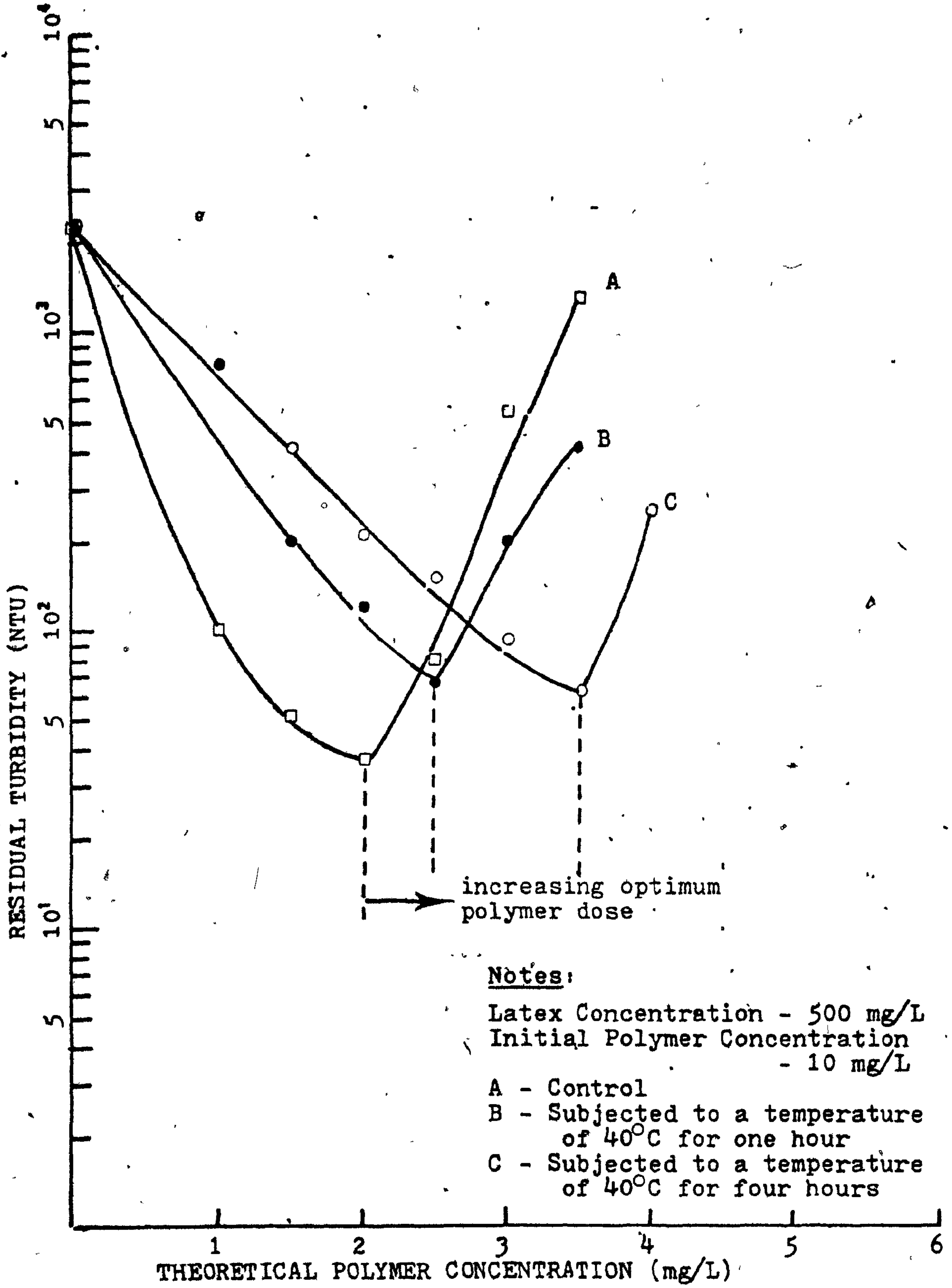
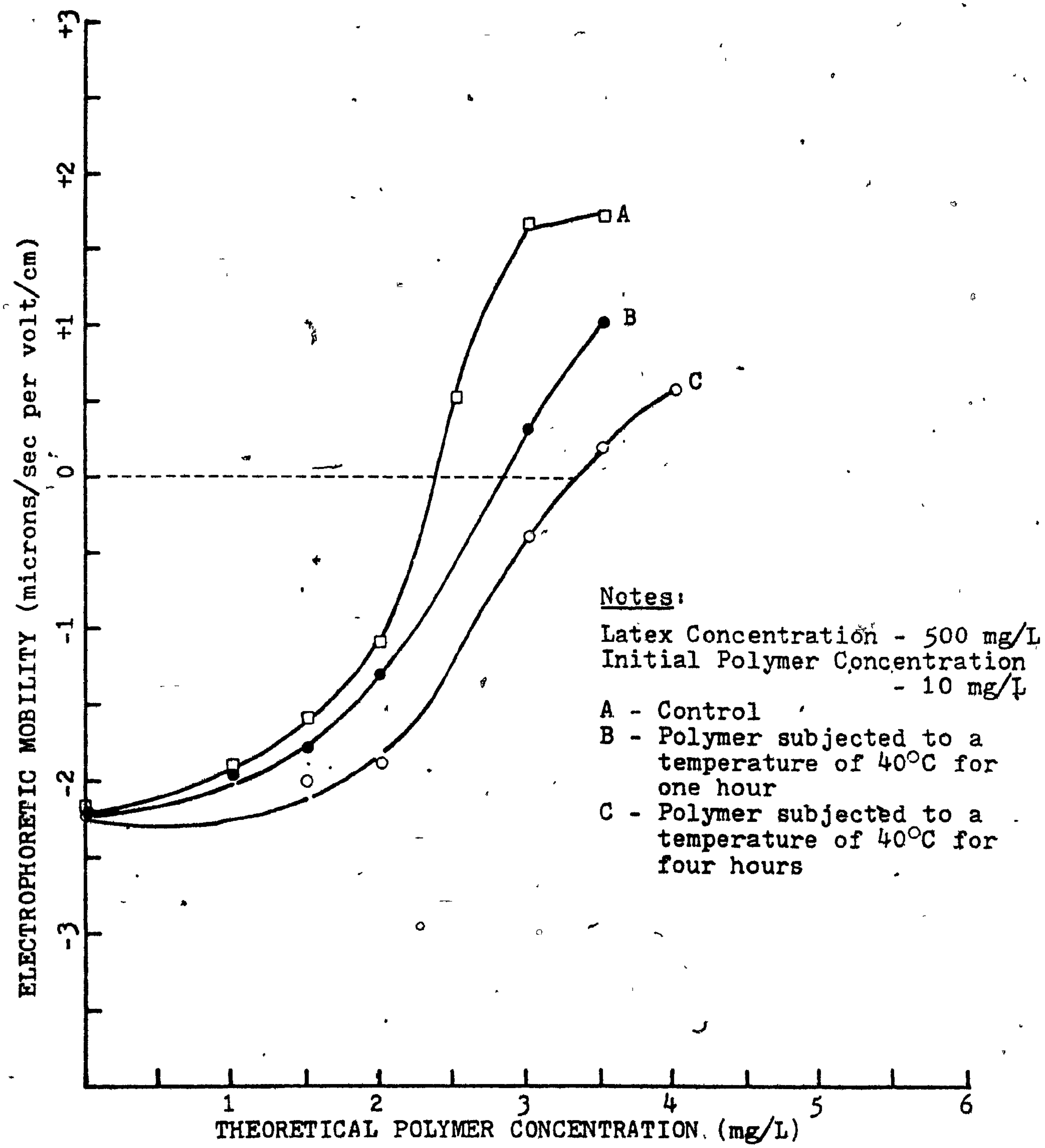


