THE EFFECTS OF BRANCHING AND OTHER PHYSICAL PROPERTIES OF ANIONIC POLYACRYLAMIDES ON THE FLOCCULATION OF DOMESTIC SEWAGE

by

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I. INTRODUCTION

In recent years there has been an increased emphasis on the reduction of water polluting material that enters streams and lakes from all sources, in particular from sewage treatment plants. This emphasis has prompted the search for chemical additives to improve the operation of existing treatment facilities. As a part of this search, an in-plant demonstration was conducted in Cleveland which showed that anionic polyacrylamide significantly improved primary clarification in the waste treatment scheme.

To this point in time, very little information has been published regarding the effect of the variable properties of anionic polyacrylamide on its flocculation activity for domestic sewage. The properties which can be expected to vary between commercial sources are average molecular weight, molecular weight distribution, degree of hydrolysis of the amide groups, degree of branching of the polymer structure and the presence of impurities.

Upon examination of the Bridging Theory of LaMer and co-workers, it is obvious that these variables could and do have an effect on the flocculation activity of anionic polyacrylamides.

The one most notable property of anionic polyacrylamide which has not been studied with respect to flocculation activity is branching. The purpose of this investigation was to determine the effect of branching of the molecular structure on the flocculation activity of anionic polyacrylamides for domestic sewage in the primary clarification process.

II. LITERATURE REVIEW

The following survey of available literature gives a general coverage of publications which are concerned with the production of anionic polyacrylamide, application of this polymer to the flocculation of sewage, light scattering for polymer characterization, and the polymer bridging theory as a flocculation mechanism. There is little previously published information regarding the major relevant area of interest, namely, the effect of branching on the flocculation activity of anionic polyacrylamide.

The Polymer Bridging Mechanism

The polymer Bridging Mechanism is an important, relatively new theory which is useful in understanding from a physical standpoint the nature of many coagulation and flocculation processes.

Introduction. The use of synthetic organic polymers as flocculation aids in the treatment of water and wastewater has been rapidly increasing. It has been observed that the most economical treatment was obtained with anionic polymer, even though the solid particles in the sewage were often negatively charged (1). It was obvious that these observations could not be explained by a simple electrostatic model. LaMer and co-workers have developed a bridging theory which provided an acceptable qualitative model for the ability of polymers to destabilize colloidal dispersions (2). The first step in understanding the Bridging Model is to describe and understand the mechanism of particle transport and removal.

Mechanism. When considering coagulation it is important to

distinguish between two separate and distinct steps. First, the particles must have been brought or transported into contact to effect the possible formation of larger particles. Second, the particles to be aggregated must have been able to adhere to each other when brought into contact (2). Both particle transport and destabilization may be brought about in several ways.

Destabilization of a colloidal suspension may be accomplished by three different mechanisms. Destabilization can be brought about by an "indifferent" electrolyte through compression of the electrical double layer surrounding the collodial particle, it may occur through neutralization of the charge on the particle by the specific adsorption of a coagulant of opposite charge, or it can occur through the formation of a polymeric molecular bridge between two colloidal particles (2). The contacts between particles may have occurred by Brownian Diffusion, agitation and fluid motion, and by differential settling. Before moving into the actual Bridging Theory, the term flocculation must be defined and understood.

Flocculation. There exists in the literature today, a considerable amount of misrepresentation between the two terms, coagulation and flocculation. For the purpose of this dissertation, these terms must be defined. To coagulate, comes from a Latin word meaning to "drive together", whereas to flocculate, means to form a floccule, a material similar to a tuft of wool or a loose fibrous structure. From this point on, the term flocculation will be restricted to a special case of coagulation in which the final structure, usually promoted by the bridg-

ing action of macromolecules, is a loose three dimensional network having pores which permit easy filtration (3). At this point, the polymer Bridging Theory will be discussed.

Theory. Various properties of colloidal dispersions have been used to follow the change from dispersed to flocculated phase. Some of the more important parameters are turbidity of supernate, sediment volume, subsidence ratio, and filtration rate (3). The last operation involves a measurement of the time to refilter a given volume of supernate solution through a deposited cake of flocculated particles. In the flocculated state the rate of filtration approaches its maximum value, whereas in the dispersed state it is a minimum (3). The following theoretical development by LaMer and Healy (3) correlated the bridging model with the filtration rate parameter.

The following sections are divided into three main categories, namely, polymer and surface parameters, flocculation reaction parameters, and filtration rate parameters. They are presented in this order so that each step of the theory can be expounded and eventually lead to the concluding proof of the filtration rate technique for quantitative evaluation of the anionic polyacrylamide's use in sewage flocculation.

Polymer and Surface Parameters: A polymer molecule may be considered to consist of an average of τ segments, and β of these segments per molecule adsorb and occupy surface sites previously occupied by solvent molecules. It may be assumed that a polymer segment is equal in size to a surface site. The term $(\tau-\beta)$ is, therefore, the number of extended segments per polymer molecule.

Next, assume in a unit volume that (P_o-P) moles of polymer concentrate at the interface, where P_o is the added polymer and P is the residual in solution after adsorption. Then $(P_o-P)N$ molecules concentrate at the interface, where N is Avagadro's number. Therefore, since each polymer has τ segments, then $(P_o-P)N\tau$ segments concentrate at the interface. If the fraction β/τ were adsorbed and occupied surface sites, then:

$\beta(P_o-P)N\tau/\tau$ = number of surface sites covered, and

(I) $\beta(P_o-P)N/sS_\theta = \theta$ = fraction of surface sites covered,

where:

s = the number of surface adsorption sites per unit area, and

S_θ = the surface area of the adsorbent.

Equation (I) can be rearranged to the following form:

(II) $P = P_o-K\theta/\beta$, where $K = sS\theta/N$.

It was found that in many polymer-solid adsorption systems, that the adsorption equation of Langmuir described the experimental data. According to Langmuir, the fraction of the adsorbate, θ, is related to the equilibrium concentration of polymer in the solution, P, as follows:

(III) $\theta = bP/(1 = bP)$, where b is a constant.

From Equations (II) and (III), it may be shown that the fraction of the surface covered by the polymer is related to the initial concentration of polymer by the following equation:

(IV) $\theta = P_o/[b^{-1}(1 = bK/\beta) + P_o(1 + bK/\beta)^{-1}]$

The significance of the preceeding development lies in the fact

that there is now an expression for the fraction of the surface covered by the polymer which can be related to the filtration rate parameter, which in turn will allow the optimum polymer dose, P_o, to be quantitatively determined. But before moving to the filtration rate, the flocculation reaction parameters must be discussed.

Flocculation Reaction Parameters: The model that was assumed and used to describe the polymer flocculation was developed by Smellie and LaMer (4) and was extended by Healy and LaMer (5). It was postulated that one end of a polymer chain, attached at its other end to a solid particle, then attached itself to an uncovered surface on a second particle, producing a network that leads to flocculation.

The rate of floc formation, $-dn_o/dt$, expressed as a decrease in the number of primary particles, was dependent upon the product $\theta(1-\theta)$ and was given by:

$$-dn_o/dt = K_1 n_o^2 \theta(1-\theta) \qquad \text{(V)}$$

The bridging mechanism advocated here involved a bimolecular process where $n_o\theta$ represented the "concentration" of active species containing flocculant, and $n_o(1-\theta)$ represented the "concentration" of species with open surfaces able to react with the first species not containing flocculant.

This equation was not able to explain the overall behavior of the system. It was observed that the system first flocculated, and then either increased time of agitation or with increased polymer concentration, the system redispersed. It was then assumed that the flocs grew according to Equation (V) until the floc of m primary particles, known

as the critical floc was attained. At this point, an empirical equation was used, since the specific reactions involved were not well characterized.

Therefore, for a given degree of agitation, A, a given total concentration, and a constant floc shape, the drag on the floc varied approximately with the floc size where this was defined by the floc radius R. The increase of primary particles with time was expressed, with reference to the drag on the floc, as

(VI) $dn_o/dt = K'_2 R$, where K_2 was a constant, and $K'_2 = K_2[\theta(1-\theta)]^{-1}$.

This equation had to satisfy certain boundary conditions:

A. When no polymer was adsorbed ($\theta=0$) the A_m floc disintegrated spontaneously, and dn_o/dt approached infinity;

B. When the surface was fully covered ($\theta=1$), polymer bridges were unable to form, and dn_o/dt approached infinity; and,

C. At half surface coverage ($\theta=.5$), the bridging model predicted that the A_m floc, or any floc, would have maximum stability, the dn_o/dt attained its maximum value for any given R.

The optimum floc size under any given set of conditions was shown to occur when the rates of floc formation and destruction were equal. Also the steady state floc size was shown to be

(VII) $R = K_1/K_2 n_o^2 \theta^2 (1-\theta)^2$.

In conclusion, the most important point in this section was that at half surface coverage, the floc would have maximum stability. This result of the bridging model will be important in the following sec-

tion which relates to the filtration rate parameters.

Filtration Rate Parameters: The filtration rate, Q, was shown to be inversely proportional to the square of the specific area, S, of the solids in the filter cake. When a slime was flocculated, the effective specific area was reduced to smaller values corresponding to increased filtration rates,

(VIII) $Q = K/S^2$

If Q_o is the filtration rate of an untreated dispersion, and r is the radius of the primary particles, then it was shown from Equations (VII) and (VIII) that

(IX) $Q-Q_o = (Q_o/r^2)\ (K_1^2/K_2^2)\ W^4\theta^4(1-\theta)^4.$

Equation (IX) shows immediately that at $\theta = .5$ [$\theta^4(1-\theta)^4 = 1/256$] a maximum in $(Q-Q_o)$ is achieved.

At this point, it was possible to express the filtration rate for a given added concentration of polymer in terms of the fundamental parameters b for the surface, and β and τ for the polymer. The fraction θ, given by Equation (III), can be substituted into Equation (IX) to yield a relationship between Q and P_o. It was found experimentally that at $P_o = P_m$, the filtration rate passed through a maximum, denoted by Q_m. The parameter P_m was defined as the optimum concentration of polymer under a given set of conditions.

(X) $Q-Q_o = [(Q_o/r^2)\ (K_1^2/K_2^2)\ W^4\ (bP/(1 + bP)^4\ (1-bP/(1+ bP)]^4$

the optimum point was the point (P_m,Q_m), $dQ/dP_o = 0$, at $P_o = P_m$.

In summary, the practical significance of this Bridging Theory lies in the fact that one can relate the optimum polymer dose needed in

the physical system to a qualitative parameter, the refiltration rate. In addition, this optimum polymer dose corresponds to the optimum solids removal as proven by studies on synthetic samples (3). At this point in the discussion, several aspects still need further clarification, namely, the controlling factors and their rates, electrical charge interactions and the multipositive cation effect.

Discussion. From the preceeding bridging theory, several aspects were found to warrant additional description. It must be stated at this point that the adsorption parameter, b, the number of segments adsorbed per molecule, β, and the number of extended segments per molecule ($\tau-\beta$) were the controlling factors in determining the adsorption-flocculation behavior for the polymer-solid system when P_o, A, time of agitation, and polymer molecular weight were varied from a physical viewpoint (5).

Next, when considering the relative rates of flocculation, the rate of adsorption of polymer promoting the flocculation was considered to consist of two steps (5,6). The reasoning behind this is still in the realm of intuition and physical experience borrowed from other processes and systems, because at the present time, no methods have been developed to measure these component consecutive rate processes. The first step, attachment of part of the polymer molecule to the surface, must have been fast, and the second step, unrolling of the polymer on the surface as a thin film, must have been slow and was the rate determining step. Thus the bridging process was considered slow because a polymer adsorbed on one particle must find another particle

that had a free surface available to complete the bridge.

One area of interest to colloidal suspensions was not taken into account in the polymer Bridging Theory. The following section discusses the electrical charge interactions as viewed by LaMer. LaMer concluded in 1951 that in flocculation studies electric charge was a secondary factor compared to the chemical adsorption of polymers with subsequent bridging as the main factor in polymeric flocculation. The fact that negatively charged polymers when acting on negatively charged colloidal particles induced more rapid and complete flocculation than did many positively charged polymers on the same particles offered seemingly incontrovertable evidence that chemical attractions between polymer and particle, when acting at short distances, overbalanced long range electrostatic effects (5).

Finally, in the middle of the 1960's, an additional school of thought formed with regard to anionic polymers and their flocculation of anionic colloidal particles. This school believed that a multipositive cation was needed between the colloid and the polymer, and their assumption was proven to be correct (7,8). Black's results showed that flocculation by an interparticle bridging mechanism was the principle mode of action of anionic polymers in dilute clay (negative) suspensions. A sufficient concentration of counterions must have been initially present in or added to the suspension; however, in order to reduce particle-particle, polymer-particle, and adsorbed polymer-polymer repulsive forces, so that interparticle bridging could occur (7), Sommerauer proposed the mechanism of the multipositive cation action (8):

A. Ca^{+2} ions accumulate in the double layer. This step is fast, and is accompanied by a compression of the double layer.

B. The approach of the partially surface active anionic polymer to surface is thus facilitated.

C. Complex formation between Ca^{+2} in the double layer and the functional groups on the surface, lower the electrochemical free energy of attachment. Correspondingly, the extent of adsorption is increased.

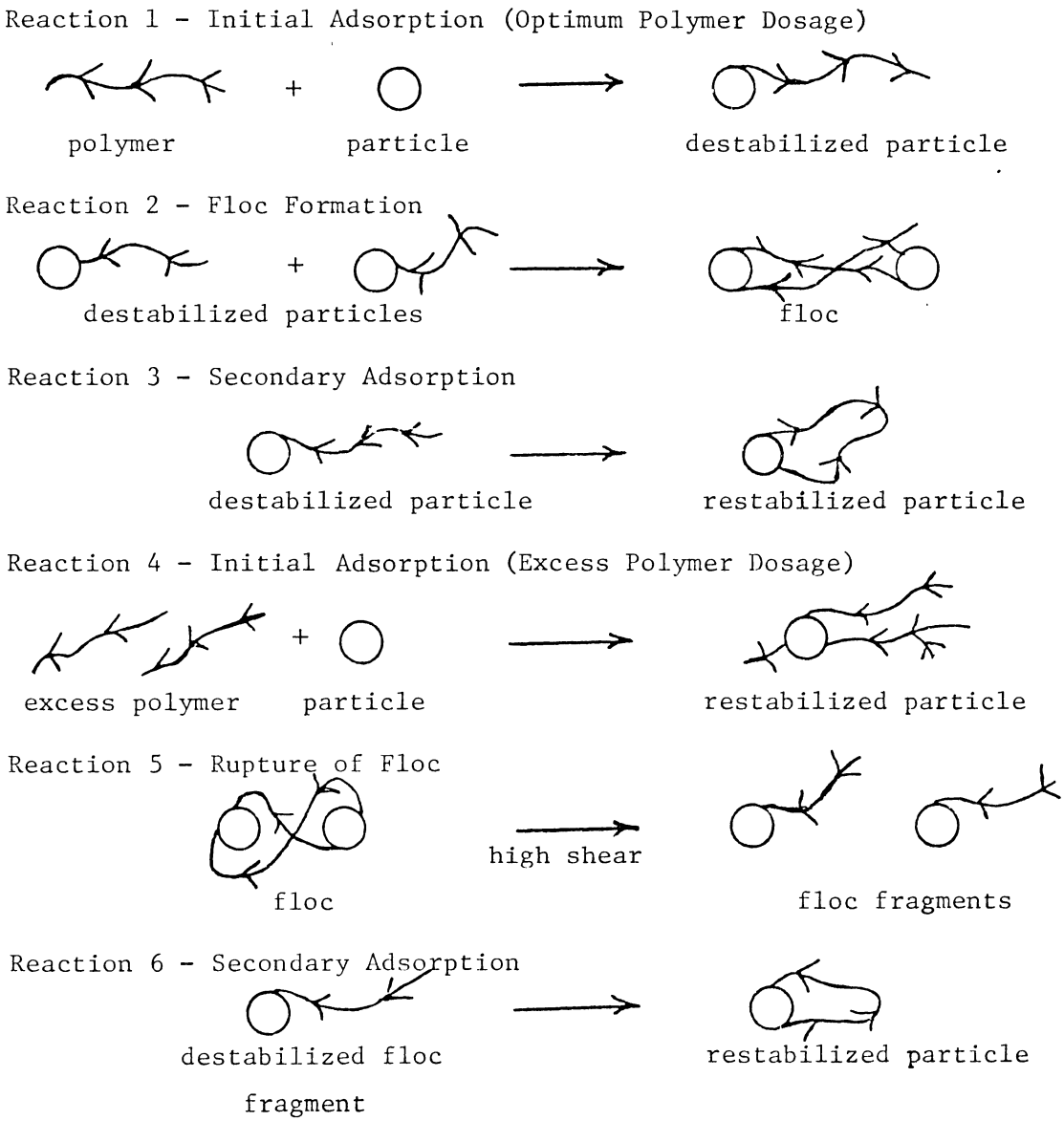
D. Now, as proposed by LaMer, individual particles are bridged together through polymer chains.

It must be remembered that the multipositive cation effect is not a contradiction of the Bridging Theory, but a complement to it.

In summary, the bridging model was pictorially simplified by O'Melia (2) showing the effect of several parameters (Figure 1). To be effective in destabilization, a polymer molecule must contain chemical groups which can interact with sites on the surface of the colloidal particle. When a polymer molecule comes into contact with a colloidal particle, some of these groups adsorb at the particle surface, leaving the remainder of the molecule extending out into the solution (Reaction 1). If a second particle with some vacant adsorption sites contact these extended segments, attachment can occur (Reaction 2). A particle-polymer-particle complex is thus formed, in which the polymer serves as a bridge. If a second particle is not available, in time the extended segments may eventually adsorb on other sites on the original particle, so that it is no longer capable of

Figure 1

The Bridging Model



serving as a bridge (Reaction 3).

Dosages of polymer which are sufficiently large to saturate the colloidal surfaces produce a restabilized colloid since no sites are available for the formation of polymer bridges. In other words, it is possible to overdose the system with polymer (Reaction 4). Under certain conditions, a system which has been destabilized and aggregated can be restabilized with extended agitation, due to the breaking of polymer surface bonds and the folding back of the extended segments on the surface of the particle (Reactions 5 and 6).

Light Scattering

The subject of light scattering for molecular weight determination and analysis of branching is grouped in the following section.

Theory. Of the many methods that have been used in the characterization of the physical chemistry properties of polymers, the light scattering technique has been one of the most useful. The following discussion was designed only to give the reader a basic introduction to light scattering. For a detailed theoretical analysis, the reader is referred to the literature available (9, 10, 11).

