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DEVELOPMENT OF IMPROVED MOBILITY CONTROL AGENTS  
FOR SURFACTANT/POLYMER FLOODING

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## I. ABSTRACT

Surfactant/polymer flooding is one of the enhanced oil recovery techniques expected to contribute appreciably to increasing production of known U. S. oil reserves. However, in order for this technique to experience large-scale commercial application, improved efficiency of the process is necessary. The objective of this laboratory work is to develop improved mobility control agents that are more effective than the commercial polymers currently used in this process.

The work reported here constitutes the second year of a three year project. Work during the first year has been reported previously.<sup>1</sup> During the second year of the project, the baseline testing of commercial products was completed. These baseline tests with polymers include studies on mobility control, retention, and shear degradation in Berea cores, the effect of common ions on rheological properties, thermal stability, microbial degradation, and surfactant-polymer interactions. These data are used for comparison of the commercial agents at standardized sets of conditions, and are also used to evaluate new, modified, or improved polymers.

Work was also initiated on the synthesis, characterization, and preliminary screening of new and modified polymers. The modified materials consist of polymers analogous to the commercially available synthetic polymers as well as other polymer types, with specific structural alterations. Testing of these analogs provides systematic correlations of polymer performance with polymer structure. This preliminary testing consists of measurements of shear degradation and viscosity loss in NaCl brines by the use of a simplified screening procedure.<sup>1</sup> Promising candidates are subsequently evaluated in more detail with procedures similar to the baseline testing of commercial products. Structural changes in the polymer molecules needed to correct inadequacies that exist with commercial products are currently under investigation.

To date, a number of potential structure-utility relationships have been observed. Solution viscosities of all nonionic polymers tested are essentially insensitive to changes in NaCl concentration. Increasing the charge-to-mass ratio (degree of hydrolysis) of either polyacrylamides or N-alkyl analogs enhances the ability of these polymers to build viscosity in low salinity NaCl brines. However, such polymers are increasingly subject to viscosity loss as the salinity is increased. Above a certain critical molecular weight, polymers become more susceptible to shear degradation. Many of the polymers that possess stiffer backbones exhibit improved brine and shear stability. The results of these studies will be used to develop an improved mobility control polymer in the next phase of this project.

## II. HISTORY OF PROJECT

This project resulted from our response to a Department of Energy Request for Proposal. The project is designated DOE Number DE-AC19-78BC00047 (formerly EW-78-C-19-0047). The three-year program began on September 29, 1978. DOE will contribute \$223,613 or 50% of the total project cost.

During the first year, the initial stage of the project (Phase 1) included a literature survey of surfactant/polymer flooding, a summary of the current status of DOE-sponsored polymer and surfactant/polymer field projects, and a survey of oil industry personnel regarding difficulties encountered in the use of commercially available polymers. The purpose of the tasks included in Phase 1 is to delineate clearly the strengths and weaknesses of the commercial polymers so that the laboratory tests in the second phase are designed to measure and compare the factors considered to be of greatest importance. All of this background work was completed and reported in our first annual report.<sup>1</sup>

During the second year of the project, the Phase 2 baseline screening tests were completed, and Phase 3 work commenced on the synthesis, characterization, and preliminary screening of new or modified polymers. Results of these Phase 3 studies will be used to design and synthesize an improved mobility control polymer in the fourth and final phase of the project. During the last year of the contract, the improved polymer will be thoroughly tested in order to provide an improved mobility control agent for surfactant/polymer flooding.

## III. INTRODUCTION

Two principal types of polymers are currently used for polymer flooding: synthetic polymers called partially hydrolyzed polyacrylamides (HPAM) and biologically-produced polysaccharides known as xanthan gum (XG). The generalized structures of these two polymers are shown in Figures 1 and 2, respectively. Although both types of materials have been successfully used in field applications, each suffers limitations that cause process inefficiencies or loss of cost effectiveness. Problems common to both polymer types include difficulties encountered with injecting polymers, especially where the reservoir permeability is low; interactions between surfactants and polymers; degradation caused by the presence of oxygen; and availability of bactericides which are compatible with the polymers. Problems specific to the use of XG include bacterial degradation, injection well impairment, and filtration requirements. Problems encountered primarily with HPAM include viscosity loss in brine, especially brines containing calcium and magnesium ions, and the necessity for special handling to prevent degradation by shearing. Although field tests are being conducted with both types of polymers, the majority of the field projects are using HPAM, probably because of economic considerations.

The goal of the laboratory work in this project is to develop mobility control agents that are more effective than the polymers currently used in surfactant/polymer flooding applications. This report summarizes the progress for each phase of the project during the first two years of work.

#### IV. SUMMARY OF PROGRESS

##### A. PHASE 1: SURVEY AND ASSESS APPLICATION DATA

The first phase of the project is an assessment of published information regarding problems encountered with polymers currently used for surfactant/polymer flooding. Details of this work are reported in our first annual report.<sup>1</sup>

##### B. PHASE 2: BASELINE LABORATORY SCREENING

A series of screening tests was designed using the information acquired in Phase 1. The areas of investigation include: (1) rheological properties, (2) temperature stability, (3) bacterial degradation, (4) surfactant-polymer interactions, and (5) flow tests in Berea sandstone cores. Tests have been conducted on as many of the commercially available mobility control polymers as deemed necessary for this purpose. Table 1 lists the polymers tested during the first and second year of the project.