Figure 8.3. Flocculation Ability of Preheated Polymers (40°C)



Notes:

Latex Concentration - 500 mg/L
Initial Polymer Concentration - 10 mg/L
A - Control
B - Polymer subjected to a temperature of 40°C for one hour
C - Polymer subjected to a temperature of 40°C for four hours

Figure 8.4. Effect of Preheated Polymers on Electrophoretic Mobility (40°C)

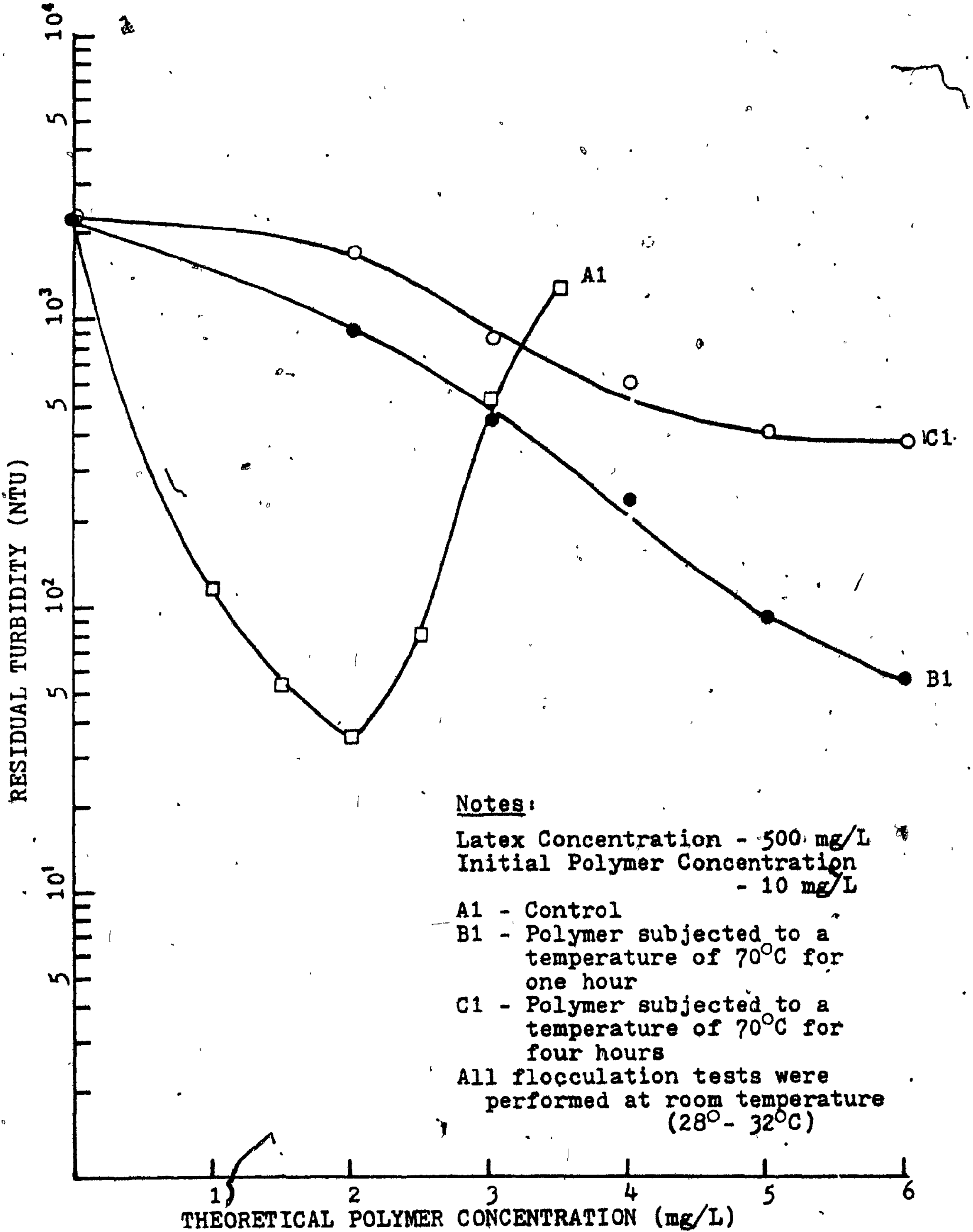


Figure 8.5. Flocculation Ability of Preheated Polymers (70°C)

Notes:

Latex Concentration - 500 mg/L
Initial Polymer Concentration
- 10 mg/L
A1 - Control
B1 - Polymer subjected to a temperature of 70°C for one hour
C1 - Polymer subjected to a temperature of 70°C for four hours
All flocculation tests were performed at room temperature (28° - 32°C)

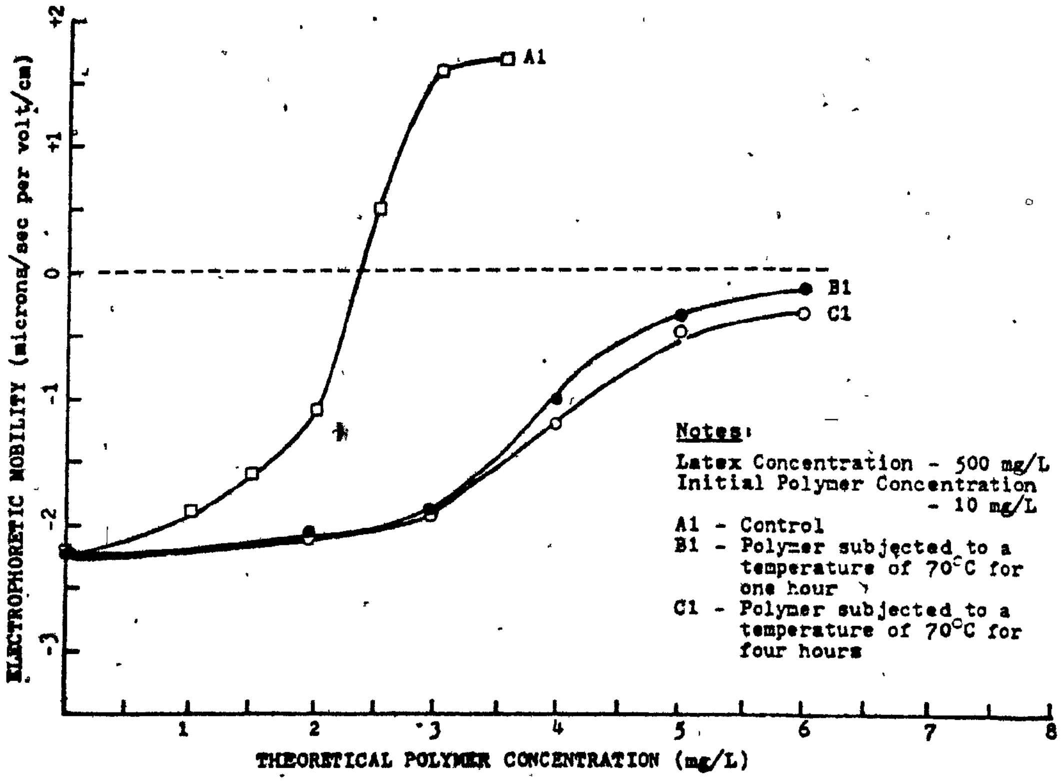


Figure 8.6. Effect of Preheated Polymers on Electrophoretic Mobility (70°C)

Figure 8.4 shows the effect of preheated polymers on the EM. It can be seen that a theoretical polymer concentration of 2.4 mg/L, yielded zero EM on curve A. In the case of curves B & C, (1 and 4 hour storage respectively, at 40°C) zero EM was obtained at 2.8 and 3.2 mg/L theoretical polymer concentrations respectively. Thus more polymer was required in the case of preheated polymer solutions for optimum flocculation to occur and also to bring the EM to zero.