Experimental data on the light scattering characteristics of polymer solutions have been evaluated to give the weight average molecular weight of the dissolved polymer, the size of the polymer molecule in solution (radius of gyration), and the chemical potential of the solvent.

The basis of light scattering measurements is very simple. A beam of monochromatic light is passed through a polymer solution, and

the intensity of the light scattered in various directions as it emerges from the solution is measured. The degree of scattering of the light beam is related to the size and number of particles in solution (12).

The fundamental expression for the determination of the weight of a particle in a fluid by light scattering is

(XI) $$Hc/\tau = 1/M$$

The equation relates weight concentration, c, and turbidity, τ, to the particle weight, M, by means of a proportionality constant H, which includes the refractive index effect (12).

However, since most systems of interest are not ideal, an extended form of the above equation has to be used to adjust for deviation from ideal behavior:

(XII) $$\frac{Hc}{\tau} = \frac{1}{M} + 2Bc + 3Dc^2 + \ldots$$

The constants B and D are the second and third virial coefficients, similar to those of the osmotic pressure equation (12).

Zimm's Method. Zimm has devised a method of determining molecular sizes and shapes from scattered light measurements made at various angles and polymer concentrations. These measurements were extrapolated to zero angle and concentration on a chart where $y(c,\theta)$ was plotted against $x(c,\theta)$. The intercepts of these two extrapolated lines should have been identical and were equal to the reciprocal of the weight average molecular weight. The slopes of these lines also gave information that led to the size of the molecule in solution and to its solvent interaction properties.

Zimm used the Pavelich Regression Model,

$$\text{(XIII)} \qquad \frac{Hc}{\tau} = \frac{1}{M} + 2Bc + 3Dc^2 + \frac{1}{3M}\left(4\pi r_g \frac{N}{\lambda}\right)^2 \operatorname{Sin}^2\frac{\theta}{2} + G_1 \operatorname{Sin}^4\frac{\theta}{2} + G_2 c \operatorname{Sin}^2\frac{\theta}{2}$$

This regression equation was rewritten into least squares form,

$$\text{(XIV)} \qquad y = A_1 + A_2 c + A_3 c^2 + A_4 s^2 + A_5 s^4 + A_6 cs^6$$

where:

$y = y_{ij}$ = measured light intensities at concentration i and angle j,

$c = c_i$ = concentration i, and

$s^2 = \operatorname{Sin}^2\frac{\theta}{2}$ j = Sine squared of 1/2 angles j of the scatter.

Once the coefficients of the regression equation were found, the properties of the polymer were:

$M = 1/A_1$ = weight average molecular weight

$B = A_2/2$ = second virial coefficient

$D = A_3/3$ = third virial coefficient, and

$r_g = \left(\frac{\lambda}{4\pi N}\right)\left(\frac{3A_4}{A_1}\right)^{1/2}$ = radius of gyration

where:

λ = wavelength of light in the median of refractive index N,

N = refractive index of the mixture.

In conclusion, it must be stated that the previously described light scattering theory was dependent on two essential conditions (13).

1. That the polymer molecules were isotropic, and

2. That a finite but not too large difference existed between refractive indices of the solution and the solvent.

The first condition was satisfied if the polymer configuration was approximated by the random coil model. The second condition set practical limits on the solvents which were used for a particular polymer. The refractive index differences have been shown to cause scattering. Obviously, the larger the difference in refractive indices, the larger was the degree of scattering.

Finally, the problem of clarification of the solutions and solvent from dust must be mentioned. Generally speaking, centrifuging and/or filtering the liquids through sintered glass discs was proven successful, but it cannot be stressed too highly that great care has to be taken if large errors due to the presence of dust were to be avoided (13).

Anionic Polyacrylamides

The subject of the polymer is grouped under three headings: polymerization kinetics, production, and properties.

Kinetics of Formation. Before the production kinetics of the polymer was studied, the chemical structure of the monomer and the polymer had to be discerned. These results are shown in Figure 2.

The actual production of acrylamide polymer is normally carried out in solution (water) by a process known as chain polymerization. A shorthand notation for this process is (14):

Initiation:

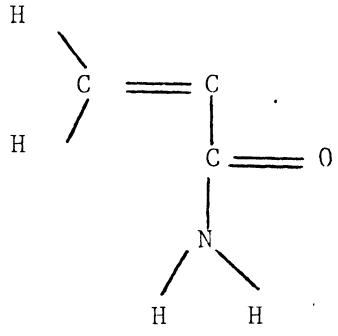
(XV) $I \xrightarrow{R_i} 2R\cdot$ (free radical production)

and $R\cdot + M \xrightarrow{R_2} RM\cdot$

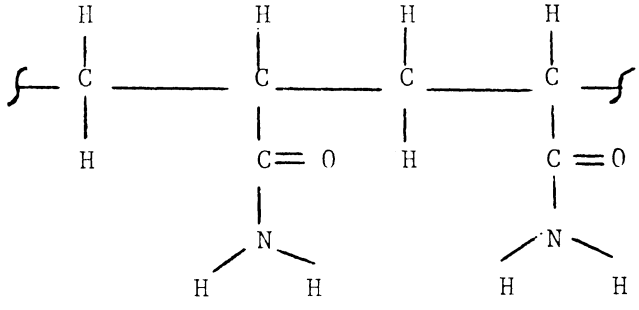
Figure 2

Structure Of The Monomer and Polymer Forms

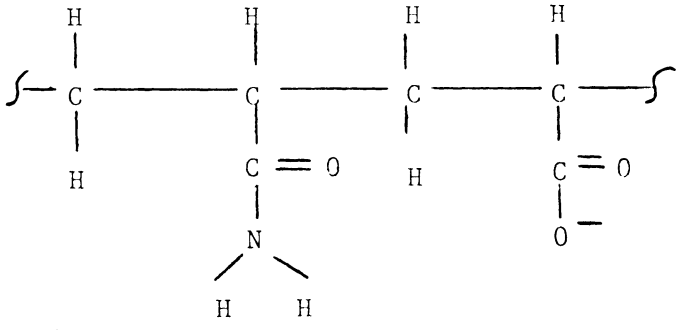
Monomer:



Non Ionic Polyacrylamide:



Anionic Polyacrylamide:
(Hydrolyzed)



Propagation:

(XVI) $RM\cdot + M \xrightarrow{R_p} RM_2\cdot$

or $RM_n\cdot + M \xrightarrow{R_p} RM_{n+1}\cdot$

Termination:

(XVII) $RM_n\cdot + RM_m\cdot \xrightarrow{R_t} R_2M_{n+m}$ (coupling)

or $RM_n\cdot + RM_m\cdot \xrightarrow{R_t} RM_n + RM_n$ (disproportionation)

where:

I = initiator concentration

R·'s = radical concentrations

M = monomer concentration

RM's = polymer concentrations, and

R_1, R_2, R_p, and R_t = reaction rates.

The kinetic model consistent with this mechanism is simple provided the following assumptions are valid:

1. The reaction proceeds slowly enough that a steady state is reached, where the radical population does not change rapidly with time.

$$\frac{d[R\cdot]}{dt} = \frac{d[M\cdot]}{dt} = 0$$

Material balances then give

(XVIII) $$2\ R_i[1] - R_2[R\cdot]\ [M] = \frac{d[R\cdot]}{dt} = 0$$

2. The propagation reaction occurs so much more often than the others that it is effectively the only consumer of monomer.

$$\text{Rate of polymerization} = R_p = \frac{-d[M]}{dt} = k_p[M\cdot]\ [M]$$

Under these conditions, a first-order dependence on monomer and half-order dependence on initiator is indicated:

$$(XX) \qquad R_p = R_p\left(\frac{R_i}{R_t}\right)^{\cdot 5} [M]\,[I]^{\cdot 5}$$

If only a certain fraction, f, of the initiator fragments can successfully react with monomer:

$$R_p = R_p\left(\frac{fR_i}{R_t}\right)^{\cdot 5} [M]\,[I]^{\cdot 5}$$

Finally, from R_p a simple approximation of the molecular weight that can be expected may be calculated by using a new term, the kinetic chain length, V_n. It is defined as a number of monomer units converted per initiating radical so that:

$$(XXI) \qquad V_n = \frac{\text{rate of monomer consumption}}{\text{- rate of radical formation}} = \frac{R_p}{2R_i[I]}$$

In summary, by relating various reported values of R_p/R_t from the literature with the half lives of the initiators, the desired molecular weight can be calculated before experimentation.

Production. Anionic polyacrylamide has been produced by the co-polymerization of acrylamide and acrylic acid (15) and various other methods (16-26). However, a commonly used commercial process involved a simultaneous homo-polymerization and hydrolysis of acrylamide in an alkaline, aqueous solution. The typical catalyst is a free radical initiator, and some of the typical hydrolyzing agents are sodium carbonate and sodium hydroxide. The resulting polymer is a high molecular weight, high charge density polyelectrolyte with an upper limit of hydrolysis ranging from about 25 percent (27) when sodium hydroxide was used to greater than 40 percent when sodium

carbonate was used.

In addition, polyacrylamide has been hydrolyzed after polymerization using caustic, which converted an uncharged polymer to an anionic polyelectrolyte (28). Michaels has reported that the hydrolysis of polyacrylamide using sodium hydroxide was increased to more than 60 percent at the amide groups by using a large excess of caustic, and by boiling and evaporating the reacting solution (29).

Gleason, Miller, and Sheats (30) in a study which used radiotagged monomer reported the formation of branched molecular structure during the polymerization of acrylamide in aqueous solution using a redox catalyst. A sodium meta bisulfate-sodium persulfate redox pair were used to produce both the linear and the branched fractions. The polymerization temperatures were 50°C for the linear formation and 78°C for the branched formation. The monomer concentrations for both formations were approximately the same, but the catalyst concentrations at 78°C were 10 percent of those used at 50°C.

Properties. Anionic polyacrylamide has been available either in aqueous solution or in the dry form as a flaky powder. Carr had listed most of the commercial names, properties, and manufacturers of polyelectrolytes, including anionic polyacrylamide, which have been marketed in the United States (3).

In general, polyacrylamide has been characterized as a very high molecular weight, stable, and water soluble polymer. Norris regarded 200,000 as a low molecular weight and 20 million as an extremely high molecular weight for polyacrylamide (15). Riddick has stated that most

anionic, natural and synthetic, polymers which were used in water treatment flocculation range from 500,000 to 1,000,000 or higher in molecular weight (32). O'Melia has stated that when anionic polymers were used, it appeared that a minimum size was necessary for these molecules to bridge the potential energy barrier between two negative colloidal particles (2). This minimum size was dependent upon such factors as the number of charged groups and the degree of branching of the polymer, the charge of the colloidal particles, and the ionic strength of the solution. Limited data has suggested that this minimum size corresponded to a molecular weight of approximately one million.

Flocculation of Domestic Sewage

The information regarding flocculation is described as it relates to theoretical mechanisms and application to primary clarification in domestic sewage treatment.

Domestic sewage has been shown to be a dilute, heterogeneous potpourri of dissolved materials and colloidal particles. The colloidal particles are usually polydispersed and have non-uniform charge intensity (33). Such colloidal particles range in size from one micron to ten angstroms in diameter and are essentially electronegative (32).

The most common scheme that has been used in the treatment of domestic sewage today consists of grit settling, primary clarification, aerated biological treatment, secondary clarification, and disinfection. The purpose of the grit chamber is to remove inorganic

solids. The next unit, the primary clarifier, is used to settle out the remaining settleable solids, normally organic in nature. The aerobic treatment unit is designed to remove most of the biodegradable and dissolved organics which are in the effluent stream of the primary clarifier. The secondary clarifier is used to remove almost all of the settleable solids from the aerobic treatment unit. Finally, the effluent from the secondary clarifier is normally disinfected with chlorine before being discharged to surface waters. In this research, the polyacrylamides were used to increase the efficiency of the primary clarifier.

Theoretical Mechanisms. In studies that use clay suspensions, many researchers have concluded that the addition of some multivalent cation was necessary for the initiation of coagulation of the electronegative colloidal particles to form settleable aggregates (34). Subsequently, the anionic polyelectrolyte was adsorbed on the surface of two or more aggregates to form larger aggregates referred to as flocs. (This mechanism is called the bridging mechanism, and was referred to earlier in the Literature Review.) The noted effect of bridging was an increase in the rate of settling (28).

Whatever the mode of polymer attachment, the configuration of the polymer molecule at the liquid-solid interface will influence the bridging action. Warrenton and Miller (35) have demonstrated that long chain anionic polymer can remove turbidity better than short chain polymers. Michaels (29) has shown in controlled hydrolysis experiments that anionic polymers should possess a sufficient number of charged

sites to extend the polymer chain thus allowing interparticle bridging to occur. If, however, the charge density of the polymer is too large, adsorption on the negative surface will have been reduced or inhibited. This phenomena was illustrated by Michaels (29) in Figure 3.

Application to Primary Clarification. A significant improvement in rate and degree of flocculation of domestic sewage was achieved by using both anionic polyacrylamide and a multivalent cation (36). However, polymer flocculants were only effective in improving removal of gross solids and colloidal solids. Soluble organic matter was not removed by polyelectrolytes, but passed through the primary clarifier and into the aerobic biological treatment unit.

In a full-scale demonstration at the Cleveland Easterly Treatment Plant, which was authorized under a Federal Water Pollution Control Administration Grant, a commercial anionic polyacrylamide, Purifloc A-23, was used in the primary clarifier operation (37). At an optimum dosage of 0.25 ppm, addition of the polymer was found to increase the suspended solids and biochemical oxygen removal in the primary clarifier by thirty-nine and thirty-five percent. The sewage to the plant contained enough multivalent metal cations from the cities' industries that no cation addition was necessary.

Summary

From the information presented in the previous sections concerning this investigation, it can readily be discerned that the polymer Bridging Theory is well defined in today's literature. On the other

Figure 3

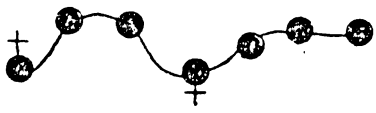
The Effect of Hydrolysis On Polyacrylamide Character

Amide

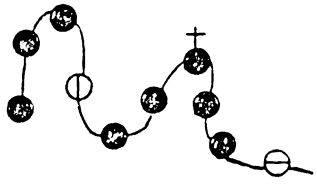
Carboxylate

Amidinium

Unhydrolyzed, Weakly Cationic, Slightly Extended Chain, Mediocre Flocculant

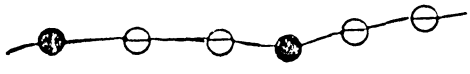


Slightly Hydrolyzed, Non Ionic, Tightly Coiled Chain, Poor Flocculant



33 percent Hydrolyzed, Anionic, Loosely Coiled Chain, Good Flocculant

67 percent Hydrolyzed, Strongly Anionic, Extended Chain, Poor Flocculant



hand, the literature concerning the actual use of polyelectrolytes in water and waste water treatment is rather limited at best. A relatively small amount of information has been published regarding the effect of molecular weight and the degree of hydrolysis on the flocculation activity of anionic polyacrylamide, but no literature has been published to this point in time regarding the effect of long chain branching in polymers on the flocculation activity in domestic sewage treatment.

As stated in the introduction, the purpose of this thesis is to investigate the effect of branching on flocculation activity for anionic polyacrylamides. In addition, the effect of optimum polymer dosage versus weight average molecular weight will be determined for the flocculation studies for both linear and branched fractions. In conclusion, the reason for this study is that the effect of branching versus linearity on anionic polyacrylamide flocculation is not known.

III. DESCRIPTION OF EXPERIMENTAL METHODS

The following sections discuss, in detail, the experimental methods used to produce, to characterize, and to evaluate the linear and branched polyacrylamides used in the flocculation studies.

Polymer Production

The main parameters in the polymerization process which were controlled to produce the varied structures of the anionic polyacrylamides, were the reactant levels, nitrogen purge, and temperature control.

Reactant Levels. Two previous studies of the polymerization of acrylamide were presented in the literature which used the same redox couple as this investigation (25, 30). Unfortunately, their reported molecular weights were too low to be considered useful in the flocculation of domestic sewage. Therefore, the catalyst levels had to be drastically reduced to attempt to achieve the desired molecular weight. The redox catalyst levels were varied from .0200 to .0041 grams of ammonium persulfate and .0048 to .0010 grams of sodium metabisulfite. In all the reactions, the volume of distilled and deionized water used as the polymerization medium was 2.5 liters. Also for each reaction, 250 grams of acrylamide was used as the monomer concentration. In order to speed up the polymerization rate, an accelerator of ferrous sulfate was added in levels between .0007 and .0100 grams to several of the reactions. All the reagents were used as received without any purification steps.

The polymerization reactor was all pyrex and was stirred con-

tinuously with a stainless steel shaft and a three bladed mixer. Before addition of the monomer and catalysts, the solvent was passed through a 0.45 micron filter to remove the dust.

Nitrogen Purge. The basic purpose of the nitrogen purge was to remove all traces of dissolved oxygen from the monomer and water solution prior to the addition of the redox couple. Any traces of dissolved oxygen would have oxidized the metabisulfite ion at a rate faster than the redox couple reaction to produce the free radicals necessary for the opening of the acrylamide double bond in the polymerization reaction.

The nitrogen used in this investigation was supplied with an oxygen content guaranteed not to exceed 10 ppm by volume. Since the catalyst levels were so small, it was necessary to scrub out the remaining oxygen in the nitrogen by bubbling it through an ammonium vanadate and zinc amalgam scrubbing system where the vanadium ions were oxidized by the dissolved oxygen (32).

In the experimental work, the solution of monomer was purged for one hour before the catalyst addition and the purging was continued during the reaction. All the reagents were used as supplied without further purification.

Temperature Control. The need for an accurate means of controlling the reaction temperature was discussed earlier by Gleason, Miller and Sheats (30). They observed that the monomer-redox pair system used in this investigation formed a linear polymer at 25 degrees and a branched polymer at 78 degrees centigrade. The method of heat-

ing the reaction vessel was an electrically heated jacket which, although very slow in response to a change in electrical input, was adequate for heating the monomer solutions to their respective temperatures.

Since the heat evolved in the polymerization reaction was rather high and rapid, a quick and reliable method of cooling the reaction mixture was needed. Therefore, the reactor was modified so that a glass cooling coil was added to the inside to insure quick cooling with ordinary tap water. The cooling coil was constructed in the V.P.I. & S.U. glass blowing shop. The final system was capable of maintaining the desired temperature within one centigrade degree.