Figures 8.5 & 8.6 are similar to figures 8.3 & 8.4, but the polymer solutions were subjected to 70 °C instead of 40°C. Figure 8.5 shows that at a theoretical polymer concentration of 2.0 mg/L, the residual turbidities corresponded to 900 and 1700 NTU for curves B1 & C1 respectively. Above 2.0 mg/L, the residual turbidity continued to decrease for curves B1 & C1, but increased for curve A1, implying that restabilization occurred in the case of curve A1. At a concentration of 6.0 mg/L, residual turbidities corresponded to 55 and 380 NTU for curves B1 & C1 respectively. No experiments were conducted higher than 6.0 mg/L theoretical polymer concentration to obtain the optimum polymer dose (or lowest turbidity) in the case of curves B1 & C1, because of the practical difficulty of maintaining the latex concentration constant. (It was demonstrated previously that the actual polymer concentration decreases in the case of preheated polymers. Hence in order not to decrease the actual polymer concentration still further by dilution, a more concentrated latex suspension has to be pipetted to make-up a constant latex solids concentration. However, when working with latex concentrations greater than 1%, there will be a loss of solids by adhesion of latex particles to the walls of the pipette. Hence it is difficult at this level to maintain the solids or latex concentration constant. It should be noted that the results would be meaningless if the latex concentration is not maintained the same for all the experiments.) Curves B1 and C1 in figure 8.6 show that at a concentration of 6.0 mg/L, an EM of zero was still not attained.

The decreased effectiveness of stored and preheated polymers as a flocculant could be due to the decrease in charge of the polymer, scission of weak links, or the disappearance of aggregates. All of the above cases in one way or another decrease the sweeping volume of polymer coils. (Sweeping volume is the volume traced by the tips of the chains if the chain spins about its centre point in three dimensions). The strength of a polymeric bridge between two particles depends upon the number and average strength of the polymer-surface bonds that are formed at the weaker end of the bridge. For the strongest bridge, a polymer coil would have to be adsorbed so that the maximum possible ratio of its' functional groups are bonded to the surface and so that there is an equal sharing of the bonding between the two particles.

A high sweeping volume of the polymer coils increases the probability of immediate interparticle adsorption that is necessary for the formation of a strong bridge. If the polymer molecule has the opportunity of predominantly bonding to one particle in a compressed coiled conformation, it will be able to become only weakly attached to a second particle. A decrease in the sweeping volume of the polymer coils will decrease the probability of interparticle adsorption. The polymer molecule will have time to coil out to a single particle and a weaker bridge results. If such is the case poor flocculation will result.

8.3 Conclusions:

The decrease in the measured polymer concentration that occurred with dilute polymer solutions during short term storage and due to the effect of temperature, was paralleled by a decrease in the effectiveness of the polymer in promoting, the flocculation of a polystyrene latex suspension. This decrease in the flocculation activity is attributed to a weakening of the interparticle bridging by a change from a strong adsorption of the bridging polymer between two particles to a strong adsorption of the bridging polymer to one particle but weak adsorption of the bridging polymer to the other particle.

CHAPTER 9

Summary, Practical Implications, and Future Research

9.1 Summary:

Polystyrene latices were used as a standard suspension owing to their highly spherical shape, uniform size and colloid stability. These have been used in flocculation studies with a high molecular weight cationic polymer. Polymer/latex reactions were found to be extremely rapid. The polymer/latex weight ratio increased by as much as three times to reach optimum flocculation when the latex concentration was less than 50 mg/L. The results obtained by flocculation of the latex suspension are consistent and can be reproduced with reasonable accuracy, enabling the development of a definite relationship between polymer dosage and the pertinent solution variables such as turbidity, EM etc. Attainment of these relationships allowed achievement of one of the objectives, which was to measure very low polymer concentrations (in the parts per billion range) in a sample.

Vacuum distillation used for concentrating dilute polymer solutions results in partial or full breakdown of polymers because of the temperature effects. Filtration of high molecular weight polymers through 0.45 microns filter paper results in a large percentage loss of polymer on the filter paper and the percentage loss is dependent on the polymer concentration.

The effect of storage of polymer solutions varied with respect to polymer concentration. In the case of dilute polymer solutions, the polymer concentration decreased in the first two days and remained steady later. For concentrated polymer solutions (>100 mg/L), the polymer concentration increased slightly in the first two days and then remained steady. This phenomenon has been attributed to the fact that time is an important criterion in reaching an equilibrium between the entanglement and disentanglement processes.

The effect of high temperatures (40-70°C) on polymer solutions is a rapid stage, followed by a slow stage, of degradation. The effect is minimal for concentrated polymer solutions (>1000 mg/L) and degradation is inversely proportional to the concentration of the polymer.

The effectiveness of stored and preheated polymers on the flocculation activity of latex suspensions decreases when compared to fresh polymers. Greater polymer dosage is required in the case of stored and preheated polymer solutions for optimum flocculation to occur and also to bring the EM to zero.

In summary, this research enabled the development of a method for the detection of cationic polymer concentrations as low as 0.1 mg/L with reasonable accuracy by relating the polymer dosage to the flocculation activity of the latex suspension. It also gave an additional insight into what happens during short term storage and at elevated temperatures on dilute and concentrated polymer solutions.

9.2 Practical Implications:

This study is believed to have the following significant implications in the water and waste treatment fields.

i) A simple method has been presented to detect concentrations of unmodified cationic polymers in process or treated waters (i.e., waters with impurities which would rule out TOC or chromatographic methods) to 0.1 mg/L with high reproducibility. This method not only detects the low polymer concentrations but also provides insight into the behavior of the polymer with respect to its flocculation activity.

ii) Undesirable effects were noticed by both short-term storage of dilute polymer solutions and subjecting these polymers to elevated temperatures (especially in the case of acrylamide based cationic polymers). These cases could easily occur when:

a) concentration of polymer is done by flash evaporation in order to detect trace amounts of polymer present in the effluent.

b) polymer solutions are prepared in advance of of application and stored at elevated temperatures in order to reduce viscosity and allow more convenient application. This case was observed in one waste treatment plant where the polymer is stored at 70°C for 3 days in order to reduce viscosity.

9.3 Further Research:

Some additional research that could be carried out on this topic is suggested below:

1) Effects of Storage:

The effects of storage should be studied over an extended period, say 30-60 days, to check whether there is any further breakdown of polymer, especially in the case of dilute polymer solutions. Electron microscope studies are required to determine what type of aggregates form or disappear during storage. Studies should be continued on the same basis for different polymers of different molecular weights to see whether the same phenomenon is occurring.

2) Concentrating Cationic Polymers:

The ion-exchange method could be a promising method for concentrating cationic polymers if a proper solvent is found for eluting the polymer from the resin. By this method the possibilities of breaking down the polymer while concentrating will be minimized.

3) Effect of Chlorine and Ozone on Polymer Solutions:

Chlorine and ozone are extensively used as disinfectants in water and wastewater treatment. Some of the studies that can be conducted concerning the effect of chlorine and ozone on polymer solutions include:

i) The effect of chlorine and ozone upon the breakup of cationic polymers using liquid chromatography.

ii) The effectiveness of chlorinated and ozonated polymer solutions on the flocculation activity of polystyrene latex suspension when compared to the fresh polymer.

iii) The effect of residual polymers on the chlorine and ozone demand.

4) Toxicity:

Toxicity studies which should be carried out include:

i) The potential toxic effect of ozonation or chlorination of polymer solutions in comparison to the toxic effect of the polymer alone.

ii) It was proved in this thesis that there was a decrease of charge on the polymer in the case of preheated polymers. Further research should be conducted on the preheated polymers to check the effect of charge on the toxicity to fish.

REFERENCES

1) APHA - AWWA - WPCF ; "Standard Methods for the Examination of Water and Waste water"; 15th ed., (1980).

2) Benedek, A., Bansci, J.J., and Rupke, J.W.G.; "Use of Polyelectrolytes for Overloaded Clarifiers"; J. Water Poll. Control Fed., 47,10,2447 (1975).

3) Biesinger, G.E., Lemke, A.E., Smith, W.E., and Tyo, R.M.; "Comparative Toxicity of Polyelectrolytes to Selected Aquatic Animals"; J. Water Poll. Control Fed.,48,1,183 (1976).

4) Birkner, F.B and Morgan, J.J.; "Polymer Flocculation Kinetics of Dilute Colloidal Suspensions"; J. Am. Water Works Assoc., 60,2,175 (1968).

5) Birkner, F.B and Edwald, J.K.; "Nonionic Polymer Flocculation of Dilute Clay Suspensions"; J. Am. Water Works Assoc., 61,12,645 (1969).

6) Black, A.P., Birkner, F.B., and Morgan, J.J.; "Destabilization of Dilute Clay Suspensions with Labelled Polymers"; J. Am.Water Works Assoc., 57,12,1547 (1965).

7) Ibid, Black, A.P. (1965), p1547

8) Black, A.P and Vilaret, M.R.; "Effect of Particle Size on Turbidity Removal"; J. Am. Water Works Assoc., 61,4,209 (1969).

9) Bolker, H.I.; "Natural and Synthetic Polymers, An Introduction"; Marcel Dekker, Inc., N.Y. (1974).

10) Burke, J.T and Dajani, M.T.; "Organic Polymers in the Treatment of Industrial Wastes"; Proc. 21st Ind. Waste Conf., Purdue Univ., 303 (1966).

11) Busch, P.L and Stumm, W.; "Chemical Interactions in the Aggregation of Bacteria Bioflocculation in Waste Treatment"; Env. Sci. and Tech., 2,1,49 (1968).

12) Business News; "Water Treatment Chemicals Use to Grow Strongly"; Chem & Eng. News, 59,22,12 (1981).

13) Check, T.G.; "Polymers Cut Cost of Phosphorus Removal"; Water & Waste Engg., 8,23 (1976).

14) Chinal, S.N and Schneider, W.C.; "Shear Dependence of Viscosity-Molecular Weight Transitions. A Study of Entanglement Effects"; J. Polymer Sci., 3,,1359 (1969).

15) Cohen, J.M.; "Natural and Synthetic Polyelectrolytes as Coagulant Aids"; J. Am. Water Works Assoc., 50,6,463 (1958).

16) Committee Report; "State of the Art of Coagulation"; J. Am. Water Works Assoc., 63,2,99 (1971).

17) Croll, B.T.; "The Determination of Acrylamide in Polyelectrolytes by Extraction and Gas Chromatographic Analysis"; Analyst, 96,1,67 (1971).

18) Croll, B.T and Simkins, G.M.; "The Determination of Acrylamide in Water by Using Electron Capture Gas Chromatography"; Analyst, 97,4,281 (1972).

19) Crummett, W.B and Hummel, R.A.; "The Determination of Traces of Polyacrylamides in Water"; J. Am. Water Works Assoc., 55,2,209 (1963).

20) Dixon, J.K., La Mer, V.K., Li, C., Messinger, S., and Linford, H.B.; "Effect of the Structure of Cationic Polymers on the Flocculation and the Electrophoretic Mobility of Crystalline Silica"; J. Colloid and Interface Sci., 23,4 (1967).

21) Dixon, J.K and Zielyk, M.W.; "Control of the Bacterial Content of Water with Synthetic Polymeric Flocculants"; Env. Sci. and Tech., 3,6,551 (1969).

22) Ibid, Dixon, J.K. (1969), p551

23) Flock, H.G and Rausch, E.G.; "Application of Polyelectrolytes in Municipal Waste Treatment"; Water Soluble Polymers; ed: Bikales N.M., Plenum Press (1973).

24) Furusawa, K. et al; "Detection of Anionic Polyacrylamide by GPC"; Chem. Lett., 314 (1978).

25) Garwood, J.; "Polyelctrolytes in Sewage Treatment"; Effluent and Water Treat., 380 (July 1967).

26) Gehr, R.; "The Role of Polymers in Dissolved Air Flotation"; Ph.D Thesis, Univ of Toronto (1980).

27) Ibid, Gehr, R. (1980), p50

28) Goodwin, J.W., Hearn, J., Ho, C.C., and Ottewill, R.H.; "Studies on the Preparation and Characterisation of Monodisperse Polystyrene Latices. iii) Preparation without Added Surface Active Agents"; J. Colloid and Polymer Sci., 252,484 (1974).

29) Goppers, V and Straub, C.P.; "Polyelectrolyte Persistence in a Municipal Water Supply"; J. Am. Water Works Assoc., 68,6,319 (1976).

30) Ibid, Goppers, V. (1976) p319

31) Gregory, J.; "Flocculation of Polystyrene Particles with Cationic Polyelectrolytes"; Trans. Faraday Soc., 65,2260 (1969).

32) Gutcho, S.; "Waste Treatment with Polyelectrolytes"; Pollution Control Review No. 8 (1972).

33) Habiban, M.T and O'Melia, C.R.; "Particles, Polymers and Performance in Filtration"; Am. Soc. of Civ. Eng., 101,EE4,567 (1975).

34) Healy, T.W and La Mer, V.K.; "The Adsorption-Flocculation Reactions of a Polymer with an Aqueous Colloidal Dispersion"; J. Phys. Chem., 66,10,1835 (1962).

35) Heller, W and Pugh, T.; "Steric Stabilization of Colloidal Solutions by Adsorption of Flexible Macromolecules"; J. Polymer Sci., 48,203 (1960).

36) Hudson Jr, H.E and Wagner, E.G.; "Conduct and Uses of Jar Tests"; J. Am. Water Works Assoc., 73,4,218 (1981).

37) Iler, R.K.; "Relation of Particle Size of Colloidal Silica to the Amount of a Cationic Polymer Required for Flocculation and Surface Coverage"; J. Colloid and Interface Sci., 37,2 (1971).

38) Jolley, R.L.; "Concentrating Organics in Water for Biological Testing"; Env. Sci. and Tech., 15,8,874 (1981).