Precipitation and Stabilization

The precipitation of the polyacrylamides was carried out by non-solvent addition technique (33). In this investigation, the entire reaction mass was placed in a five liter vessel and agitated vigorously while methyl alcohol, a non-solvent, was added until no more visible milky white polymer precipitated from the resulting alcohol water solvent. The solvent was then removed from the polymer by vacuum filtration.

The stabilization of the polymer was accomplished in the same step as the precipitation. First, the agitation was brought about by the addition of filtered lab air. The oxygen was able to react with the remaining metabisulfite ions to oxidize them, therefore, rendering them unable to form the necessary free radicals with the persulfate ions which could attack the chain with resulting degradation. Next,

the persulfate ions, which have been shown to degrade the polyacrylamide chains, were removed by a reaction with the non-solvent methyl alcohol, in the following manner (34):

$$SO_4^- + CH_3OH \rightarrow HSO_4^- + \dot{C}H_2OH$$

$$\dot{C}H_2OH + S_2O_8^{=} \rightarrow HSO_4^- + SO_4^- + RC\overset{O}{\underset{H}{}}$$

The final step in the stabilization, was the removal of solvent traces by vacuum drying at 90 to 95 degrees Fahrenheit for approximately ten hours (35).

Hydrolysis

The percentage of hydrolysis of polyacrylamide samples was determined by dissolving a weighed sample in water, acidifying the resulting solution with a strong mineral acid, hydrochloric acid, to a pH of 3 or less, and back titrating with a standard solution of a strong base, sodium hydroxide, using an electronic pH meter. The number of equivalents of base required to bring the polymer solution from a pH of 3.3 to 7.0 equaled the number of equivalents of combined acrylic acid moieties in the sample. As a baseline value, a sample of unpurified acrylamide was used to determine a value for the number of equivalents of base used for a sample with no hydrolysis (36).

The reactions which were carried out to achieve the desired degree of hydrolysis were allowed to react for twenty-four hours after the base addition before reprecipitation and stabilization.

The pH meter used in this part of the investigation was calibrated using individual prepared buffers of citric acid and disodium phosphate (37).

Storage

The problems in the storage of both the hydrolyzed and raw polyacrylamides were solved rather easily by storing the dry forms of all the samples at temperatures below 50 degrees Fahrenheit and above 32 degrees Fahrenheit in the absence of light (38).

Polymer Characterization

The polymer characterization by use of the light scattering photometer was a complicated procedure which included selection of solvent, selection of calibration medium, Rayleigh Ratio determination, calibration of the differential refractometer, and the characterization of the polyacrylamides.

Solvent Selection. The solvents that have been used in light scattering analysis employing the common calibration mediums have been discussed extensively in the literature (39-50). The solvent that was selected in this study was a 0.10 molar sodium chloride solution in distilled water. The purpose for this selection was twofold; namely, it has been used with tungstosilicic acid (the calibration medium), and with the polyacrylamides the ionic strength of the 0.10 molar salt solution was used to approximate the ionic strength of the sewage in which the polymers were to be evaluated.

Calibration Medium. The calibration of the light scattering instrument was accomplished by using tungstosilicic acid ($H_4SiW_{12}O_{40}$, F.W. 2956). It was chosen because it had a fairly high molecular weight, along with long term stability in solution. In addition, Kerker and co-workers had investigated its properties on a similar

photometer to the one used in this investigation (43, 47-49).

The tungstosilicic acid was purified by the following method (39). The acid was dissolved in as little deionized water as possible. To this solution, a 1:1 solution of hydrochloric acid was added and the tungstocilicic acid extracted with di-ethyl ether. The ether was removed from the ether acid complex by evaporation in a vacuum oven at one hundred degrees Fahrenheit and 29 inches of mercury.

Rayleigh Ratio Determination. No mention of the Rayleigh Ratio of a 0.10 molar sodium chloride solution was found in the literature up to the period of this investigation. Since Kerker had successfully used this solvent in his investigations of tungstosilicic acid, it was decided to take the light scattering data with varying concentrations of the acid and extrapolate back to zero concentration and calculate the value of K in Kc/R_θ (ordinate of the Zimm Plot) and then solve for the Rayleigh Ratio (R_θ) of the solvent since the molecular weight of the tungstosilicic acid was known.

Differential Refractometer Calibration. As discussed previously in the Literature Review, the refractive index gradient of the polymer-solvent system had to be determined in order to evaluate the weight average molecular weight and the radius of gyration. Therefore, calibration solutions for the refractometer were made up using distilled water and potassium chloride which was dried for 48 hours at 103 degrees centigrade. The standards were produced in accordance with the Brice Phoenix Differential Refractometer Manual (51).

Light Scattering Analysis. The analysis of the polyacrylamides for weight average molecular weight and radius of gyration was performed in the manner outlined in the "Light Scattering Operation Manual CM - 1000A" (52). The polymer was dissolved and aged for eighteen hours in the 0.1 molar sodium chloride solvent for the analysis before being filtered through an 1.2 micron filter to remove dust and polymer aggregates. The solvent used in this step, and all succeeding steps, was previously passed through a 0.45 micron filter.

A cylindrical cell, C-101, of forty milliliters volume was used in all of the light scattering runs. At the conclusions of each day's work, the cell was acid cleaned and then rinsed ten times with 0.45 micron filtered deionized water before being stored away.

The wavelength of light, 5461 A°, used in this investigation was chosen because it was the largest available on the equipment and thus minimized the error. The polymers were all scanned on the photometer between twenty-five and ninety degrees and at either four, five, or six concentrations of polyacrylamides. The varying concentrations of polymer were obtained by diluting the original concentration directly in the cell. For each of the light scattering runs, the temperature at the sample in the cell was maintained at $25^{\pm}.1°C$.

The program used to reduce the raw data from the light scattering runs is presented in the Appendix.

Optimum Polymer Doses and Jar Tests

This section describes the experimental procedures employed to determine the optimum polymer doses of the various polyacrylamides, and

also the jar tests used to evaluate the suspended solids removal and the chemical oxygen demand reductions using the optimum polymer doses.

Sewage Parameters. As previously discussed in the Literature Review, dilute solutions of anionic polyacrylamides tend to degrade in solution due to residual persulfate levels remaining from the polymerization process. In order to avoid any problems related to this feature, the polymers were aged for the same time period and under the same conditions imposed in the light scattering analysis. The net result of these restrictions was that only a few polymer solutions could be made up daily due to equipment limitations. Therefore, to insure validity to these tests, certain limits had to be applied to the sewage that was to be tested. Accordingly, a ten day survey of raw sewage from the Christiansburg Treatment facility, samples picked up at 7:00 a.m., was undertaken to determine acceptable limits for hardness, suspended solids, and chemical oxygen demand. The main problem to be eliminated, was the effect of rain on the sewage parameters.

Polymer Make-up. All polymer solutions were made up so that one milliliter delivered one milligram of polymer. The solutions were made up in distilled water and aged.

Flocculation. All the flocculation tests that were used in the optimum dose determinations and the jar tests were run on one liter of sewage at room temperature. The flocculation consisted of a thirty second rapid mix at 70 revolutions per minute and a fifteen minute slow mix at ten revolutions per minute. During the rapid mix sequence, the

cations were added and then the polymers. Following the end of the slow mix period, the sample was allowed to settle for ten minutes.

Cation Level. Before running the refiltration tests for the optimum polymer doses of the various polyacrylamides, an investigation of the minimum cation level necessary for adequate bridging was conducted. The tests were conducted using constant doses of Purifloc A-23 (commercially available anionic polyacrylamide) while varying the calcium cation dosage and then running the refiltration studies on each cation level.

Refiltration. After the samples had settled for ten minutes, 800 milliliters of the clarified sewage was decanted off. The remaining 200 milliliters were then filtered under 14.5 inches of mercury, and the filtered sewage collected. The collected sewage was then refiltered through the deposited cake at a vacuum of 14.5 inches of mercury and the time required to collect 100 milliliters was recorded. This process was continued by varying the polymer dose at a constant hardness level until a maximum refiltration rate had been found which implied the optimum polymer dose.

Jar Tests. These tests were run separately from the optimum polymer dose tests due to time and storage limitations. Essentially, the optimum polymer doses were again applied to acceptable sewage and the suspended solids and chemical oxygen demand reductions were determined. Each dose was tested five times so that a reasonable number of experimental values were obtained for statistical analysis.

At the conclusion of the first set of jar tests, it was decided

to run another series of tests at a higher solids level for comparison with the previous results of a selected group of polymers. The optimum polymer doses were scaled up based on the solids ratio of the different samples. In addition, the samples were settled for twenty minutes instead of ten minutes.

IV. RESULTS

The results obtained in this investigation are given in the following section. They are divided into three sections: polymerization and light scattering results, optimum polymer doses and the chemical oxygen demand and suspended solids reduction when testing with the optimum dose.

Polymerization and Light Scattering Results

The polymerization conditions, the degree of hydrolysis, and the results of the light scattering are presented in Table I. The raw data and the refractive index-concentration gradients obtained from the light scattering work for the various polymer fractions are presented in the Appendix in Table VIII. Figure 4 is a log-log plot of the relationship of the radius of gyration and the weight average molecular weight. The purpose of this figure was to illustrate the result that there was no true branched or linear groups of polymers based on the initial reaction temperatures. If there had been a distinct group of linear polymers all of the polymers that were produced at twenty-five degrees centigrade should have had radii of gyration larger than those produced at seventy-eight degrees centigrade. In the Appendix, Figure 8 and Table IX present the calibration data for the light scattering equipment using tungstosilicic acid.

TABLE I. POLYMERIZATION AND LIGHT SCATTERING RESULTS **

REACTION	TEMPERATURE °C	METABISULFATE LEVEL gms	PERSULFATE LEVEL gms	PER CENT CONVERSION	FINAL DEGREE OF HYDROLYSIS PER CENT	WEIGHT AVERAGE MOLECULAR WEIGHT gms/mole	ERROR AS A PER CENT OF MOLECULAR WEIGHT ***	RADIUS OF GYRATION A°
1-25-25	25	.0048	.0200	34	25.1	1,514,000	18.51	1747
1-25-35	25	.0048	.0200	34	35.0	1,192,000	22.97	1693
2-25-25	25	.0142	.0595	75	24.8	191,000	11.25	1100
2-25-35	25	.0142	.0595	75	35.0	151,500	13.41	1164
3-25-25	25	.0710	.2960	35	25.2	605,500	14.92	3993
3-25-35	25	.0710	.2960	35	35.2	340,400	27.13	2825
4-25-25	25	.0024	.0100	64	25.0	8,224,000	8.94	6055
4-25-35	25	.0024	.0100	64	34.8	18,205,000	4.16	8977
1-78-25	78	.0048	.0200	39	25.0	325,000	8.89	1709
1-78-35	78	.0048	.0200	39	35.0	306,400	8.81	1571
2-78-25	78	.0142	.0595	70	24.9	171,600	14.51	1329
2-78-35	78	.0142	.0595	70	34.7	189,500	13.97	1431
4-78-25	78	.0010	.0041	18	25.1	836,700	19.72	4217
4-78-35	78	.0010	.0041	18	33.9	765,000	15.36	3896
4a-78-25	78	.0024	.0100	21	24.9	3,470,000	15.45	2009
4a-78-35	78	.0024	.0100	21	35.0	3,316,000	16.29	2027

** The following conditions were constant for all the reactions:
a) 2.5 liters of deionized water passed thru a .45 micron filter
b) 250 grams of acrylamide
c) Reaction mixture was purged for one hour before catalyst addition, and then continued for course of reaction.

*** Possible error in the intercept of the Zimm plot by double extrapolation.

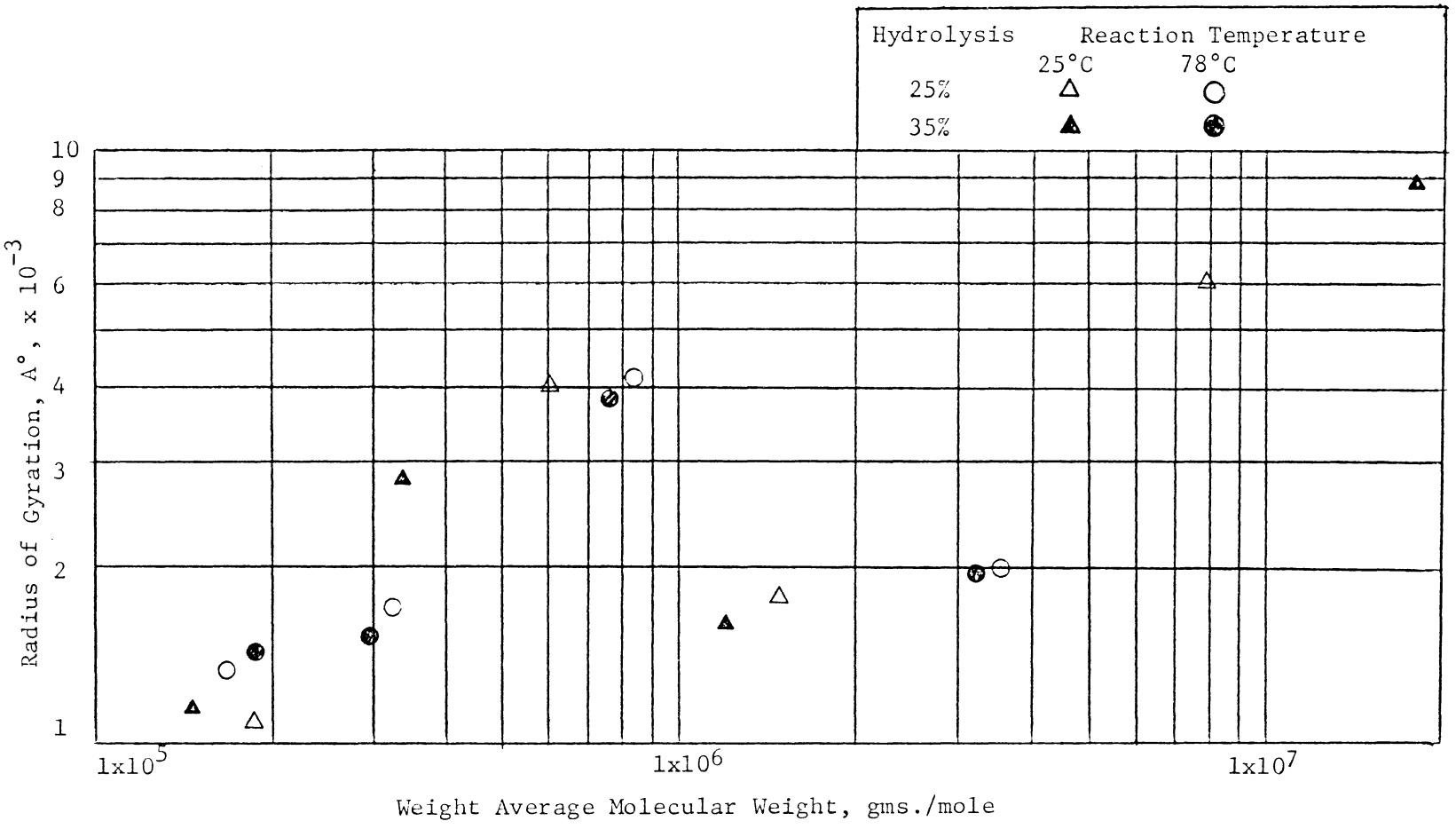


Figure 4 The Relationship Between the Weight Average Molecular Weight and the Radius of Gyration

Optimum Polymer Dose and Jar Test

The results of the optimum polymer dosage tests and the flocculation jar tests are presented in this section.

Sewage Survey. Upon completing the ten day survey the acceptable limit for solids was set at a minimum of 40 milligrams per liter and hardness at a minimum of 170 milligrams per liter as calcium carbonate. The above mentioned levels of hardness and suspended solids were selected so that any samples with valves lower would not be used in this investigation. This restriction reduced the possibility of the influence of heavy rainfall on this phase of the experimental work.

Divalent Cations. Figure 5 represents the relationship between the divalent cation level and the refiltration rate parameter for the determination of the minimum divalent cation concentration necessary to achieve satisfactory bridging of the anionic polyacrylamides to the suspended solids. The minimum acceptable divalent cation level was found to be approximately 110 milligrams per liter as Ca^{++}. The supporting data for this figure can be found in the Appendix in Table X.

Optimum Polymer Dosages. Table II lists the results of the refiltration tests for the determination of the optimum polymer dosages. Figure 6 is a plot of the relationship between the weight average molecular weights and the optimum polymer dose of the polyacrylamide fractions. The complete summary of all the related data

can be found in the Appendix in Table X. Figure 7 is included to illustrate the data taken for each polymer fraction and the method by which the optimum dose was determined by finding the maximum re-filtration rate. Table III is the sequential analysis of varients (anova) table for the effect of weight average molecular weight and the effect of the radius of gyration given the effect of the weight average molecular weight on the optimum polymer dosages. The single and multiple regressions were based on the logs of weight average molecular weight and the logs of the radius of gyration correlated against the optimum polymer dosages. This transformation was necessary due to the fact that the linearity of all variables is the major assumption necessary for prediction when using the statistical models described in the Appendix.

The anova results were that the optimum polymer dose regression on the weight average molecular weight was highly significant, $\alpha=0.01$, and the additional correlation on the radius of gyration given the effect of the weight average molecular weight was also significant but at a lower level, $\alpha=0.15$.

Jar Tests. The results of the jar tests in which the solids and chemical oxygen demand reductions were studied using the optimum polymer doses are presented in Table IV through VII. The four tables present an anova of the results to determine if there was any difference among the treatments employing the optimum polymer doses. Duncan's Multiple Range test is also presented to compare the treatment means. The purpose of Duncan's test was to examine

the removal for each polymer fraction to see if they differed from each other. Those polymer fractions commonly underlined are not significantly different, and can be assumed to yield the same removal. The total summary of the data is presented in Tables XI and XII in the Appendix.

For all the solids and chemical oxygen demand reductions the F statistics were highly significant indicating that there was a difference among the treatment means.

As previously mentioned in the end of the Experimental Methods Section, two solids levels were employed in this investigation. Tables IV and V which were the solids and chemical oxygen demand reductions were run on the lower solids level which was the same as that employed in the refiltration studies. The Duncan's analysis of both the anova's were complicated and the results will be examined in the Discussion section.

Tables VI and VII are a comparison of a group of polymers on the different suspended solids levels to determine again if branching has an effect on solids removal. These polymers were selected because of the relatively small difference in the weight average molecular weights and the large differences in the radii of gyration. The lower solids level, Table VI, showed no distinct trend with respect to the removals and the radius of gyration. The results employing the higher solids and scaled up polymer doses did show a distinct trend in that the polymers with the larger radii of gyration removed more solids.