39) Josephs, R and Feitelson, J.; "Interactions of Polyelectrolytes. A Turbidimetric Method for the Estimation of Ionized Polymers"; J. Polymer Sci., 1(A),3385 (1963).

40) Kane, J.C., La Mer, V.K., and Linford, H.B.; "Filtration and Electrophoretic Mobility Studies of Flocculated Silica Suspensions"; J. Am. Chem. Soc., 86,3450 (1964).

41) Kawamura, S and Tanaka, Y.; "Applying Colloid Titration Techniques to Coagulant Dosage Control"; Water and Sewage Works, 113,9,348 (1966).

42) Klass, C.P., Sharp, A.J., and Urick, J.M.; "Polyelectrolyte Retention Aids"; TAPPI, CA Report No. 57 (1975).

43) Koral, J. et al; "The Adsorption of Polyvinyl Acetate"; Phys. Chem., 62,541 (1958).

44) Kragh, A.M and Langston, N.B.; "The Flocculation of Quartz and Other Suspensions with Gelatin"; J. Colloid Sci., 17,101 (1962).

45) La Mer, V.K and Healy, T.W.; "Adsorption-Flocculation Reactions of Macromolecules at the solid-liquid Interface"; Rev. Pure and Appl. Chem., 13,112 (1963).

46) Lindquist, G.M and Stratton, R.A.; "The Role of Polyelectrolyte Charge Density and Molecular Weight on the Adsorption and Flocculation of Colloidal Silica with Polyethyleimine"; J. Colloid and Interface Sci., 55,1,45 (1976).

47) Michaels, A.S.; "Aggregation of Suspensions by Polyelectrolytes"; Ind. Eng. Chem., 46,1485 (1954).

48) Michaels, A.S and Morelos, O.; "Polyelectrolyte Adsorption by Kaolinite"; Ind. Eng. Chem., 47,1801 (1955).

49) Mortensen, J.L.; "Adsorption of Hydrolyzed Polyacrylonitrile on Kaolinite. ii) Effect of Solution Electrolytes"; Soil Sci. Soc. Am. Proc., 21,385 (1957).

50) Ockershausen, R.W and Peterman, C.J.; "A Discussion of the Paper, Zeta-Potential Measurements in the Control of Coagulation Chemical Doses"; J. Am. Water Works Assoc., 56,2,224 (1964).

51) Packham, R.F.; "Polyelectrolytes in Water Clarification"; Proc. of the Soc. for Water Treatment and Examination., 16,88 (1967).

52) Packter, A.; "Interaction of Montmorillonite Clays with Polyelectrolyte"; Soil Sci., 83,335 (1957).

53) Particle Size Analyzer-7991 Catalogue, Leeds & Northup, Largo, Fl 33543.

54) Personal Communication; Langley, J.G., Allied Colloids Ltd., Bradford, England (April, 1982).

55) Poduska, R.A., Hicks, J.E., and Howard, J.W.; "Polymer Addition for Effluent Quality Control'; J. Water Poll. Control Fed., 51,11,2615 (1979).

56) Pressman, M.; "Cationic Polyelectrolytes as Prime Coagulants in Natural Water Treatment"; J. Am. Water Works Assoc., 59,2,169 (1967).

57) Process Design Manual for Suspended Solids Removal; U.S.EPA., Technology Transfer, Washington, D.C. (1975).

58) Pugh, T.L and Heller, W.; "Coagulation and Stabilization of Colloidal Solutions with Polyelectrolytes"; J. Polymer Sci., 47,219 (1960).

59) Riddick, T.M.; "Zeta-Potential and its Applications to Difficult Waters"; J. Am. Water Works Assoc.,53,8,1007 (1961).

60) Roberts, K., Wennerberg, A.M., and Friberg, S.; "The Influence of Added Saccharide, Protein and Lipid on the Sedimentation of E.coli Bacteria using Aluminium Sulfate and Polyacrylamides"; Water Research, 8,1,61 (1974).

61) Ruehrwein, R.A and Ward, D.W.; "Mechanisms of Clay Aggregation by Polyelectrolytes"; Soil Sci., 73,485 (1952).

62) Silberberg, A., and Katchalsky, A.; "Temperature-Dependence of Light Scattering and Intrinsic Viscosity of Hydrogen Bonding Polymers"; J. Polymer Sci., 23,259 (1957).

63) Simha, R., and Frisch, H.L.; "The Adsorption of Flexible Macromolecules"; J. Phys. Chem., 58,507 (1954).

64) Spraggs, L.D., Gehr, R., and Hadjinicolaou, J.; "Polyelectrolyte Toxicity Tests by Avoidance Studies"; Poster Presentation, 11th International Conference, International Association on Water Pollution Research, Cape Town, March 29-April 2, 1982.

65) Stumm, W. and O'Melia, C.R.; "Stoichiometry of Coagulation"; J. Am Water Works Assoc., 60,5,514 (1968).

66) Swift, D.L and Friedlander, S.E.; "The Coagulation of Hydrosols by Browniam Motion and Laminar Shear Flow"; J. Colloid Sci., 19,621 (1964).

67) Tenney, M.W., Echelberger Jr, W.F., Schuessler, R.G., and Pavoni, J.L.; "Algal Flocculation with Synthetic Organic Polyelectrolytes"; Applied Microbiology, 18,6,965 (1965).

68) Teot, A.S.; "The Use of Polymer Science in Preventing Water Pollution"; Ann. N.Y. Acad. Sci., 155,593 (1969).

69) Treweek, G.P and Morgan, J.J.; "Determination of Flocculant Effectiveness in Aggregating Suspended Particulate Matter"; J. Water Poll. Control Fed., 51,7,1859 (1979).

70) Tsubouchi, M., Mitsushio, H., and Yamasaki, N.; "Determination of Cationic Surfactants by Two-Phase Titration"; Anal. Chem., 53,1957 (1981).

71) Turbidimeter HACH Bulletin 2100 A-6ED, HACH Chemical Company, IOWA, USA.

72) Wang, L.K and Shuster, W.W.; "Polyelectrolyte Determination at Low Concentration"; Ind. Eng. Chem., Prod. Res. Dev., 14,4 (1975).

73) Weber Jr. W.J.; "Physicochemical Processes for Water Quality Control"; p61-109 (Coagulation and Flocculation), Wiley-Interscience (1972).

74) Welday, J.M and Baumann, R.E.; "Polymer Characterization Based on Zeta Potential and Filtration Resistance"; J. Am. Water Works Assoc., 71,12,726 (1979).

75) Wimberley, J.W and Jordan, D.E.; "Short Communications"; Analytica Chimica ACTA, 56,308 (1971).

76) Yeh, H.H and Ghosh, M.M.; "Selecting Polymers for Direct Filtration"; J. Am. Water Works Assoc., 73,4,211 (1981).

77) Zeta Meter Inc., Zeta Meter Manual, 2nd Ed., (1968).

78) Gehr, R and Henry, J. G.; "The Adsorption Behaviour of Cationic Polyelectrolytes in Dissolved Air Flotation"; Wat. Sci. Tech., v14, Capetown, 689 (1982).

79) Operating Manual # 168 D, Buchi Evaporators Model R; Brinkmann Instruments, Westbury, N.Y.