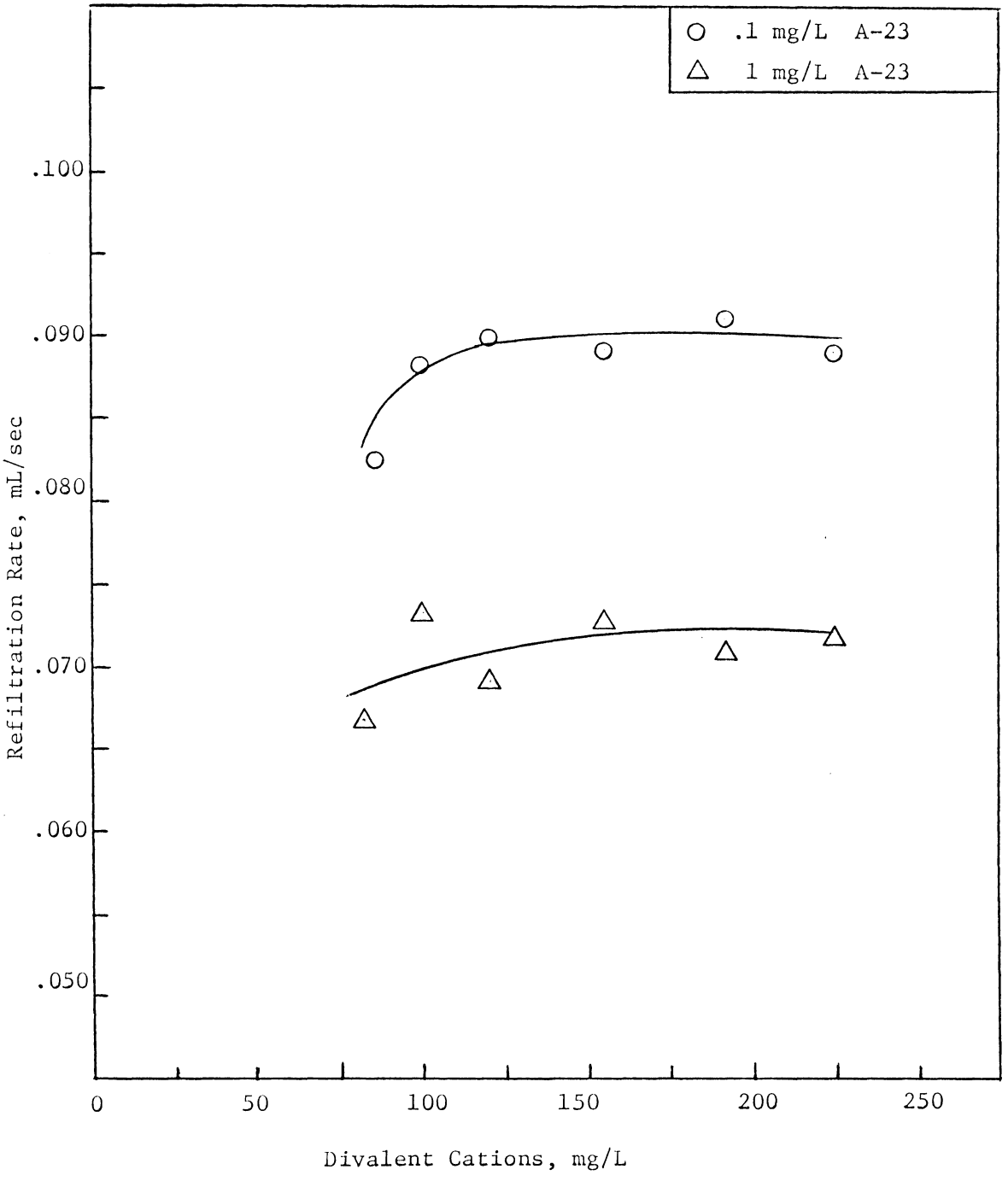


Figure 5. Determination of Minimum Divalent Cation Level for the Bridging of Anionic Polyacrylamides to Anionic Sewage Solids

TABLE II. OPTIMUM POLYMER DOSES FOR THE POLYACRYLAMIDES

POLYMER FRACTION	WEIGHT AVERAGE MOLECULAR WEIGHT gms/mole x 10^{-6}	RADIUS OF GYRATION $\mathring{A}$	OPTIMUM POLYMER DOSE mg/l
1-25-25	1.514	1747	1.2
1-25-35	1.192	1693	1.2
2-25-25	.191	1100	2.3
2-25-35	.151	1164	2.5
3-25-25	.605	3993	1.5
3-25-35	.340	2825	1.6
4-25-25	8.224	6055	0.3
4-25-35	18.221	8977	0.2
1-78-25	.325	1709	1.9
1-78-35	.306	1571	1.9
2-78-25	.171	1329	2.4
2-78-35	.189	1431	2.4
4-78-25	.836	4217	1.4
4-78-35	.765	3896	1.6
4a-78-25	3.470	2009	1.0
4a-78-35	3.320	2027	0.9

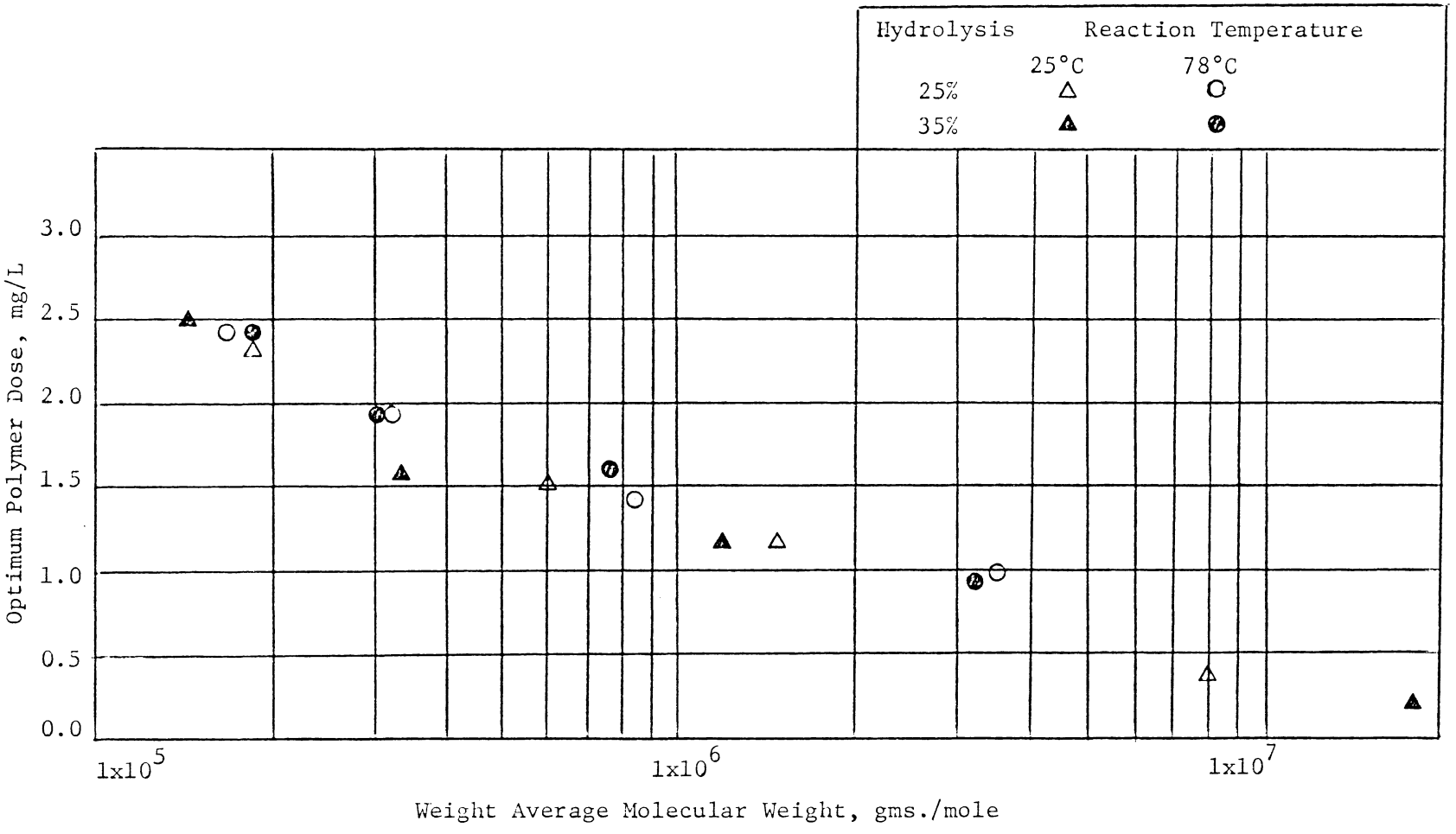


Figure 6 The Relationship Between the Optimum Polymer Dose and the Weight Average Molecular Weight

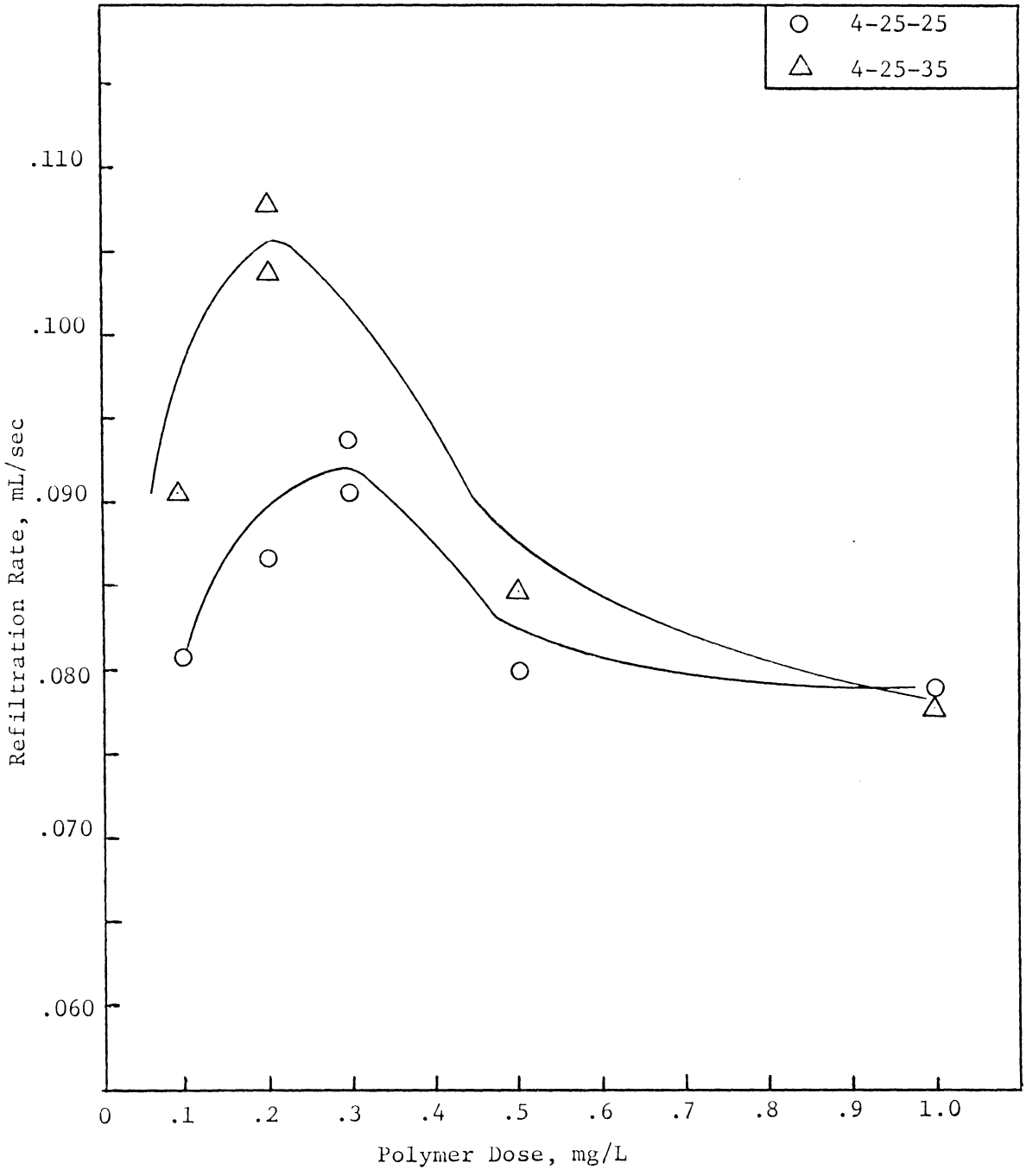


Figure 7 Determination of Optimum Polymer Dose for Polyacrylamides 4-25-25 and 4-25-35

TABLE III. ANOVA ANALYSIS OF OPTIMUM POLYMER DOSES IN SEQUENTIAL ANALYSIS AT LOWER SOLIDS LEVEL

SOURCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARES	F VALUE
Regression Due to Both Variables	2	7.2195	3.6098	165.580**
Regression Due to Weight Average Molecular Weight	1	7.1598	7.1598	328.430**
Regression Due to Radius of Gyration Given the Effect of Weight Average Molecular Weight	1	.0597	.0597	2.738***
Residual	14	.3050	.0218	
Total	16			

F TABULATED VALUES NECESSARY FOR SIGNIFICANCE

DEGREES OF FREEDOM	αPROTECTION LEVEL	F VALUE
(2,14)	.05*	3.74
	.01**	6.51
(1,14)	.01*	4.60
	.05**	8.86
	.01***	2.43

TABLE IV. ANOVA ANALYSIS OF PER CENT CHEMICAL OXYGEN DEMAND REMOVALS EMPLOYING THE OPTIMUM POLYMER DOSES AND DUNCAN'S MULTIPLE RANGE TESTS AT LOWER SOLIDS LEVEL

SOURCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARES	F VALUE
Treatment	15	5547.6	371.3	39.9**
Error	64	596.6	9.3	
Total	89	6144.2		

F TABULATED VALUE NECESSARY FOR SIGNIFICANCE

DEGREES OF FREEDOM	α PROTECTION LEVEL	F VALUE
(15,64)	.05*	1.84
	.01**	2.35

DUNCAN'S MULTIPLE RANGE TEST AT ONE PER CENT (POLYMER AND REMOVAL)

4A-78-35	4A-78-25	1-25-35	4-25-25	4-25-35	1-25-25	4-78-35	4-78-25	1-78-25	
34.86	34.70	24.01	19.00	18.84	17.14	16.39	15.56	14.12	(A)

3-25-25	1-78-35	3-25-35	2-78-35	2-78-25	2-25-35	2-25-25	
13.88	13.64	10.09	9.09	8.72	6.75	6.51	(A)

TABLE V. ANOVA ANALYSIS OF PER CENT SOLIDS REMOVALS EMPLOYING THE OPTIMUM POLYMER DOSES AND DUNCAN'S MULTIPLE RANGE TESTS AT LOWER SOLIDS LEVEL

SOURCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARES	F VALUE
Treatment	15	4839.0	321.2	21.6**
Error	64	959.5	14.8	
Total	89	5798.5		

F TABULATED VALUE NECESSARY FOR SIGNIFICANCE

DEGREES OF FREEDOM	αPROTECTION LEVEL	F VALUE
(15,64)	.05*	1.84
	.01**	2.35

DUNCAN'S MULTIPLE RANGE TEST AT ONE PER CENT (POLYMER AND REMOVAL)

4-25-25	4A-78-25	4-25-35	1-25-35	4A-78-35	1-25-25	4-78-35	4-78-25	3-25-25	
29.74	26.34	24.60	24.28	24.17	21.09	20.87	16.12	13.14	(A)

3-25-35	1-78-35	1-78-25	2-25-35	1-78-25	2-25-25	2-78-25	
10.92	8.94	8.89	8.74	8.17	8.11	5.82	(A)

TABLE VI. COMPARISON OF SELECTED POLYMER FRACTIONS AT THE LOWER SOLIDS LEVEL USING OPTIMUM POLYMER DOSES AND DUNCAN'S MULTIPLE RANGE TESTS

SOURCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARES	F VALUE
Treatment	6	594.2	99.0	6.07**
Error	28	456.2	16.3	
Total	34	1050.4		

F TABULATED VALUE FOR NECESSARY SIGNIFICANCE

DEGREES OF FREEDOM	αPROTECTION LEVEL	F VALUE
(6,28)	.05*	2.45
	.01**	3.53

DUNCAN'S MULTIPLE RANGE TEST AT FIVE PER CENT (POLYMER AND REMOVAL)

3-25-25	4-78-25	4-78-35	1-25-25	4A-78-35	1-25-35	4A-78-25
13.1	18.2	20.9	21.1	24.2	24.3	26.3

TABLE VII. COMPARISON OF SELECTED POLYMER FRACTIONS AT THE HIGHER SOLIDS LEVEL USING SCALED OPTIMUM POLYMER DOSES AND DUNCAN'S MULTIPLE RANGE TESTS

SOURCE	DEGREE OF FREEDOM	SUM OF SQUARES	MEAN SQUARES	F VALUE
Treatment	6	1667.4	277.9	33.5**
Error	28	232.8	8.3	
Total	34	1900.4		

F TABULATED VALUE FOR NECESSARY SIGNIFICANCE

DEGREES OF FREEDOM	αPROTECTION LEVEL	F VALUE
(6,28)	.05*	2.45
	.01**	3.53

DUNCAN'S MULTIPLE RANGE TEST AT FIVE PER CENT (POLYMER AND REMOVAL)

1-25-35	4A-78-35	4A-78-25	1-25-25	4-78-35	4-78-25	3-25-25
21.9	22.7	24.1	26.7	37.5	37.6	37.6

V. DISCUSSION

The results obtained in this investigation are discussed in the following chapter. The discussion is divided into three sections: polymerization and light scattering results, optimum polymer doses, and chemical oxygen demand and suspended solids reduction when testing with the optimum polymer dose.

Polymerization and Light Scattering

The discussion of the polymerization and light scattering results is given in the following sections.

Effect of Catalyst Levels on the Molecular Weight. The effect of the catalyst levels on the polymerization of the acrylamide was as expected: namely, the lower the levels of the metabisulfite and persulfate, the higher the weight average molecular weight of the resulting polymer chain.