APPENDIX - A

Colloid Titration Method

The colloid titration method used in this study for detection of polymers is that developed by Wang and Shuster (72). This method is applicable to both cationic and anionic polymers. As only one cationic polymer was used in the study, only the method used for detection of cationic polymers was described in section 3.5. A slight modification was made to the method in the detection of the end point of the titration. Instead of determining the color change visually, a dip-in-probe colorimeter (PC 800 Brinkman Colorimeter) was used. For determining the correct wave length to be used, percentage transmittance at different wave lengths were determined for titrated and untitrated samples by a Beckman DB.Spectrophotometer. Figure A.1 shows that, at 620nM wavelength, there was a large difference in percentage transmittance between the titrated and untitrated samples. Hence, a 620nM filter was used in the colorimeter for all titrations. The titration was considered to be complete when a large change in percentage transmittance had occurred, as can be seen in figure A.2. This refined method was used in all experiments of this thesis where measurements were made by colloid titration.

It can be seen from the calibration curve in figure A.3 that there was a linear relationship between polymer concentration and titrant volume with a coefficient of regression of 0.99. The reproducibility of results was very

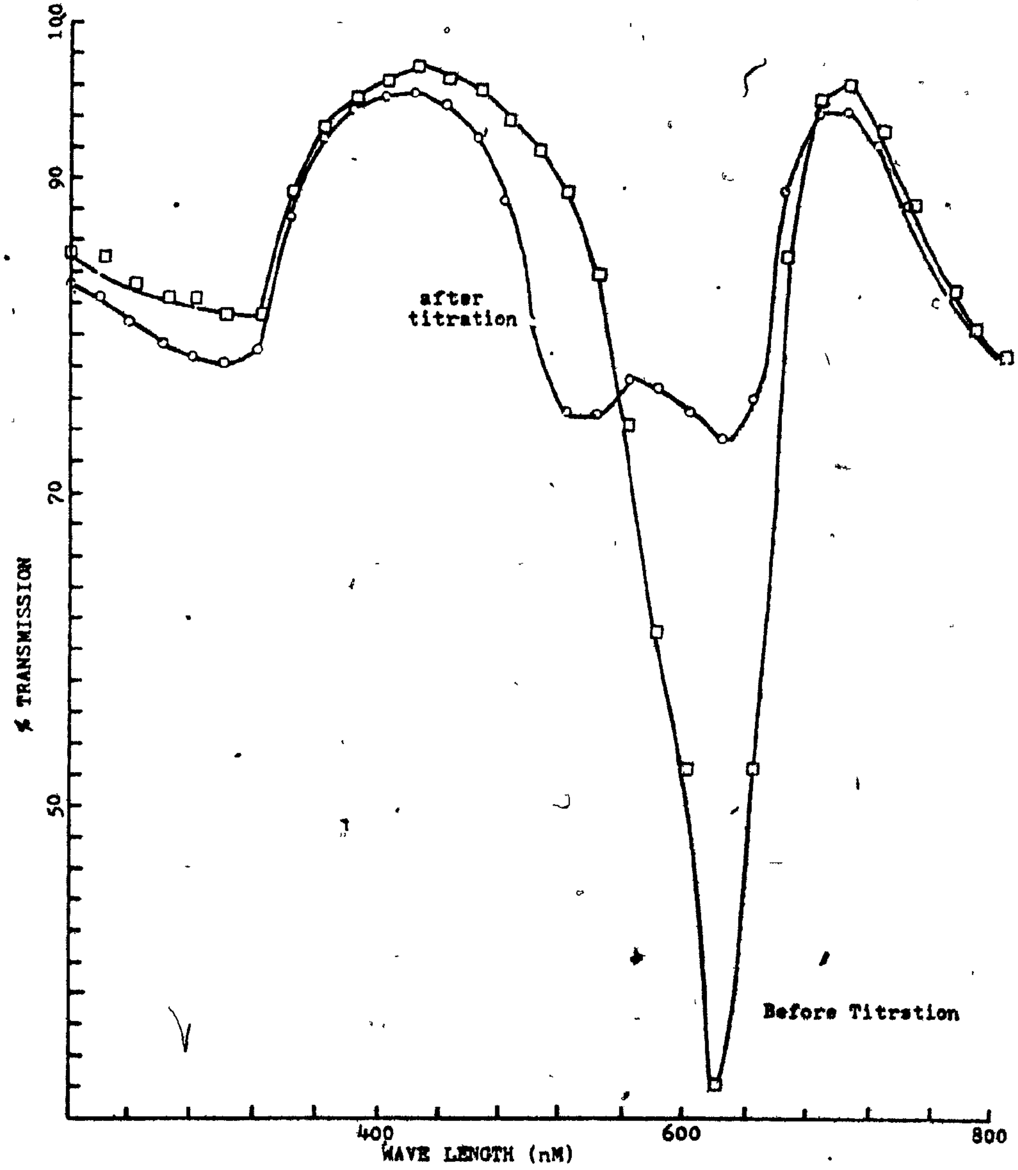
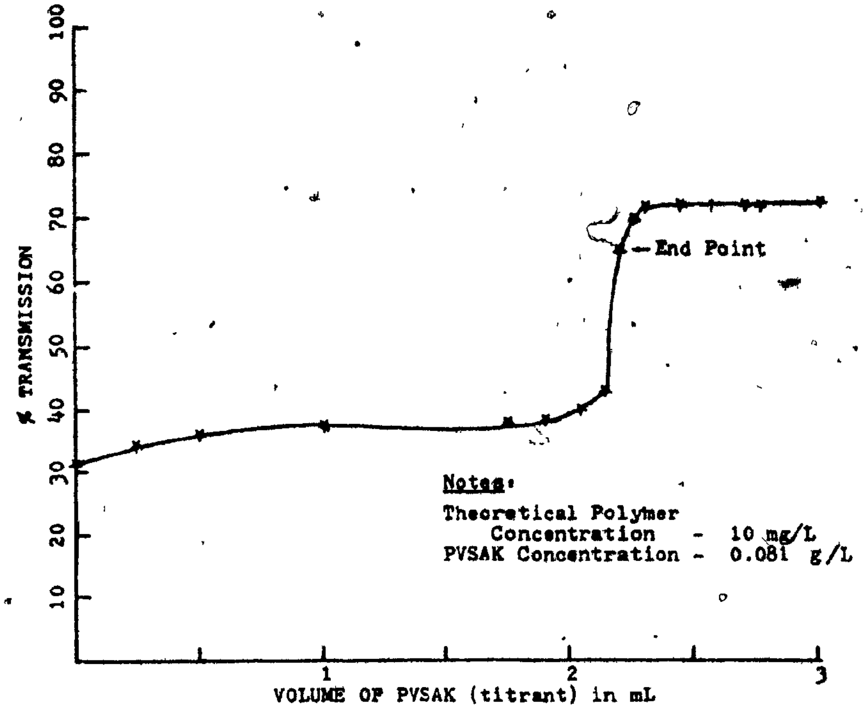


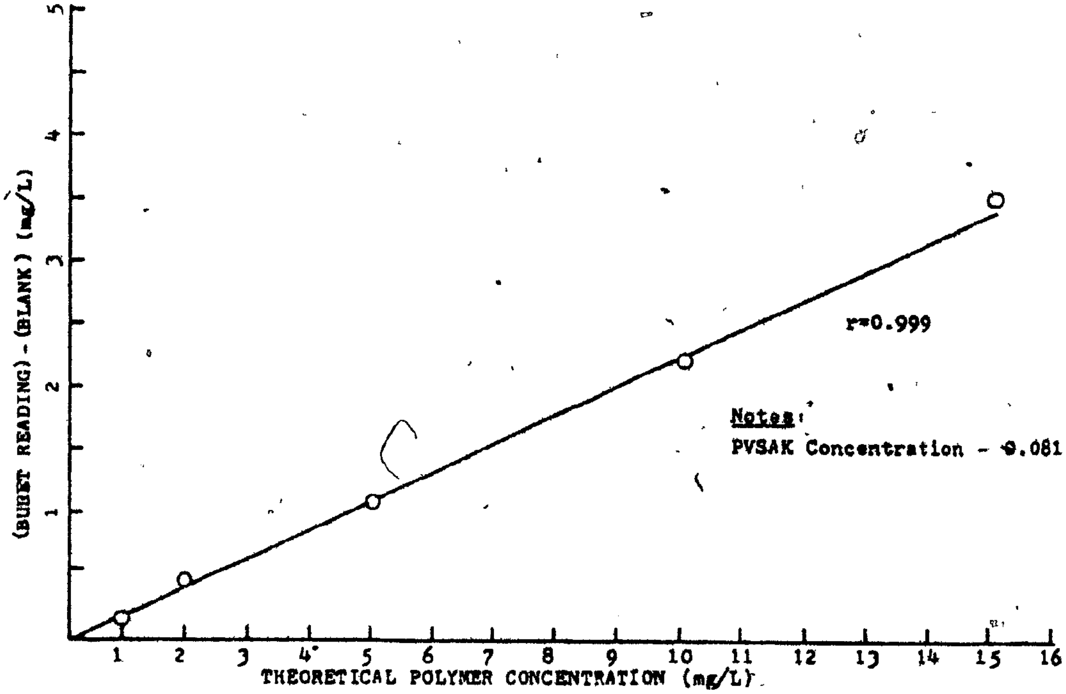
Figure A.1. Wave Length Versus % Transmission



Notes:

Theoretical Polymer
Concentration - 10 mg/L
PVSAK Concentration - 0.081 g/L

Figure A.2. Colorimetric Titration Curve



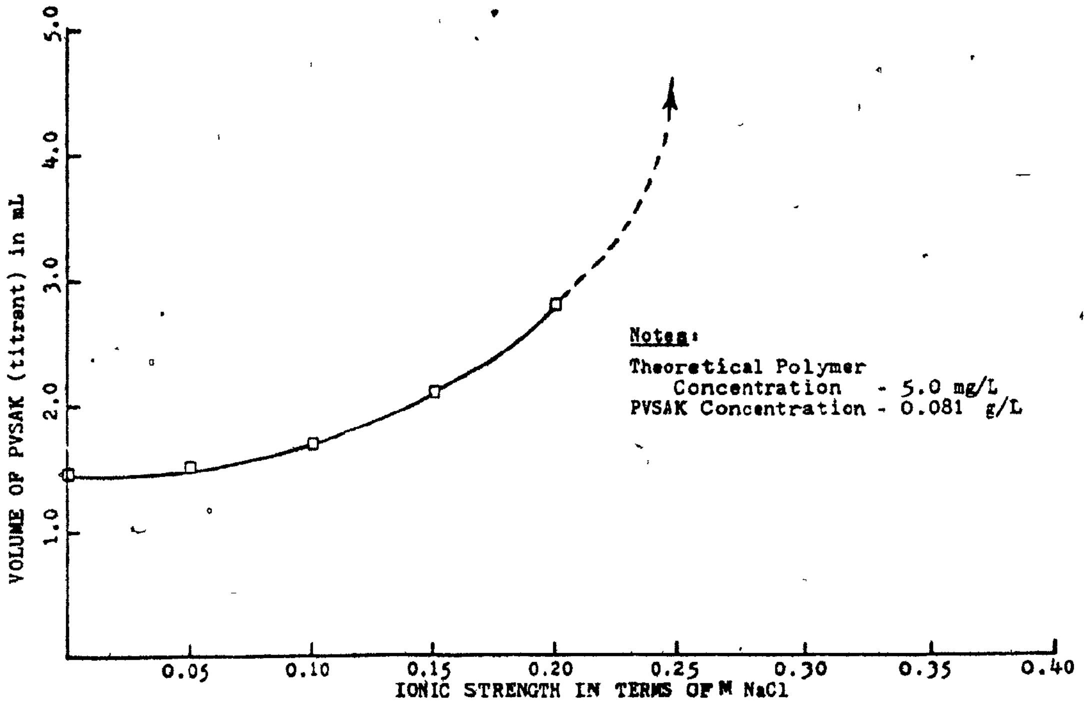
Notes:

PVSAK Concentration - 0.081 g/L

Figure A.3. Calibration Curve for Polymer A Obtained by Modified Colloid Titration Method good and the accuracy was ±0.1 mg/L. By this refined method, the minimum polymer concentration that can be detected accurately without any interpolations is 1.0 mg/L.

A.1 Limitations:

Figure A.4 shows the effect of ionic strength (in terms of M NaCl) on results from the colloid titration method. This shows that the colloid titration method is problematic when the ionic strength of the sample is greater than 0.2M in terms of NaCl. In general, the ionic strength of samples used in experiments in this thesis was 31.8 micro-mhos ($0.80*10^{-3}$M in terms of NaCl).



Notes:

Theoretical Polymer
Concentration - 5.0 mg/L
PVSAK Concentration - 0.081 g/L

Figure A.4. Effect of Ionic Strength on the Colloid Titration Method

APPENDIX - B

VISCOSITY MEASUREMENTS

The decrease in effective polymer concentration due to short-term storage and temperature elevation has been reported in the thesis. Viscosity measurements were performed to conclude whether this decrease was due to polymer breakdown or not. Viscosity measurements were done by measuring the efflux times at 25 °C in an Ubbelohde viscometer. The results obtained are tabulated in table B.1. It can be seen that the relative viscosities and efflux times were decreased in the case of stored and preheated polymers for polymers equal to or below 0.3 mg/L. However, in the above experiment, the sample charge was not reduced. Charge is known to affect the efflux time and hence the calculated viscosity. Hence a set of experiments was done with the charge reduced by addition of 1M NaCl. It was found that efflux times obtained by the blank (solvent) and the sample were the same. This was attributed to the fact that the viscometer is not sensitive at these low polymer concentrations (after the charge effects had been reduced).

No further experiments were conducted. It is therefore still uncertain whether the decrease in effective polymer concentration had occurred due to actual physical breakdown of the polymer into subunits, or whether the cationic charge had been reduced. Either of these occurrences would have caused increased efflux times for the polymer solutions without NaCl addition.

TABLE B.1: Effect of Storage and Elevated Temperatures on Viscosity of Dilute Polymer Solutions

Efflux time in 1/100 minute							
Storage Time	Fresh	1st day	2nd day	5th day	6th day	A	B
Polymer Concentration (mg/L).							
0.0 (solvent)	155						
0.1	168 (1.084)	166 (1.071)	163 (1.052)	164 (1.058)	162 (1.045)		
0.2	194 (1.252)	190 (1.225)	187 (1.206)	186 (1.200)	186 (1.200)	(1.09)	(1.01)
0.3	210 (1.355)	203 (1.309)	201 (1.296)	201 (1.296)	202 (1.303)		
0.5	244 (1.574)	244.5 (1.577)	243 (1.567)	243 (1.567)	244 (1.574)		
1.0	325 (2.096)	325.5 (2.096)	326 (2.100)	326 (2.100)	325 (2.096)		

Notes for Table B.1:

A: Polymer solution subjected to 70°C for 1 hour
B: Polymer solution subjected to 70°C for 4 hours
Solvent is distilled water
Values in brackets indicate viscosities calculated by the formula: $\eta_r = \eta/\eta_o = t/t_o$

where η_r = viscosity ratio
t = efflux time of sample
t_o = efflux time of solvent

APPENDIX - C

LIST OF CANADIAN WATER AND WASTEWATER TREATMENT PLANTS

This survey covers water and waste treatment plants using polyelectrolytes as coagulants in four Canadian provinces. The survey uses information obtained from two major manufacturers selling polyelectrolytes (Allied Colloids and Calgon Corp. of Canada).