Effect of Temperature on the Molecular Weight. In this investigation for each catalyst level, the polymerization was carried out at two temperatures, 25 and 78 degrees Centigrade. In all cases the resultant molecular weight was greater for the 25 degree Centigrade polymerization. This difference in the resultant weight average molecular weights was more pronounced for the lower catalyst levels.

Effect of Catalyst Levels and Temperature on the Radius of Gyration. These results were not as obvious as the molecular weight results. There was no distinct trend with respect to the radius of gyration and the catalyst levels and temperature. Figure 4 represents

the relationship between the weight average molecular weight and the radius of gyration. From this figure it is evident that there is not a distinct branched or linear group of polymers. This result is possibly due to the gel effect (Trommsdorf Effect) such that in cases of high conversion an autoacceleration occurs in the polymerization process. Since the autoacceleration is controlling, the reaction turns viscous, thus causing less mixing and a resultant loss of temperature control in the reactor. With the loss of temperature control, the tendency for branching is increased with the metabisulfite and persulfate redox couple. Therefore there is not a distinct set of linear and branched polymers.

Effect of Degree of Hydrolysis on the Radius of Gyration and the Weight Average Molecular Weight. Each polymer fraction was divided and hydrolyzed to 25 and 35 percent based on the monomer. The light scattering results showed no correlation between the degree of hydrolysis and the radius of gyration or the weight average molecular weight.

Light Scattering Analysis and Error. Assuming a one percent error in the most variable inputs (refractive index-concentration gradients, solvent calibration, concentration of polymer, angle, and the millivolt readings) to the light scattering analysis for a single point of the Zimm Plot an approximately eight percent error may result in the determination of the weight average molecular weight. With regard to this value the errors expressed as a percent of the weight average molecular weight are very reasonable.

Summary. Although there was not a distinct group of linear and branched polymers due to the probable gel effect, the results of the light scattering for the various polymer fractions revealed both a wide range in molecular weights (1.5×10^5 to 1.8×10^7 gms./mole) and molecular size (1100 to 8977 A°). Therefore the effect of weight average molecular weight and the molecular size can still be evaluated on the flocculation of domestic sewage with the analyzed material.

Optimum Polymer Dose and Jar Tests

The results are discussed in detail in the succeeding sections for all topics related to the use of synthesized polymers as flocculation agents.

Divalent Cations. As previously discussed in the Literature Review, the presence of multivalent cations is mandatory for effective bridging to occur. In this investigation divalent calcium had to accumulate in the double layer and subsequently depress it so that a bridge was able to form from the anionic sewage particles through the divalent cations to the anionic polyacrylamides. Figure 5 illustrated the importance of the divalent cations: namely, below one hundred milligrams per liter as Ca^{++} there were not enough cations present for satisfactory bridging to be accomplished.

This part of the investigation utilized Dow Purifloc A-23 as the polymer to test the divalent cation effect. The only published report using this polymer on domestic sewage referred to data

collected at the Cleveland, Ohio, Easterly Treatment Plant. The investigation reported no values on multivalent cation level because they had a substantial cation source in their waste flow due to numerous metal plating facilities on their sewage collection system. Therefore, no comparison of the amount of multivalent cation necessary to accomplish satisfactory bridging was available in the literature for comparison.

Optimum Polymer Doses. In this section two questions must be answered concerning the optimum polymer doses for the various polyacrylamide fractions. First, what is the effect of the weight average molecular weight on the optimum polymer dose? Second, what is the effect of the radius of gyration on the optimum polymer dose? Table II and Figure 6 relate the optimum polymer doses for the various polyacrylamides used in this investigation. The only trend that can be readily gleaned from this data is that as the weight average molecular weight decreases the optimum polymer dose increases. In order to answer the previously stated questions, a statistical test commonly called analysis of variance was employed to allow determination as to whether the relationship between the weight average molecular weight and the effect of the radius of gyration given the effect of the weight average molecular weight on the optimum polymer dose were statistically significant.

The results of the anova test are given in Table III. In this anova the optimum polymer dose was correlated with the logs of the weight average molecular weight and radius of gyration. The

reason for this transformation is that the anova variables must be linear with respect to each other by definition for the anova to be statistically valid.

The first item to be discussed is the regression due to the weight average molecular weight. The F statistic in this case was 328.43, and this is highly significant, at the 99 percent confidence level. This essentially means that the effect of the weight average molecular weight is very important in determining the optimum dose parameter. The second item to be examined is the regression due to both variables. Again the F statistic, 165.58, is highly significant, but note that the F statistic is now less than the case where only the weight average molecular weight is correlated. The regression due to the radius of gyration given the effect of the weight average molecular weight is significant but at a lower level of acceptance, α=0.15. Essentially this means that in this anova, the radius of gyration of the various polyacrylamides does have a statistical bearing on the total regression model. With the weight average molecular weight, the model in simplified terms implies that a ninety-nine percent probability exists that the molecular weight is important in the regression. With the effect of the radius of gyration the model implies that an eighty-five percent probability exists that the radius of gyration is important in the regression. This lower significance level is the reason why the regression due to both variables was less than that due only to the weight average molecular weight.

If Figure 4, which is a plot of the relationship between the weight average molecular weight and the radius of gyration, is again examined, a wide variation of the radius of gyration is noted for the various polyacrylamide fractions. This fact again supports the acceptance of the lower significance level of 0.15 for the effect of the radius of gyration given the effect of the weight average molecular weight. The wide differences in sizes of the polymers of the polymers will have an effect on the optimum polymer doses because polymers of similar molecular weights and different sizes will have different limiting rates of shear in the floc production stage.

In conclusion the two questions previously discussed have been answered through the statistical analysis. First, the effect of the weight average molecular weight was found to be very important with regard to the optimum polymer doses. The optimum polymer doses increases as the weight average molecular decreases. This trend is easily recognized in Figure 6. Second, the effect of the radius of gyration was also found to be important with regard to the optimum polymer dose. For similar molecular weights and different radius of gyrations, the larger radius of gyration the lower the optimum polymer dose. For example a polymer with a molecular weight of 325,000 grams per mole and a radius of gyration of 1709 angstroms had an optimum polymer dose of 1.9 milligrams per liter, while a polymer with a molecular weight of 340,000 grams per mole and 2825 angstroms had an optimum polymer dose of 1.6 milligrams per liter. The second conclusion therefore implies that the extent of branching

of the polymer chain has an effect on the optimum polymer dose.

Jar Tests. In this section two questions must be answered. First, what is the effect of the optimum polymer doses of the various polyacrylamides on the suspended solids and chemical oxygen demand removals in the flocculation of domestic sewage? Second, what is the effect of varying the degree of hydrolysis from twenty-five to thirty-five percent on the above parameters?

In the anovas for the percent removals of solids and chemical oxygen demand, Tables IV and V, the F statistic in both cases was highly significant. This automatically eliminated the possibility that the optimum polymer doses were all just as efficient in removing solids and chemical oxygen demand. It must be remembered that the optimum polymer dose as described in the Literature Review only implies the highest solids removal for that individual polymer. The differences in the suspended solids removals for the optimum polymer dosages might be attributable to one of several factors. First, the different polymer fractions may by nature of their physical properties have varying residual amounts of polymer left in solution and therefore not be used in bridging. Second, the molecular weight distributions of the polymers may have an effect on the bridging. Finally, the size or radius of gyration of the polymer molecule in solution may greatly affect the shear strength of the floc particles.

With regard to the chemical oxygen demand and solids anovas it was worthwhile to note that the eight polymers with the highest percent removals were the eight largest polymers, greater than 675,000

grams per mole, with respect to weight average molecular weight, but the eight polymers were ranked differently in the respective Duncan's test. In addition the remaining eight polymers, which were the smallest, were also ranked differently in both the solids and chemical oxygen demand removal analysis.

With regard to the degrees of hydrolysis, no distinction was discerned with regard to Duncan's test. In both the solids and chemical oxygen demand removals neither one of the degrees of hydrolysis consistently showed any better effect on the removals. Therefore the conclusion was drawn that there was no appreciable difference between twenty-five and thirty-five percent hydrolysis of the polyacrylamides in the solids or chemical oxygen demand removals in domestic sewage.

At the conclusion of the previous jar tests it was decided to investigate several selected polymers on a higher solids level to check the effect of large radius of gyration differences and relatively small weight average molecular weight differences. Seven polymers were chosen. Three "linear" polymers, 4-78-35, 4-78-25, and 3-25-25, and four "branched" polymers, 1-25-25, 4A-78-25, 4A-78-35, and 1-25-35 were investigated on the higher solids level.

Tables VI and VII are the comparisons of the selected polymers on the lower, previously used solids level and the higher solids level respectively. The results of the lower solids level test revealed no trend with respect to the size differences. But the results of the higher solids comparison demonstrated the fact that with

relatively small differences in the weight average molecular weights, the more linear polymers yielded a higher solids removal. For example in the flocculation tests a polymer of 836,000 grams per mole and 4217A° removed an additional thirty-seven percent of the suspended solids, while a polymer of 3,316,000 grams per mole and 2027A° removed only an additional twenty-three percent of the suspended solids. Therefore long chain branching in anionic polyacrylamides decreases the solids removal during flocculation.

The higher solids level part of the investigation was aided due to the fact of an improved mutual agglomeration due to the physical presence of a larger amount of solids. The chemical oxygen demand removal results are presented in Tables XI and XII in the Appendix. Those results showed no trends with respects to removals and therefore were not included.

In the Cleveland Easterly Treatment Plant study using Dow Purifloc A-23, it was reported that the addition of polymer increased the suspended solids removal in the primary clarifier by thirty-nine percent on raw sewage of about 160 milligrams per liter of suspended solids. The maximum removal obtained in this investigation was thirty-seven percent on raw sewage of 152 milligrams per liter. Therefore, the polymers synthesized for this investigation were as a whole satisfactory with respect to suspended solids removal.

VI. CONCLUSIONS

The investigation of the effect of branching and other properties of anionic polyacrylamides on the flocculation of domestic sewage led to the following conclusions:

1. As the weight average molecular weight increased the optimum polymer dose decreased (α=0.01).
2. For polymers of similar molecular weights and differing radius of gyrations, as the radius of gyration increased the optimum polymer dose decreased (α=0.15).
3. There was no statistically significant difference in the degree of treatment between twenty-five and thirty-five percent hydrolyzed polymers.
4. For polymers of similar molecular weights and differing radius of gyration, the "linear" polymers were more efficient in removing suspended solids. Therefore, long chain branching in anionic polyacrylamides decreased the flocculation efficiency in domestic sewage.

VII. SUMMARY

The first two phases of this investigation were concerned with the polymerization, hydrolysis and characterization of the polyacrylamides to be used in the flocculation studies. The results of the characterization by light scattering revealed a group of polymers varying in weight average molecular weight from 18,205,000 to 151,000 grams per mole, radius of gyration ranging from 8977 to 1100 angstroms, and degrees of hydrolysis of twenty-five and thirty-five percent.

The main purpose and final phase of this investigation was to determine the effects of molecular weight and radius of gyration, or branching, on the flocculation of domestic sewage. Prior to this determination several other parameters were evaluated. First, the minimum concentration of divalent cation was established as required to facilitate bridging. This cation level was found to be at least 110 milligrams per liter as calcium. Following the cation determination, the optimum polymer dose for each of the sixteen polymers was determined by using the refiltration parameter.

The optimum polymer doses were then correlated against the logs of the weight average molecular weight and the radius of gyration. The regression demonstrated that the effect of the weight average molecular weight was highly significant (α=0.01), and the effect of the radius of gyration was also significant (α=0.15). In a qualitative manner, the optimum polymer dose increased as the weight average molecular weight decreased, and for polymers of similar molecular weights and widely varying radius of gyrations, the larger

the radius of gyration resulted in a lower optimum polymer dose than the smaller polymer. Accordingly it was concluded that branching of the polymer chain, which is related to the radius of gyration, had significant effects on the flocculation of domestic sewage. For example in a flocculation test a polymer of 836,000 grams per mole and 4217 angstroms removed an additional thirty-seven percent of the suspended solids, while a polymer of 3,316,000 grams per mole and 2027 angstroms removed only an additional twenty-three percent of the suspended solids. Therefore long chain branching in anionic polyacrylamides decreased the suspended solids removal during flocculation.

In addition it was determined that optimum polymer doses for the various polymers did not result in the same levels of suspended solids and chemical oxygen demand reductions. Finally, there were no appreciable treatment effects for the different degrees of hydrolysis.

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IX. APPENDIX

This section contains the computer program utilized in the light scattering data reduction, tables containing basic data, a section describing the statistics used in this investigation, and a description of the materials and apparatus employed in this investigation.

```
      DIMENSION POLY(10),SOL(10),CONC(7),ANGLE(11),Y(7,11),A(8),          A0005
     AXX(7,11),Z(7,7)  ,ANGL(11)  ,TT(7,11)
C                                                                         A0015
C     READ IN NAME OF POLYMER, B OR L, FRACTION NUMBER, 40 UNITS          A0020
C                                                                         A0025
 9999 READ(5,1) (POLY(K),K=1,10)                                          A0030
    1 FORMAT(10A4)                                                        A0035
      WRITE(6,9998)(POLY(K),K=1,10)                                       A0040
 9998 FORMAT(1H1,5X,10A4)                                                 A0045
C                                                                         A0050
C     READ IN NAME OF SOLVENT, 40 UNITS                                   A0055
C                                                                         A0060
      READ(5,1) (SOL(K),K=1,10)                                           A0065
      WRITE(6,9997)(SOL(K),K=1,10)                                        A0070
 9997 FORMAT(///,5X,10A4)                                                 A0075
C                                                                         A0080
C     NC--NO. OF CONCENTRATIONS, INCLUDING ZERO                           A0085
C     NR--NO. OF READINGS AT A GIVEN CONCENTRATION, ANGLES                A0090
C                                                                         A0095
      READ(5,2) NC,NR                                                     A0100
    2 FORMAT(2I10)                                                        A0105
      WRITE(6,9996)    NC,NR                                            A0110
 9996 FORMAT( //,5X,'NO. OF CONCENTRATIONS IS',I4,/,5X,'NO. OF ANGLES I   A0115
     AS ',I4//)                                                           A0120
C                                                                         A0125
C     RINDEX--REFRACTIVE INDEX OF SOLVENT, UNITS                          A0130
C     DNDC--REFRACTIVE INDEX CONCENTRATION GRADIENT, UNITS/(GM/CC)        A0135
C     PR90--RAYLEIGH RATIO AT 90 DEGREES                                  A0140
C     WAVELT--WAVELENGTH OF LIGHT IN VACUO IN ANGSTROMS                   A0145
C     SOLINT--CALIBRATION IN MILLEVOLTS, PURE SOLVENT AT 90 DEGREES       A0150
C     XSF--ABSCISSA SCALE FACTOR, SPREADS ABSCISSA                        A0155
C                                                                         A0160
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```
      READ(5,3) RINDEX,DNDC,RR90,WAVELT,SCLINT,XSF                      AC165
    3 FORMAT(2F10.4,E10.3,3F10.4)                                       AC170
      WRITE(6,9995) RINDEX,DNDC,RR90,WAVELT,SCLINT,XSF                  AC175
 9995 FORMAT(///5X,'REFRACTIVE INDEX OF SOLVENT IS ',F10.4/             AC180
     A5X,'REFRACTIVE INDEX CONCENTRATION GRADIENT IS ',F10.4/           AC185
     B5X,'RAYLEIGH RATIO AT 90 DEGREES IS ',E10.3/                      AC190
     C5X,'WAVELENGTH OF LIGHT IN VACUUM IN ANGSTROMS IS ',F10.4/        AC195
     D5X,'CALIBRATION IN MILLIVOLTS, PURE SOLVENT AT 90 DEGREES IS ',   AC200
     EF10.4/5X,'ABSCISSA SCALE FACTOR IS ',F10.4///)                    AC205
C                                                                       AC210
C     CONC(I)--CONCENTRATIONS FROM ZERO, GRAMS PER MILLILITER           AC215
      READ(5,6) (CONC(I),I=1,NC)                                        AC220
    6 FORMAT(6F10.6)                                                    AC225
      WRITE(6,9994) (CONC(I),I=1,NC)                                    AC230
 9994 FORMAT(5X,'THE CONCENTRATIONS IN GRAMS PER MILLILITER ARE ',//    AC235
     A5X,6F10.6////)                                                    AC240
C                                                                       AC245
C     ANGLE(I)--ANGLES AT WHICH VARIOUS MEASUREMENTS WERE MADE, DEGREES AC250
C                                                                       AC255
      READ(5,4) (ANGLE(I),I=1,NR)                                       AC260
    4 FORMAT(11F6.0)                                                    AC265
      WRITE(6,9993) (ANGLE(I),I=1,NR)                                   AC270
 9993 FORMAT(5X,'ANGLES FOR ANALYSIS IN DEGREES ',5X,/,5X,11F5.0////)   AC275
C                                                                       AC280
C     Y(I,J)--LIGHT INTENSITIES AT VARIOUS ANGLES MEASURED AT A         AC285
C             PARTICULAR CONCENTRATION, STARTING WITH SOLVENT           AC290
C                                                                       AC295
      DO 7 I=1,NC                                                       AC300
    7 READ(5,4) (Y(I,J),J=1,NR)                                         AC305
      DO 777 I=1,NC                                                     AC306
      DO 777 J=1,NR                                                     AC307
  777 TT(I,J)=Y(I,J)                                                    AC308
```

```
      WRITE(6,9992)                                                    AC310
 9992 FORMAT(5X,'LIGHT INTENSITIES, ANGLES ACROSS, CONC. DOWN '/)      AC315
      DO 9991 I=1,NC                                                   AC320
 9991 WRITE(6,9990) (Y(I,J),J=1,NR)                                    AC325
 9990 FORMAT(5X,11F7.0)                                               AC330
C                                                                     AC335
C     OPK= OPTICAL CONSTANT                                           AC340
C                                                                     AC345
      OPK=2.*(3.1416*DNDC*RINDEX)**2*SOLINT/(WAVELT**4*6.0231E-9*RS90) AC350
      DO 8 I=2,NC                                                     AC355
      CON=CONC(I)*XSF                                                 AC360
C                                                                     AC365
C     GENERATE ABSCISSAS AND ORDINATES                                AC370
C                                                                     AC375
      DO 8 J=1,NR                                                     AC380
      ANG=ANGLE(J)*0.017453293                                        AC385
      SINE=SIN(ANG*0.5)                                               AC390
      XX(I-1,J)=SINE*SINE+CON                                         AC395
      SINE=SIN(ANG)                                                   AC400
      COSINE=COS(ANG)                                                 AC405
      DIV=SINE/(COSINE*COSINE+1.0)                                    AC410
      TT(I,J)=CONC(I)*OPK/((Y(I,J)-Y(1,J))*DIV)                       AC414
      Y(I,J)=CONC(I)*OPK/((Y(I,J)-Y(1,J))*DIV)                        AC415
C                                                                     AC420
C     SET UP MATRIX OF NORMALIZED REGRESSION EQUATION                 AC425
C                                                                     AC430
C     REGRESSION EQUATION THAT WILL BE NORMALIZED                     AC435
C                                                                     AC440
C     H*C/TAU = K*C/RTHETA = 1/M+2*B*C+3*D*C*C+1/(3*M)*CON1*SINE(A/2)**2  AC445
C                    +CON2*SINE(A/2)**4+CON3*C*SINE(A/2)**2           AC450
C                                                                     AC455
       SY=0.                                                          AC460
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 SCY=0.                                                          A0465
 SC2Y=0.                                                         A0470
 SS2Y=0.                                                         A0475
 SS4Y=0.                                                         A0480
SCS2Y=0                                                          A0485
SC=0.                                                            A0490
SC2=0.                                                           A0495
SS2=0.                                                           A0500
SS4=0.                                                           A0505
SCS2=0.                                                          A0510
SC3=0.                                                           A0515
SCS4=0.                                                          A0520
SC2S2=0.                                                         A0525
SC4=0.                                                           A0530
SC2S4=0.                                                         A0535
SC3S2=0.                                                         A0540
SS6=0.                                                           A0545
SS8=0.                                                           A0550
SCS6=0.                                                          A0555
DO 101 I=2,NC                                                    A0560
DO 101 J=1,NR                                                    A0565
ANG=ANGLE(J)*.017453293                                          A0570
SINE=SIN(ANG*.5)                                                 A0575
SINE2=SINE*SINE                                                  A0580
SINE4=SINE2*SINE2                                                A0585
CONCN2=CONC(I)*CONC(I)                                           A0590
SY=Y(I,J)+SY                                                     A0595
SCY=Y(I,J)*CONC(I)+SCY                                           A0600
SC2Y=Y(I,J)*CONCN2+SC2Y                                          A0605
SS2Y=Y(I,J)*SINE2+SS2Y                                           A0610
SS4Y=Y(I,J)*SINE4+SS4Y                                           A0615
SCS2Y=Y(I,J)*CONC(I)*SINE2+SCS2Y                                 A0620
```

```
      SC=CONC(I)+SC                                                    A0625
      SC2=CONCN2+SC2                                                   A0630
      SS2=SINE2+SS2                                                    A0635
      SS4=SINE4+SS4                                                    A0640
      SCS2=CONC(I)*SINE2+SCS2                                          A0645
      SC3=CONC(I)*CONCN2+SC3                                           A0650
      SCS4=CONC(I)*SINE4+SCS4                                          A0655
      SC2S2=CONCN2*SINE2+SC2S2                                         A0660
      SC4=CONCN2*CONCN2+SC4                                            A0665
      SC2S4=CONCN2*SINE4+SC2S4                                         A0670
      SC3S2=CONC(I)*CONCN2*SINE2+SC3S2                                 A0675
      SS6=SINE4*SINE2+SS6                                              A0680
      SS8=SINE4*SINE4+SS8                                              A0685
  101 SCS6=CONC(I)*SINE4*SINE2+SCS6                                    A0690
      Z(1,1)=(NC-1)*NR                                                 A0695
      Z(1,2)=SC                                                        A0700
      Z(1,3)=SC2                                                       A0705
      Z(1,4)=SS2                                                       A0710
      Z(1,5)=SS4                                                       A0715
      Z(1,6)=SCS2                                                      A0720
      Z(1,7)=SY                                                        A0725
      Z(2,1)=SC                                                        A0730
      Z(2,2)=SC2                                                       A0735
      Z(2,3)=SC3                                                       A0740
      Z(2,4)=SCS2                                                      A0745
      Z(2,5)=SCS4                                                      A0750
      Z(2,6)=SC2S2                                                     A0755
      Z(2,7)=SCY                                                       A0760
      Z(3,1)=SC2                                                       A0765
      Z(3,2)=SC3                                                       A0770
      Z(3,3)=SC4                                                       A0775
      Z(3,4)=SC2S2                                                     A0780
```

```
      Z(3,5)=SC2S4                                                      A0785
      Z(3,6)=SC3S2                                                      A0790
      Z(3,7)=SC2Y                                                       A0795
      Z(4,1)=SS2                                                        A0800
      Z(4,2)=SCS2                                                       A0805
      Z(4,3)=SC2S2                                                      A0810
      Z(4,4)=SS4                                                        A0815
      Z(4,5)=SS6                                                        A0820
      Z(4,6)=SCS4                                                       A0825
      Z(4,7)=SS2Y                                                       A0830
      Z(5,1)=SS4                                                        A0835
      Z(5,2)=SCS4                                                       A0840
      Z(5,3)=SC2S4                                                      A0845
      Z(5,4)=SS6                                                        A0850
      Z(5,5)=SS8                                                        A0855
      Z(5,6)=SCS6                                                       A0860
      Z(5,7)=SS4Y                                                       A0865
      Z(6,1)=SCS2                                                       A0870
      Z(6,2)=SC2S2                                                      A0875
      Z(6,3)=SC3S2                                                      A0880
      Z(6,4)=SCS4                                                       A0885
      Z(6,5)=SCS6                                                       A0890
      Z(6,6)=SC2S4                                                      A0895
      Z(6,7)=SCS2Y                                                      A0900
C                                                                       A0905
C     SOLVE FOR MATRIX COEFFICIENTS -- A(I)                             A0910
C                                                                       A0915
      NROW=6                                                            A0920
      NCOL=7                                                            A0925
      IROW=1                                                            A0930
      JCOL=1                                                            A0935
C                                                                       A0940
```

```
C       SEARCH FOR LARGEST VALUE OF Z(I,J) IN FIRST COLUMN                A0945
C                                                                         A0950
  201   II=IROW                                                           A0955
        JJ=JCOL                                                           A0960
        J=JCOL                                                            A0965
        BIGZ=Z(II,JJ)                                                     A0970
        DO 203 I=IROW,NROW                                                A0975
         IF(ABS(Z(I,J))-ABS(BIGZ)) 203,203,202                            A0980
  202   BIGZ=Z(I,J)                                                       A0985
        II=I                                                              A0990
        JJ=J                                                              A0995
  203   CONTINUE                                                          A1000
C                                                                         A1005
C       INTERCHANGE ROWS TO PLACE LARGEST VALUE OF Z(I,J) ON DIAGONAL     A1010
        I=IROW                                                            A1015
        DO 204 J=JCOL,NCOL                                                A1020
        A(J)=Z(I,J)                                                       A1025
        Z(I,J)=Z(II,JJ)                                                   A1030
        Z(II,JJ)=A(J)                                                     A1035
  204   JJ=JJ+1                                                           A1040
        II=IROW+1                                                         A1045
        JJ=JCOL+1                                                         A1050
        J=JJ                                                              A1055
C                                                                         A1060
C       REDUCE MATRIX BY TRIANGULAR DECOMPOSITION METHOD                  A1065
C                                                                         A1070
        DO 205 I=II,NROW                                                  A1075
        FACTOR=Z(I,JJ-1)/BIGZ                                             A1085
        DO 205 J=JJ,NCOL                                                  A1090
  205   Z(I,J)=Z(I,J)-Z(IROW,J)*FACTOR                                    A1095
        IROW=IROW+1                                                       A1100
        JCOL=JCOL+1                                                       A1105
```

```
      IF(NROW-IROW) 206,206,201                                          A1110
C                                                                        A1115
C     REGRESSION EQUATION COEFFICIENTS A(I)                              A1120
C                                                                        A1125
  206 A(NROW)=Z(NROW,NCOL)/Z(NROW,NROW)                                  A1130
      IROW=NROW                                                          A1135
      N=NROW-1                                                           A1140
  207 FACTOR=0.                                                          A1145
      DO 208 J=IROW,NROW                                                 A1150
  208 FACTOR=Z(N,J)*A(J)+FACTOR                                          A1155
      A(N)=(Z(N,NCOL)-FACTOR)/Z(N,N)                                     A1160
      IF(N-2) 210,209,209                                                A1165
  209 N=N-1                                                              A1170
      IROW=IROW-1                                                        A1175
      GO TO 207                                                          A1180
C                                                                        A1185
C     CALCULATE DESIRED POLYMER PROPERTIES                               A1190
C                                                                        A1195
  210 AWMWT=1./A(1)                                                      A1200
      SVC=A(2)/2.0                                                       A1205
      TVC=A(3)/3.0                                                       A1210
      RADGYR=SQRT(ABS(A(4)/A(1)*3.0))*WAVELT/(4.0*3.1415927*RINDEX)      A1215
      WRITE(6,218) A(1),A(1),A(2),A(3),A(4),A(5),A(6)                    A1220
  218 FORMAT(1H1,5X,26HZIMM PLOT Y-AXIS INTERCEPT,17X,2H= ,E13.6//5X     A1225
     A35HCOEFFICIENTS OF REGRESSION EQUATION   ,3X,7HA(1) =  ,E13.6/     A1230
     B43X,7HA(2) = ,E13.6/43X,7HA(3) = ,E13.6/                           A1235
     C43X,7HA(4) = ,E13.6/43X,7HA(5) = ,E13.6/43X,7HA(6) = ,E13.6//)     A1240
      WRITE(6,219) AWMWT,SVC,TVC,RADGYR                                  A1245
  219 FORMAT(5X,31HWEIGHT AVERAGE MOLECULAR WEIGHT,12X,2H= ,E13.6//      A1250
     A5X,45HSECOND OSMOTIC PRESSURE VIRIAL COEFFICIENT = ,E13.6//        A1255
     B5X,45HTHIRD OSMOTIC PRESSURE VIRIAL COEFFICIENT  = ,E13.6//        A1260
     C5X,26HAVERAGE RADIUS OF GYRATION,17X,2H= ,E13.6)                   A1265
```

```
C                                                                       A1270
C       CALCULATE THE STANDARD ERROR OF ESTIMATE                        A1275
C                                                                       A1280
      DEV=0.0                                                           A1284
      SSD=0.                                                            A1285
      DATA=NC*NP-2                                                      A1290
      JC=1+NR                                                           A1291
      ANGL(1)=0.0                                                       A1292
      DO 537  I=1,NP                                                    A1293
      J=1+I                                                             A1294
  537 ANGL(J)=ANGLE(I)                                                  A1295
      DO 538  I=1,JC                                                    A1296
      J=I                                                               A1297
  538 ANGLE(J)=ANGL(I)                                                  A1298
      DO 220 I=2,NC                                                     A1299
      DO 220  J=1,JC                                                    A1300
       XZT=ANGLE(J)*.01745329*0.5                                       A1304
       YC=SIN(XZT)                                                      A1305
      YC=YC*YC                                                          A1310
      YC=A(1)+CONC(I)*A(2)+CONC(I)*CONC(I)*A(3)+YC*A(4)+YC*YC*A(5)+     A1315
     ACONC(I)*YC*A(6)                                                   A1320
      DO 539 K=1,NR                                                     A1321
      KK=K+1                                                            A1322
  539 Y(I,KK)=Y(I,K)                                                    A1323
      IF((I-1)*(J-1))  220,220,213                                      A1324
  213 K=J-1                                                             A1325
  540 DEV=(1./Y(I,J))-(1./YC)                                           A1326
  220 SSD=DEV*DEV+SSD                                                   A1330
      SEE=SQRT(SSD/DATA)                                                A1335
      WRITE(6,221) SEE                                                  A1340
  221 FORMAT(/5X,26HSTANDARD ERROR OF ESTIMATE,17X,2H= ,E13.6)          A1345
      PERC=SEE*100.*A(1)                                                A1350
```

```
      WRITE(6,223) PERC                                                  A1355
  223 FORMAT(5X,43HERROR AS PERCENT OF WGHT. AVG. MOL. WGHT.   ,2H= ,    A1360
     AF9.4)                                                              A1365
  222 FORMAT(1H1)                                                        A1370
  505 DO 530 I=1,NC                                                      A1380
      IF(I-4)  503,503,503                                               A1385
  503 WRITE(6,222)                                                       A1390
  506 WRITE(6,507) CONC(I)                                               A1395
  507 FORMAT(//5X,15HCONCENTRATION =,F9.5,7H GMS/ML //                   A1400
     A6X,5HANGLE,5X,8HABSCISSA,5X,10HCALCULATED,6X,8HOBSERVED/           A1405
     B30X, 8HORDINATE,7X,8HORDINATE/)                                    A1410
      JO=1+NR                                                            A1415
  508 DO 523 J=1,JO                                                      A1420
      K=J-1                                                              A1425
      XXP=ANGLE(J)*0.5*.017453293                                        A1431
      XXX=SIN(XXP)                                                       A1432
      XXX=XXX*XXX                                                        A1435
      XXY=CONC(I)*XSF+XXX                                                A1440
      YY=A(1)+A(2)*CONC(I)+A(3)*CONC(I)*CONC(I)+A(4)*XXX+                A1445
     AA(5)*XXX*XXX+A(6)*CONC(I)*XXX                                      A1450
  515 IF(J-1) 516,519,516                                                A1455
  516 IF(I-1) 519,519,521                                                A1460
  519 WRITE(6,520) ANGLE(J),XXY,YY                                       A1465
  520 FORMAT(F11.1,F12.3,4X,F13.5,3X,F13.6)                              A1470
      GO TO 523                                                          A1475
  521 WRITE(6,520) ANGLE(J),XXY,YY,TT(I,K)                               A1480
  523 CONTINUE                                                           A1485
  530 CONTINUE                                                           A1490
      READ(5,531) NIPPO                                                  A1495
  531 FORMAT(5X,I4)                                                      A1500
      IF(NIPPO)  532,532,9999                                            A1505
  532 STOP                                                               A1510
      END
```

TABLE VIII. PRELIMINARY LIGHT SCATTERING DATA

POLYMER	CONC. gm/ml	MILLIVOLTS AT VARIOUS ANGLES								REFRACTIVE INDEX - CONCENTRATION GRADIENT
		25	30	35	40	45	50	55	90	ml/gm
1-25-25	.000000	1461	635	279	101	60	32	22	13	.1365
	.000302	4161	2375	1714	1176	814	665	497		
	.000408	4761	2818	2014	1401	1005	828	641		
	.000538	5413	3286	2157	1682	1238	992	783		
	.000696	6329	3822	2297	1951	1423	1072	856		
	.000951	7501	4487	2864	2217	1659	1271	951		
1-25-35	.000000	1461	635	279	101	60	32	22	13	.1358
	.000352	4307	2462	1772	1209	843	687	513		
	.000469	4931	2907	2079	1445	1072	855	668		
	.000734	6595	3962	2377	2017	1471	1112	886		
	.000983	7739	4617	2961	2294	1713	1308	983		
2-25-25	.000000	1461	635	279	101	60	35	22	13	.1365
	.000351	2234	1209	836	575	471	352	283		
	.000468	2441	1357	998	708	564	429	349		
	.000625	2690	1546	1114	796	624	508	404		
	.000834	3129	1768	1208	877	720	568	465		
2-25-35	.000000	1461	635	279	101	60	35	22	13	.1383
	.000333	2122	1149	794	546	448	334	269		
	.000445	2319	1289	948	673	535	408	331		
	.000593	2656	1469	1059	755	593	482	383		
	.000792	2972	1679	1147	833	684	540	442		
3-25-25	.000000	1461	635	279	101	60	35	22	13	.1372
	.000657	2874	1361	888	561	481	357	286		
	.000877	3389	1653	1031	706	553	436	343		
	.001170	3799	1897	1186	818	638	511	409		
	.001560	4483	2177	1249	947	687	581	469		
	.002775	6268	2793	1719	1151	877	721	587		

TABLE VIII. CONTINUED

POLYMER	CONC. gm/ml	MILLIVOLTS AT VARIOUS ANGLES							REFRACTIVE INDEX CONCENTRATION GRADIENT
		25	30	35	40	45	50	55	90	ml/gm
3-25-35	.000000	1461	635	279	101	60	35	22	13	.1351
	.000636	2817	1333	870	550	471	351	280		
	.000850	3321	1619	1010	692	542	427	336		
	.001135	3723	1860	1162	802	626	501	401		
	.001513	4394	2133	1224	928	673	570	459		
	.002019	5240	2510	1422	1053	771	625	521		
4-25-25	.000000	1239	581	237	119	63	32	20	12	.1375
	.000292	5115	2318	1805	998	878	548	360		
	.000389	6267	3133	2232	1329	1097	750	511		
	.000319	7877	4309	2721	1835	1486	1031	763		
	.000692	9555	5724	3027	2365	1596	1341	959		
	.000923	13338	7230	4189	3228	2087	1818	1344		
4-25-35	.000000	1239	581	237	119	63	32	20	12	.1362
	.000300	5283	2383	1865	1001	908	563	371		
	.000401	6421	3216	2291	1370	1117	771	528		
	.000534	8092	4503	2800	1883	1513	1059	771		
	.000712	9813	5899	3099	2414	1632	1378	982		
	.000951	13789	7471	4294	3326	2152	1870	1381		
1-78-25	.000000	1296	564	247	88	53	31	20	12	.1369
	.001260	2926	1884	1283	961	748	626	525		
	.001681	3334	2103	1382	1035	835	671	588		
	.002250	3799	2271	1524	1118	887	725	617		
	.003007	4436	2565	1641	1193	915	782	654		
1-78-35	.000000	1296	564	247	88	53	31	20	12	.1372
	.001235	2838	1829	1245	932	725	608	501		
	.001646	3235	2042	1341	1000	808	655	571		
	.002205	3685	2200	1481	1085	863	707	596		
	.002947	4300	2491	1590	1161	888	758	636		