Municipality	Plant Name	Average Flow cu.m/d	Application	Flocculant Type
Province of Quebec				
Candiac	Candiac WTP	13619	Potable Water	Non ionic polyacrylamide
Contrecoeur	Centrale de Trait D'Eau	2687	Potable Water	Non ionic polyacrylamide
Dolbeau	Usine de Filtration	9987	Potable Water	Non ionic polyacrylamide
Donnacona	Usine de Traitement	5447	Potable Water	High MW Slightly Cationic
Hull City	Usine de Traitement D'Eau de Parc Mouse	68099	Potable Water	High MW nonionic
Lachute	Usine de Filtration	10895	Potable Water	Nonionic Polyacrylamide
Lauzon	Usine de Filtration	6174	Potable Water	Nonionic polyacrylamide
Lavaltrie	Usine de Filtration	522	Potable Water	Nonionic polyacrylamide
L'Assomption	Usine de Filtration	6809	Potable Water	Nonionic polyacrylamide
L'Islet	Usine de Filtration	-	Potable Water	High MW Slightly Cationic
Mirabel	Usine Depuration de St. Janvier	1452	Sludge Dewatering	High MW Slightly Cationic
Nicolet	Usine de Traitement D'Eau	5302	Potable Water	High MW Slightly Cationic

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Municipality	Plant Name	Average Flow cu.m/d	Application	Flocculant Type
Plessisville	Usine de Filtration de Plessisville	5674	Potable Water	Nonionic polyacrylamide
Quebec	Usine de Traitement	181599	Potable Water	High MW Slightly Cationic
Quebec	Imperial Oil	-	Sludge Dewatering	High MW Slightly Cationic
Repentigny	Centrale de Filtration	8217	Potable Water	Nonionic Polyacrylamide
Riveriere du Loup	Usine de Traitement	8170	Potable Water	Nonionic Polyacrylamide
Roberval	Usine de Filtration	10895	Potable Water	Nonionic Polyacrylamide
St. Agathe	Usine de Filtration	3631	Potable Water	Nonionic Polyacrylamide
St.Francois du Lac	Filtration Conventionelle	-	Potable Water	Nonionic Polyacrylamide
St. Georges (Beauce)	Usine de Filtration	2905	Potable Water	High MW Slightly Cationic
St. Lambert	Usine de Filtration	49939	Potable Water	Nonionic Polyacrylamide
Sorel	Usine de Traitement D'Eau	24520	Potable Water	Nonionic Polyacrylamide
Terrebonne	Usine de Filtration	17705	Potable Water	Nonionic Polyacrylamide
Varennes	Usine de Filtration de Varennes	6968	Potable Water	Nonionic Polyacrylamide
Vaudreuil	Usine Epuration de Vaudreuil	4085	Sludge Dewatering	High MW Slightly Cationic

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Munici-pality	Plant Name	Average Flow cu.m/d	Application	Flocculant Type
Province of Ontario				
Aylmer Town	Aylmer Municipal Plant	7590	Potable Water	High MW Nonionic
Buckingham Town	-	-	Potable Water	High MW Nonionic
Casselman Village	Casselman WTP	404	Potable Water	High MW Nonionic
Chapleau Township	Chapleau Municipal Plant	3314	Potable Water	High MW Nonionic
Chatam City	Chatam WPCP	15889	Sludge Dewatering	High MW Cationic
Durham Town	Durham Sewage Works	1098	Sludge Dewatering	High MW Cationic
Hamilton City	Woodward Avenue Sewage Treatment	239257	Sludge Dewatering	High MW Cationic
Kingston City	Kingston Water Pollution Control	54479	Sludge Dewatering	High MW Cationic
London City	-	-	Sludge Dewatering	High MW Cationic
Marmora Village	Marmora Municipal	499	Potable Water	High MW Nonionic
Midland Town	Midland WPCP	8171	Sludge Dewatering	High MW Cationic
Moosonee	Moosonee WTP	635	Potable Water	High MW Nonionic
North Bay City	North Bay WPCP	31325	Sludge Dewatering	High MW Cationic
Ottawa City	Green Creek Pollution Control Center	267859	Phosphorous Removal	High MW Nonionic
Prescott	Prescott Municipal Plant	31325	Clarification	High MW Anionic
Sarnia City	Sarnia Sewage City	39634	Phosphorous Removal	High MW Anionic
Sault Ste. Marie City	Highland Creek Plant	105781	Phosphorous Removal	High MW Anionic
St. Mary	St. Mary's Municipal Supply	3191	Potable Water	High MW Slightly Cationic

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Munici-pality	Plant Name	Average Flow cu.m/d	Application	Flocculant Type
St. Thomas City	St. Thomas Municipal WPCP	175921	Sludge Dewatering	High MW Cationic
Sudbury City	Sudbury WPCP	49939	Sludge Thickening	High MW Cationic
Toronto	Toronto Main Plant	776339	Sludge Dewatering	High MW Cationic
Toronto	Toronto Main Plant	776339	Sludge Thickening	High MW Cationic
Toronto City	Metropolitan Toronto	-	Potable Water	Poly DADMAC
-	Molson's Brewery	-	Sludge Dewatering	High MW Cationic
-	Molson's Brewery	-	Sludge Thickening	High MW Cationic
-	Ontario Hydro	-	Water Clarification	High MW Anionic
-	Chrysler Canada	-	Flotation	High MW Anionic
-	Collis Leather	-	Sludge Dewatering	High MW Cationic
-	Interlake Steel	-	Wastewater Clarificaion	High MW Anionic
-	Green Gaint of Canada	-	Sludge Dewatering	High MW Cationic
-	Metal Koting	-	Wastewater Clarification	High MW Anionic
Verner	-	-	Potable Water	High MW Nonionic
Windsor City	Little River Pollution Control Plant	100333	Sludge Dewatering	High MW Cationic
			Sludge Thickening	High MW Cationic
			Phosphorous Removal	High MW Anionic
Windsor City	Windsor City Main Plant	127555	Potable Water	High MW Slightly Cationic

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Munici-pality	Plant Name	Average Flow cu.m/d	Application	Flocculant Type
Pronvince of Saskatchewan				
	Buffalo Pound	-	Potable Water	High MW Anionic
Regina City	Regina Wastewater Treatment Plant	61516	Sludge Dewatering	High MW Cationic
Regina City	Regina Wastewater Treatment Plant	61516	Phosphorous Removal	High MW Anionic
Estevan City	Estevan WTP	3722	Potable Water	High MW Anionic
Province of Alberta				
Calgary City	Bonnybrook Sewage Treatment Plant	282097	Sludge Thickening (Flotation)	High MW Cationic
	Indian Affairs		Potable Water	High MW Anionic