TABLE VIII. CONTINUED

POLYMER	CONC. gm/ml	MILLIVOLTS AT VARIOUS ANGLES								REFRACTIVE INDEX - CONCENTRATION GRADIENT
		25	30	35	40	45	50	55	90	ml/gm
2-78-25	.000000	1296	564	247	88	53	31	20	12	.1352
	.001100	2498	1563	998	714	585	517	423		
	.001475	2894	1777	1155	864	643	575	486		
	.001962	3316	2033	1282	965	712	622	525		
	.002621	3913	2296	1423	1031	763	663	575		
2-78-35	.000000	1296	564	247	88	53	31	20	12	.1384
	.001056	2433	1520	971	644	567	510	410		
	.001416	2763	1724	1121	838	623	557	471		
	.001880	3411	1673	1244	936	691	604	509		
	.002520	3815	2229	1380	1002	741	645	557		
4-78-25	.000000	1160	527	212	126	73	48	31	12	.1386
	.000418	7099	4169	3362	2192	1834	1359	965		
	.000557	8881	5612	4217	2961	2372	1801	1346		
	.000744	10650	6685	4818	3349	2918	2006	1494		
	.000992	13831	8979	6402	4471	3795	2760	2079		
	.001322	17250	11571	8329	6037	4815	3642	2740		
4-78-35	.000000	1160	527	212	126	73	48	31	12	.1392
	.000447	7542	4435	3595	2337	1951	1443	1023		
	.000594	9392	6002	4507	3160	2532	1920	1439		
	.000793	11396	7110	5132	3561	3110	2130	1594		
	.001050	14790	9576	6810	4732	4048	2943	2221		
	.001411	18395	12362	8887	6430	5135	3872	2932		
4a-78-25	.000000	1160	527	212	126	73	48	31	12	.1368
	.000989	3702	2055	1333	990	736	635	518		
	.001300	4692	2472	1525	1097	819	719	578		
	.001735	5664	2882	1781	1224	901	803	647		
	.002314	6657	3216	1881	1328	1002	863	693		

TABLE VIII. CONTINUED

POLYMER	CONC. gm/ml	MILLIVOLTS AT VARIOUS ANGLES							REFRACTIVE INDEX - CONCENTRATION GRADIENT
		25	30	35	40	45	50	55	90	ml/gm
4a-78-35	.000000	1296	564	247	88	53	31	20	12	.1372
	.000970	3629	2015	1307	971	722	623	508		
	.001275	4600	2424	1496	1076	803	705	567		
	.001700	5553	2826	1747	1200	884	787	635		
	.002268	6527	3153	1845	1302	983	847	679		

TABLE IX

TUNGSTOSILICIC ACID CALIBRATION CHECK DATA

FOR THE LIGHT SCATTERING PHOTOMETER IN .10

MOLAR SODIUM CHLORIDE

	CONCENTRATION gms/ml	$\frac{Kc}{R_\theta} \times 10^3$	SLOPE
Run #1	.04859	.33909	0.030
	.03644	.35066	
	.02733	.35123	
	.02049	.33918	
	.01536	.37818	
	.00864	.35369	
	.00648	.31696	
	.00486	.34854	
	.00364	.35069	
	.00273	.29257	
	.00204	.36713	
	.00153	.32429	
Run #2	.04532	.37981	1.100
	.03967	.37052	
	.03465	.36817	
	.03033	.37017	
	.02655	.35962	
	.02323	.35499	

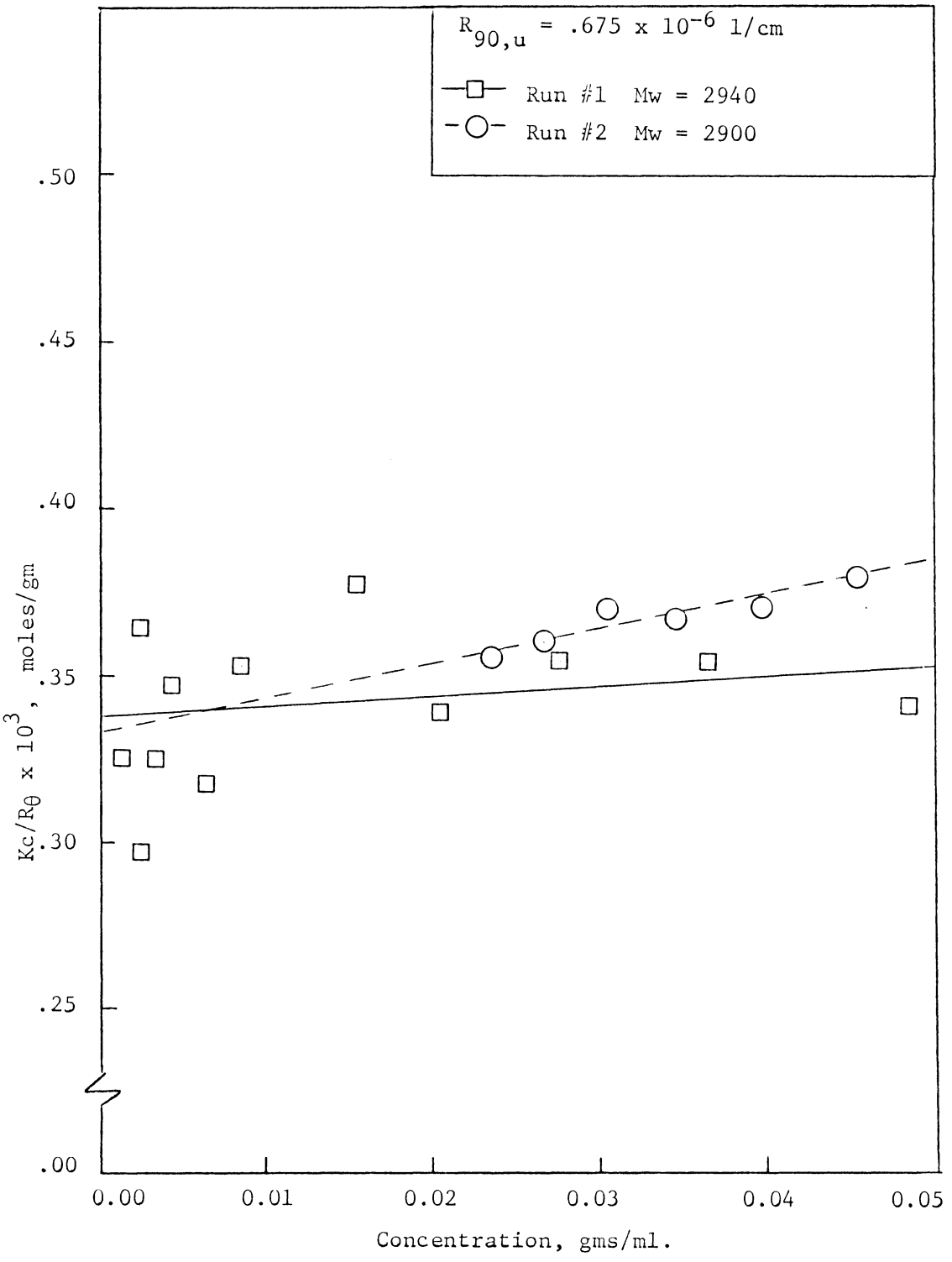

Figure 8 Light Scattering Calibration Check with Tungstosilic Acid and 0.10 Molar Sodium Chloride System

TABLE X. RESULTS OF MINIMUM DIVALENT CATION AND OPTIMUM POLYMER DOSAGE DETERMINATION

POLYMER	DIVALENT CATIONS mg/l @ Ca^{++}	SUSPENDED SOLIDS mg/l	CHEMICAL OXYGEN DEMAND mg/l	POLYMER DOSAGE mg/l	REFILTRATION RATE ml/sec
Purifloc A-23	82	54.2	63.0	0.1	.082
	118			0.1	.090
	154			0.1	.089
	190			0.1	.091
	226			0.1	.089
	100			0.1	.089
	82			1.0	.067
	118			1.0	.069
	154			1.0	.073
	190			1.0	.071
	226			1.0	.072
	100			1.0	.073
4-25-25	72	53.5	70.8		
	108			0.1	.081
	108			0.5	.080
	108			0.2	.087
	108			0.3	.091
	108			0.3	.094
	108			1.0	.079
4-25-35	77	53.5	70.8		
	108			0.1	.091
	108			0.5	.085
	108			0.2	.104
	108			0.3	.095
	108			0.2	.108
	108			1.0	.078
1-25-25	74	61.3	66.9		
	114			1.0	.070
	114			1.2	.082
	114			1.2	.079
	114			1.3	.074
	114			2.0	.068

TABLE X. CONTINUED

POLYMER	DIVALENT CATIONS mg/l @ Ca^{++}	SUSPENDED SOLIDS mg/l	CHEMICAL OXYGEN DEMAND mg/l	POLYMER DOSAGE mg/l	REFILTRATION RATE ml/sec
1-25-35	74	61.3	66.9		
	114			0.5	.068
	114			1.0	.069
	114			2.0	.066
	114			1.5	.069
	114			1.2	.077
	114			1.2	.076
	114			1.3	.071
2-25-25	83	48.3	86.6		
	119			1.0	.091
	119			2.0	.097
	119			3.0	.088
	119			2.5	.103
	119			2.2	.102
	119			2.4	.101
	119			2.3	.110
	119			2.3	.107
2-25-35	83	48.3	86.6		
	119			2.0	.095
	119			2.3	.095
	119			2.5	.104
	119			2.7	.092
	119			2.5	.105
3-25-25	74	61.3	69.2		
	113			1.0	.089
	113			1.5	.093
	113			2.0	.076
	113			1.6	.089
	113			1.8	.079
	113			1.5	.092
	113			1.7	.086

TABLE X. CONTINUED

POLYMER	DIVALENT CATIONS mg/l @ Ca^{++}	SUSPENDED SOLIDS mg/l	CHEMICAL OXYGEN DEMAND mg/l	POLYMER DOSAGE mg/l	REFILTRATION RATE ml/sec
3-25-35	74	61.3	69.2		
	113			1.0	.086
	113			2.0	.072
	113			1.5	.094
	113			1.6	.098
	113			1.7	.091
	113			1.6	.096
1-78-25	74	60.4	71.3		
	112			1.5	.087
	112			2.0	.091
	112			2.5	.083
	112			1.9	.095
	112			1.8	.091
	112			1.9	.097
1-78-35	74	60.4	71.3		
	112			1.8	.091
	112			1.9	.099
	112			1.9	.098
	112			1.7	.091
	112			2.0	.087
	112			2.5	.073
2-78-25	85	52.8	72.5		
	121			2.0	.091
	121			3.0	.086
	121			1.0	.092
	121			2.5	.092
	121			2.4	.103
	121			2.3	.094
	121			2.4	.101

TABLE X. CONTINUED

POLYMER	DIVALENT CATIONS mg/l @ Ca^{++}	SUSPENDED SOLIDS mg/l	CHEMICAL OXYGEN DEMAND mg/l	POLYMER DOSAGE mg/l	REFILTRATION RATE ml/sec
2-78-35	85	52.8	72.5		
	121			2.0	.091
	121			3.0	.087
	121			2.5	.093
	121			2.4	.097
	121			2.4	.101
	121			2.3	.093
4-78-25	75	69.2	81.3		
	119			1.0	.081
	119			2.0	.080
	119			1.5	.085
	119			1.6	.085
	119			1.4	.092
	119			1.3	.087
	119			1.4	.089
	119			1.2	.085
4-78-35	75	69.2	81.3		
	119			1.4	.085
	119			1.5	.087
	119			1.6	.094
	119			1.6	.094
	119			1.7	.089
	119			2.0	.086
4a-78-25	77	62.3	69.1		
	117			1.0	.083
	117			1.0	.083
	117			1.2	.075
	117			1.4	.073
	117			.9	.077

TABLE X. CONTINUED

POLYMER	DIVALENT CATIONS mg/l @ Ca^{++}	SUSPENDED SOLIDS mg/l	CHEMICAL OXYGEN DEMAND mg/l	POLYMER DOSAGE mg/l	REFILTRATION RATE ml/sec
4a-78-35	77	62.3	69.1		
	117			1.0	.079
	117			2.0	.072
	117			1.5	.079
	117			1.0	.080
	117			.9	.084
	117			.9	.083
	117			.7	.075

TABLE XI. RESULTS OF JAR TESTS EMPLOYING THE OPTIMUM POLYMER DOSES

POLYMER FRACTION	DIVALENT CATIONS	SOLIDS	SETTLED SOLIDS WITHOUT POLYMER	SOLIDS AFTER TEST	CHEMICAL OXYGEN DEMAND	SETTLED CHEMICAL OXYGEN DEMAND WITHOUT POLYMER	CHEMICAL OXYGEN DEMAND AFTER TEST
	mg/l @ Ca^{++}	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
4-25-25	77	65.0			78.1		
	110		50.0			69.9	
	110			37.2			58.1
	110			35.6			56.5
	110			35.6			55.0
	110			32.9			57.0
	110			34.3			55.8
4-25-35	77	65.0			78.1		
	110		50.0			69.9	
	110			38.5			56.7
	110			34.2			57.0
	110			41.5			58.3
	110			38.6			58.3
	110			35.7			55.0
4a-78-25	75	73.0			92.5		
	110		57.8			78.0	
	110			41.5			50.0
	110			44.3			51.1
	110			41.5			49.2
	110			41.5			52.3
	110			44.3			52.0

TABLE XI. CONTINUED

POLYMER FRACTION	DIVALENT CATIONS mg/l @ Ca^{++}	SOLIDS mg/l	SETTLED SOLIDS WITHOUT POLYMER mg/l	SOLIDS AFTER TEST mg/l	CHEMICAL OXYGEN DEMAND mg/l	SETTLED CHEMICAL OXYGEN DEMAND WITHOUT POLYMER mg/l	CHEMICAL OXYGEN DEMAND AFTER TEST mg/l
4a-78-35	75	73.0			92.5		
	110		57.8			78.0	
	110			45.8			49.2
	110			44.3			51.1
	110			43.8			52.3
	110			41.5			52.3
	110			45.8			49.2
1-25-35	79	54.9			68.0		
	110		45.7			60.9	
	110			38.6			49.5
	110			35.6			45.6
	110			37.8			48.7
	110			39.0			47.6
	110			35.6			47.6
1-25-25	79	54.9			68.0		
	110		45.7			60.9	
	110			37.2			47.6
	110			34.3			45.6
	110			38.6			46.6
	110			34.3			45.6
	110			35.7			47.6

TABLE XI. CONTINUED

POLYMER FRACTION	DIVALENT CATIONS	SOLIDS	SETTLED SOLIDS WITHOUT POLYMER	SOLIDS AFTER TEST	CHEMICAL OXYGEN DEMAND	SETTLED CHEMICAL OXYGEN DEMAND WITHOUT POLYMER	CHEMICAL OXYGEN DEMAND AFTER TEST
	mg/1 @ Ca^{++}	mg/1	mg/1	mg/1	mg/1	mg/1	mg/1
4-78-35	80	62.1			86.5		
	110		56.7			74.5	
	110			47.1			62.5
	110			45.5			63.0
	110			44.2			63.0
	110			47.1			63.0
	110			48.5			63.0
1-78-25	78.5	52.8			77.8		
	110		47.6			68.0	
	110			43.8			58.5
	110			43.8			56.8
	110			43.8			58.5
	110			44.3			59.0
	110			43.8			58.5
1-78-35	78.5	52.8			77.8		
	110		47.6			68.0	
	110			44.3			58.5
	110			43.8			56.0
	110			44.3			59.4
	110			43.8			59.0
	110			41.1			59.0

TABLE XI. CONTINUED

POLYMER FRACTION	DIVALENT CATIONS	SOLIDS	SETTLED SOLIDS WITHOUT POLYMER	SOLIDS AFTER TEST	CHEMICAL OXYGEN DEMAND	SETTLED CHEMICAL OXYGEN DEMAND WITHOUT POLYMER	CHEMICAL OXYGEN DEMAND AFTER TEST
	mg/1 @ Ca^{++}	mg/1	mg/1	mg/1	mg/1	mg/1	mg/1
3-25-25	75	60.7			85.3		
	110		52.8			74.5	
	110			47.1			62.5
	110			44.2			64.0
	110			47.1			66.4
	110			45.4			64.0
	110			45.4			64.0
3-25-35	75	60.7			85.3		
	110		52.8			74.5	
	110			48.5			66.4
	110			47.1			64.0
	110			47.1			65.1
	110			45.4			64.8
	110			47.1			64.0
2-78-25	75	69.2			74.0		
	110		61.5			85.5	
	110			58.5			78.0
	110			57.1			76.2
	110			58.5			80.0
	110			57.1			78.0
	110			58.5			78.0

TABLE XI. CONTINUED

POLYMER FRACTION	DIVALENT CATIONS mg/l @ Ca^{++}	SOLIDS mg/l	SETTLED SOLIDS WITHOUT POLYMER mg/l	SOLIDS AFTER TEST mg/l	CHEMICAL OXYGEN DEMAND mg/l	SETTLED CHEMICAL OXYGEN DEMAND WITHOUT POLYMER mg/l	CHEMICAL OXYGEN DEMAND AFTER TEST mg/l
2-78-35	75	69.2			94.0		
	110		61.5			85.5	
	110			55.8			76.2
	110			54.3			80.0
	110			55.8			78.0
	110			57.1			77.5
	110			57.1			76.8
2-25-25	73	80.0			76.8		
	110		67.2			73.2	
	110			63.0			69.6
	110			61.5			67.2
	110			61.5			68.4
	110			61.5			68.4
	110			60.0			68.4
2-25-35	73	80.0			76.8		
	110		67.2			73.2	
	110			60.0			68.7
	110			61.5			68.4
	110			60.0			67.1
	110			61.5			68.7
	110			60.0			68.7

TABLE XII. RESULTS OF JAR TESTS EMPLOYING SCALED UP POLYMER DOSES ON THE HIGHER SOLIDS LEVEL

POLYMER FRACTION	DIVALENT CATIONS mg/l @ Ca^{++}	SCALED OPTIMUM POLYMER DOSE mg/l	SOLIDS mg/l	SETTLED SOLIDS WITHOUT POLYMER mg/l	SOLIDS AFTER TEST mg/l	CHEMICAL OXYGEN DEMAND mg/l	SETTLED CHEMICAL OXYGEN DEMAND WITHOUT POLYMER mg/l	CHEMICAL OXYGEN DEMAND AFTER TEST mg/l
3-25-25	52.0	3.3	152.8	91.9		94.1	74.5	
	110.0				55.6			58.8
	110.0				55.6			58.8
	110.0				57.1			54.8
	110.0				58.5			54.8
	110.0				60.0			54.8
4-78-25	52.0	3.1	152.8	91.9		94.1	74.5	
	110.0				61.5			50.9
	110.0				57.1			54.8
	110.0				57.1			58.8
	110.0				54.3			54.8
	110.0				57.1			50.9
4-78-35	52.0	3.5	152.8	91.9		94.1	74.5	
	110.0				62.9			54.8
	110.0				58.5			58.8
	110.0				57.1			54.8
	110.0				54.3			62.7
	110.0				54.3			50.9

TABLE XII. CONTINUED

POLYMER	DIVALENT CATIONS mg/l @ Ca^{++}	SCALED OPTIMUM POLYMER DOSE mg/l	SOLIDS mg/l	SETTLED SOLIDS WITHOUT POLYMER mg/l	SOLIDS AFTER TEST mg/l	CHEMICAL OXYGEN DEMAND mg/l	SETTLED CHEMICAL OXYGEN DEMAND WITHOUT POLYMER mg/l	CHEMICAL OXYGEN DEMAND AFTER TEST mg/l
1-25-25	52.0	2.6	152.8	91.9		94.1	74.5	
	110.0				65.8			62.7
	110.0				68.5			66.6
	110.0				68.5			62.7
	110.0				70.0			62.7
	110.0				64.3			58.8
1-25-35	52.0	2.6	152.8	91.9		94.1	74.5	
	110.0				71.5			58.8
	110.0				73.0			58.8
	110.0				74.3			58.8
	110.0				70.0			58.8
	110.0				70.0			58.8
4a-78-25	52.0	2.2	152.8	91.9		94.1	74.5	
	110.0				67.3			54.8
	110.0				68.5			58.8
	110.0				68.5			58.8
	110.0				70.0			62.7
	110.0				74.3			58.8

TABLE XII. CONTINUED

POLYMER FRACTION	DIVALENT CATIONS	SCALED OPTIMUM POLYMER DOSE	SOLIDS	SETTLED SOLIDS WITHOUT POLYMER	SOLIDS AFTER TEST	CHEMICAL OXYGEN DEMAND	SETTLED CHEMICAL OXYGEN DEMAND WITHOUT POLYMER	CHEMICAL OXYGEN DEMAND AFTER TEST
	mg/l @ Ca^{++}	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
4a-78-35	52.0	2.0	152.8	91.9		94.1	74.5	
	110.0				75.8			50.9
	110.0				71.5			54.8
	110.0				67.3			50.9
	110.0				70.0			50.9
	110.0				71.5			58.8

STATISTICS[53,54,55]

The avowed purpose of this section is only to acquaint the reader with the basic statistical parameters and tests used to analyze the results of this investigation. There were three types of tests used and they are outlined below.

Simple Anova

The analysis of variance technique in applied statistics basically tells the investigator if there is a significant difference among groups or treatments within the total test. Simply stated this can tell you that with treatments A, B, C, D and E there are different effects, but it does not illustrate whether only one is different from the other four treatments, or whether all five are different.

In order to illustrate this technique the following example should be examined:

1. Assume that you are testing specified corn seeds on a certain classification of soil, therefore you have the following experimental results

Seed A_1	Seed B_1	Seed C_1	Seed D_1
⋮	⋮	⋮	⋮
Seed A_n	Seed B_n	Seed C_n	Seed D_n

where the number of groups or treatments, a, is equal to the number of different types of seeds, and the number of replications within a group is equal to n.

2. The steps in the calculations are outlined below.

   a. First, obtain the group sum, $\sum_{j=1}^{n} y_{ij}$

   b. Second, obtain the uncorrected group sum of squares,

   $$\sum_{j=1}^{n} y_{ij}^2$$

   c. Third, obtain the grand sum, $\sum_{i=1}^{a} \sum_{j=1}^{n} y_{ij}$

   d. Fourth, obtain the uncorrected sum of squares, $\sum_{i=1}^{a} \sum_{j=1}^{n} y_{ij}^2$

   e. Next obtain the correction factor, $C = (\sum_{i=1}^{a} \sum_{j=1}^{n} y_{ij})^2/n_i$

   f. Using the correction factor the corrected total sum of squares can be calculated $TSS = \sum_{i=1}^{a} \sum_{j=1}^{n} y_{ij}^2 - C$

   g. Now the treatment sum of squares can be calculated,

   $$TRSS = \sum_{i=1}^{a} ((\sum_{j=1}^{n} y_{ij})^2/n) - C$$

   h. Finally the error sum of squares can be obtained,

   $$ERSS = TSS - TRSS$$

3. The calculation steps outlined above were all utilized to arrive at the following anova table:

Source	Degrees of Freedom	Sum of Squares	Mean Squares	F Value
Treatment	a-1	TRSS	TRSS/(a-1)	TRMS/ERMS
Error	a(n-1)	ERSS	ERSS/a(n-1)	
Total	an-1	TSS		

degrees of freedom for F is (a-1, a(n-1))

Once you have calculated the F value for your experimental work you test for significance between the treatments by comparing your F value with the tabulated values of F at the same degrees of freedom. If the calculated F value is greater than the tabulated value, then there is at least one significant difference among the treatments.

Duncan's Multiple Range Test

If the anova test reveals a significant F value, as stated before, you can only assume that one or more of the treatments is significantly different. In order to examine each treatment with respect to the others another statistical examination must be employed.

When testing between two or more means several errors can occur. First, a Type I Error, which is a rejection of a true hypothesis, is possible. Second, a Type II Error, which is the acceptance of a false hypothesis, is also possible. Obviously, the ideal case for investigation is to minimize the probability of accepting both these errors. Duncan's multiple range test satisfies the previous requirements. This test is simply a comparison of the treatment means, ranked in order of magnitude, against Duncan's tabulated ranges for multiple comparisons based on the group sample size.

The basic method of calculation is as follows:

1. Calculate, $S_{\bar{y}} = ((ERSS/(a(n-1))/a))^{1/2}$

   where ERSS/a(n-1) is the error mean square from the simple anova

2. From Duncan's Multiple Comparison Tables select your values (SSR) based on the number of treatment means and the group sample size.

   i.e. for n=5 and a=5 at a protection level of 0.05

   SSR's 3.636 3.921 4.153 4.348

3. Next, calculate the least significant range

   $LSR = SSR(S_{\bar{y}})$

4. After arranging the treatment means in order of magnitude, compare the means, highest to lowest, and continue until significance is found. Then repeat with the next highest and continue. Never test previous non-significance.

Regression Analysis

The basic regression analysis is used to determine what fraction of the variation of a dependent variable is due to the independent variable in the system. In a multiple regression you are determining the effect of two or more independent variables on a single response of dependent variable. The basic steps is performing the multiple regression analysis is discussed below:

1. Calculate the sums, sums of squares, and the interaction terms,

   $\sum_{n} Y, \sum_{n} X_1, \sum_{n} X_2, \sum_{n} Y^2, \sum_{n} X_1^2, \sum_{n} X_2^2, \sum_{n} X_1 Y, \sum_{n} X_2 Y, \sum_{n} X_1 X_2$

where n = number of relationships

Y = dependent variables

X_1, X_2 = independent variables

2. Calculate the corrected sum of squares

$$\sum^{n} x_1^2 = \sum^{n} X_1^2 - (\sum^{n} X_1)^2/n$$

$$\sum^{n} x_2^2 = \sum^{n} X_2^2 - (\sum^{n} X_2)^2/n$$

$$\sum^{n} y^2 = \sum^{n} Y^2 - (\sum^{n} Y)^2/n$$

$$\sum^{n} x_1 y = \sum^{n} X_1 Y - \sum^{n} X_1 \sum^{n} Y/n$$

$$\sum^{n} x_2 y = \sum^{n} X_2 Y - \sum^{n} X_2 \sum^{n} Y/n$$

$$\sum^{n} x_1 x_2 = \sum^{n} X_1 X_2 - \sum^{n} X_1 \sum^{n} X_2/n$$

3. For a simple regression regression of X_1 on Y,

a. $b_1 = \sum^{n} x_1 y / \sum^{n} x_1^2$

and $\hat{Y} = \bar{Y} - b_1(X_1 - \bar{X}_1)$

where $\bar{Y}$ and $\bar{X}_1$ are the means, and $\hat{Y}$ is the predicted Y value

b. Anova Table

Regression Sum of Squares = $b_1 \sum x_1 y$

Residual Sum of Squares = $\sum y^2$ - Regression Sum of Squares

Total Sum of Square = Regression Sum of Squares + Residual Sum of Squares

Source	Degrees of Freedom	Sum of Squares	Mean Squares	F Value
Regression	1	Reg. S.S.	$\frac{\text{Reg. S.S.}}{1}$	$\frac{\text{Reg. M.S.}}{\text{Res. M.S.}}$
Residual	n-2	Res. S.S.	$\frac{\text{Res. S.S.}}{n-2}$	
Total	n-1	Tot. S.S.		

degrees of freedom of F is (1, n-2)

If F calculated is greater than the F tabulated, then a significant correlation of X_1 on Y is assumed.

c. The fraction of the variation in Y explained by X_1 is

$$r^2 = \frac{\text{Regression Sum of Squares}}{\text{Total Sum of Squares}}$$

The value of r^2 for an acceptable regression probably should be greater or equal to 0.50.

4. For a multiple regression of X_1 and X_2 on Y the following format is to be followed:

a. Find the inverse, A^{-1}, of the coefficient matrix A.

$$A = \begin{bmatrix} x_1^2 & x_1x_2 \\ x_1x_2 & x_2^2 \end{bmatrix} \qquad A^{-1} = \begin{bmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{bmatrix}$$

b. Solve for the regression coefficients and fit the equation.

$$b_1 = c_{11}\overset{n}{\Sigma}x_1y + c_{12}\overset{n}{\Sigma}x_2y$$

$$b_2 = c_{12}\overset{n}{\Sigma}x_1y + c_{22}\overset{n}{\Sigma}x_2y$$

$$b_o = \bar{Y} - b_1\bar{X}_1 - b_2\bar{X}_2$$

$$\hat{Y} = b_o + b_1X_1 + b_2X_2$$

c. Anova Table

Regression Sum of Squares = $b_1\sum_{n}x_1y + b_2\sum_{n}x_2y$

Residual Sum of Squares = y^2 - Regression Sum of Squares

Total Sum of Squares = Regression Sum of Squares + Residual Sum of Squares

Source	Degrees of Freedom	Sum of Squares	Mean Squares	F Value
Regression	2	Reg. S.S.	$\frac{\text{Reg. S.S.}}{2}$	$\frac{\text{Reg. M.S.}}{\text{Res. M.S.}}$
Residual	n-3	Res. S.S.	$\frac{\text{Res. S.S.}}{n-3}$	
Total	n-2	Total S.S.		

degrees of freedom of F value is (2, n-3)

Again if the calculated F value is greater than F tabulated, then a significant correlation of X_1 and X_2 is assumed.

d. The fraction of the variation in Y explained by X_1 and X_2

$$r^2 = \frac{\text{Regression Sum of Squares}}{\text{Total Sum of Squares}}$$

5. The only problem with the analysis up to this point is that the effect of X_1 and X_2 on Y is the only correlation parameter known. The sequential anova approach will resolve this problem

by partitioning the regression sum of squares into the effect of X_1 and the effect of X_2 given the effect of X_1.

Sequential Anova Table

Source	Degrees of Freedom	Sum of Squares	Mean Squares	F Value
Regression	2	Reg. X_1X_2	$\frac{\text{Reg. } X_1X_2}{2}$	$\frac{\text{M.S. } X_1X_2}{\text{M.S. Res.}}$
b_1	1	Reg. X_1	$\frac{\text{Reg. } X_1}{1}$	$\frac{\text{M.S. } X_1}{\text{M.S. Res.}}$
b_2/b_1	1	(Reg. X_1X_2 - Reg. X_1)	$\frac{((\text{Reg. } X_1X_2) - (\text{Reg. } X_1))}{1}$	$\frac{\text{M.S. } b_2/b_1}{\text{M.S. Res.}}$
Residual	n-3	Res. S.S.	$\frac{\text{Res. S.S.}}{n-3}$	
Total	n-1	Total S.S.		

Degrees of freedom from top to bottom (2,n-3)
(1,n-3)
(1,n-3)

In summary if all three calculated F's are significant then both X_1 and X_2 are significant in the regression equation and should be kept.

Materials

A listing of the materials used in this investigation is given in the following section.

Acrylamide. Fisher Scientific, catalog number 5521, used as the monomer on the production of the polyacrylamides.

Ammonium Persulfate. Fisher Scientific catalog number A-682, used as a catalyst in the production of the polyacrylamides.

Ammonium Vanadate. Fisher Scientific catalog number A-714, used in the oxygen scrubbing system.

Citric Acid. Fisher Scientific catalog number A-940, used as a component of the buffer in the calibration of the pH meter.

Diethyl Ether. Fisher Scientific catalog number E-138, used in the purification of Tungstosilic Acid.

Ferrous Sulfate. Fisher Scientific catalog number I-146, used as an accelerator in the production of the polyacrylamides.

Hydrochloric Acid. Fisher Scientific catalog number A-144, used in the oxygen scrubbing system.

Mercuric Chloride. Fisher Scientific catalog number M-156, used in the oxygen scrubbing system.

Methyl Alcohol. Fisher Scientific catalog number A-412, used as a non-solvent in the polymer precipitation.

Nitrogen Gas. 10 ppm by volume of oxygen, prepurified grade, supplied by Bluefield Industrial Gas, used to strip out oxygen from the polymerization reactor.

Potassium Chloride. Fisher Scientific catalog number P-217, used as a component of the refractive index standard.

Sodium Hydroxide Solution. Fisher Scientific catalog number SO-S-255, used in the hydrolysis of the polyacrylamides.

Sodium Chloride. Fisher Scientific catalog number S-271, used in the light scattering solvent.

Sodium Metabisulfite. Fisher Scientific catalog number S-244, used as a catalyst in the production of the polyacrylamides.

Sodium Phosphate. Fisher Scientific catalog number S-372, used in the preparation of the buffers used to calibrate the pH meter.

Tungstosilic Acid. Matheson, Coleman and Bell catalog number TX1618, used to calibrate the light scattering equipment.

Zinc. Fisher Scientific catalog number Z-15, used in the oxygen scrubbing system.

Standard Methods. Chemicals used in the hardness and chemical oxygen demand determinations were as listed in Standard Methods.

Apparatus

A listing of the apparatus used in this investigation is given in the following section.

Brice Pheonix Universal Light Scattering Photometer. Manufactured by Brice Pheonix Company, model BP-1000, series 1999-88, used in the light scattering work.

Constant Temperature Bath. Manufactured by MGW Lauda, $\pm$ 0.02°C., used to maintain a constant temperature on the light scattering equipment.

Cooling Coil. Manufactured at VPI&SU glass blowing shop, used to cool the polymerization reactor.

Demineralizer. Barnstead, Fisher Scientific catalog number 9-033-10, used to demineralize the water prior to addition to the polymerization reactor.

Differential Refractometer. Manufactured by Brice Pheonix Co., used to determine the refractive index-concentration gradients for the light scattering work.

Filter. Gelman filter apparatus, Fisher Scientific catalog number 9-754, used to filter the water prior to addition to the polymerization reactor.

Filter Paper, Solids. Manufactured by Whatman, GF/A, 2.1 cm., used in suspended solids determination.

Filter Paper, Refiltration. Manufactured by Whatman, #44, 2.5 cm., used in the refiltration tests for optimum polymer dosage.

Gas Dispersion Tubes. Fisher Scientific catalog number 11-138, used in the oxygen scrubbing system.

Gooch Crucible. Manufacture by Coors Co., #4, used in the suspended solids determination.

Heating Mantle. Fisher Scientific catalog number 11-847-15D, used to heat the polymerization reaction.

Mixer. Stirrer, electric, Fisher Scientific catalog number 14-502, used to stir the polymerization reactor.

pH Meter. Fisher Scientific catalog number Accumet 120, used in determining the degree of hydrolysis of the acrylamide and polyacrylamides.

Reactor. Reaction Kettle, Resin pyrex brand, Fisher Scientific catalog number 11-847D, used as the polymerization reactor.

Refractometer. Abbe 3L, Bausche and Lomb, Fisher Scientific catalog number 13-963, used to check and determine the Rw/Rc constants for the light scattering work.

Separatory Funnel. Fisher Scientific catalog number 10-423,20A, used in the purification of the Tungstosilic Acid.

Still. Distilling apparatus, Barnstead, electrically heated, Fisher Scientific catalog number 9-026B, used to distill the water prior to use in the polymerization reactor.

Strip Chart Recorder. Manufactured by Leeds and Northrup Co., "H" Azar multiple range, 0-2 mv. to 0-100 mv, used in the light scattering work.

Vacuum Oven. Fisher Scientific catalog number 13-262-5, used to dry the polymer samples to prevent the use of excessive temperatures.

Variac. Fisher Scientific catalog number 9-521, used in conjunction with the heating mantle.

Standard Methods. Equipment used for hardness and Chemical Oxygen Demand determinations were as listed in Standard Methods.

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THE EFFECTS OF BRANCHING AND OTHER PHYSICAL PROPERTIES OF ANIONIC POLYACRYLAMIDES ON THE FLOCCULATION OF DOMESTIC SEWAGE

by

Alan J. Anthony

(ABSTRACT)

The first two phases of this investigation were concerned with the polymerization, hydrolysis and characterization of the polyacrylamides to be used in the flocculation studies. The results of the characterization by light scattering revealed a group of polymers varying in weight average molecular weight from 18,205,000 to 151,000 grams per mole, radius of gyration ranging from 8977 to 1100 angstroms, and degrees of hydrolysis of twenty-five and thirty-five percent.

The main purpose and final phase of this investigation was to determine the effects of molecular weight and radius of gyration, or branching, on the flocculation of domestic sewage. Prior to this determination several other parameters were evaluated. First, the minimum concentration of divalent cation was established as required to facilitate bridging. This cation level was found to be at least 110 milligrams per liter as calcium. Following the cation determination, the optimum polymer dose for each of the sixteen polymers was determined by using the refiltration parameter.

The optimum polymer doses were then correlated against the logs of the weight average molecular weight and the radius of gyration. The regression demonstrated that the effect of the weight

average molecular weight was highly significant ($\alpha = 0.01$), and the effect of the radius of gyration was also significant ($\alpha = 0.15$). In a qualitative manner, the optimum polymer dose increased as the weight average molecular weight decreased, and for polymers of similar molecular weights and widely varying radius of gyrations, the larger the radius of gyration resulted in a lower optimum polymer dose than the smaller polymer. Accordingly it was concluded that branching of the polymer chain, which is related to the radius of gyration, and significant effects on the flocculation of domestic sewage. For example in a flocculation test a polymer of 836,000 grams per mole and 4217 angstroms removed an additional thirty-seven percent of the suspended solids, while a polymer of 3,316,000 grams per mole and 2027 angstroms removed only an additional twenty-three percent of the suspended solids. Therefore long chain branching in anionic polyacrylamides decreased the suspended solids removal during flocculation.

In addition it was determined that optimum polymer doses for the various polymers did not result in the same levels of suspended solids and chemical oxygen demand reductions. Finally, there were no appreciable treatment effects for the different degrees of hydrolysis.