##### 1. Rheological Properties

One of the most important properties of a mobility control polymer is the ability to thicken water. Economic considerations dictate that polymers must provide maximum viscosity for a minimum of polymer concentration and cost. Tests have been designed to compare viscosity enhancement for solutions of the polymers in Table 1. Each polymer is mixed according to the directions supplied by its manufacturer. For purposes of comparison, all the polymer concentrations are equal (750 mg/L) and each polymer is evaluated in at least seven different salt solutions: 0.01, 0.1, 0.3, and 2% NaCl and 0.01, 0.3, and 2% CaCl<sub>2</sub>.

The results of the viscosity screening are in agreement with previously published values. Nowhere else is such a complete set of data available at a constant set of conditions (polymer concentration, temperature, pH, and methods of measurement). The principal contribution of this work is the direct comparison of the commercially available polymers for a variety of salinity environments. Further evaluation of

interesting materials is then quickly accomplished. Rheological testing of the products listed in Table 1 was reported previously.<sup>1</sup> Other materials with interesting structures have been evaluated in similar tests; results of these tests are contained in the two sections that follow.

#### a. Rheology of Scleroglucan

Scleroglucan is a polysaccharide produced from the fermentation of D-glucose by selected species of fungi known as *Sclerotium*.<sup>2</sup> The structure of this biopolymer is shown in Figure 3.<sup>3</sup>

Rheograms of a liquid glucan polymer (trade name, JETCO Actigum CS-11-L) in NaCl and CaCl<sub>2</sub> brines were obtained. The results for a 2% NaCl solution, shown in Figure 4, are typical of rheograms at other salinities. The Power Law parameters, K and n, can be obtained from log-log plots of viscosity versus shear rate. The apparent viscosity at various shear rates in the Power Law region can be determined by the relation:

$$\mu = K(\dot{\gamma})^{n-1}$$

where

$$\mu = \text{viscosity, mPa}\cdot\text{s} \quad (\text{cP})$$

$$K = \text{Consistency Index, mPa}\cdot\text{s}^n$$

$$\dot{\gamma} = \text{shear rate, s}^{-1}$$

$$n = \text{Flow Behavior Index, dimensionless}$$

These Power Law parameters, listed in Table 2, show that the nonionic glucan polymer is very pseudoplastic (shear-thinning), and virtually insensitive to salinity or divalent calcium ion. These results may be compared to data obtained in a similar fashion with other commercially available polymers. In saline brines (>1% NaCl or CaCl<sub>2</sub>), the glucan polymer at the test concentration of 750 mg/L generates the highest solution viscosities of any of the polymers tested to date. As a result of these interesting rheological properties, this polymer was subjected to additional testing. Results of mobility control tests are contained in a subsequent section of this report.

Another rheological test of mobility control polymer solution is measurement of the time required for the solution to pass through a series of five 100-mesh screens.<sup>4-6</sup> The ratio of the polymer flow time divided by the aqueous solvent flow time will be referred to subsequently as the "screen factor". This test measures properties related to the viscoelastic nature of polymer solutions, and has been used in this project for the polymers listed in Table 1 at the same concentrations and

salinities as the viscosity measurements.<sup>1</sup> Screen factors of the glucan polymer (Table 3) suggest that this polymer is relatively inelastic. Such behavior is similar to the response observed for the familiar xanthan gum, as well as other polymers with cellulose structures.<sup>1</sup>

#### b. Rheology of AMPS Homopolymer

The sodium salt of poly(2-acrylamido-2-methylpropanesulfonic acid) has been proposed as a mobility control polymer for oil recovery applications.<sup>7</sup> Structure of the AMPS homopolymer is depicted in Figure 5. Rheograms of this polymer in NaCl brines and CaCl<sub>2</sub> brines are shown in Figures 6 and 7, respectively; rheological properties are listed in Table 4. Screen factors of the AMPS polymer solutions, while relatively unaffected by salinity, are similar in value to screen factors obtained with many of the HPAM polymers. In the standard NaCl and CaCl<sub>2</sub> brines, the AMPS homopolymer generates solution viscosities of approximately the same magnitude as Pusher 700, a commercially available HPAM-type polymer. The AMPS homopolymer appears to have slightly improved performance in the presence of high levels of calcium ion; this possibility will be evaluated further with a procedure outlined in the next section of this report.

#### c. Effect of Divalent Cations on Viscosity of HPAM Solutions

The effect of hardness ions, calcium and magnesium, on the viscosity of HPAM solutions is an area of special concern. Calcium and magnesium are commonly present in reservoir brines. Even when divalent cations are excluded from the injection water, they are picked up as the polymer slug progresses through the reservoir.

Although it is well known that the hardness ions drastically decrease viscosity of the HPAM polymers, very few data are available comparing the effect on various polymers or systematically measuring viscosities in brines which contain both sodium chloride and the hardness ions. A test has now been developed using a series of HPAM polymers in which viscosities of solutions with constant ionic strength and variable ratios of sodium to hardness ions are compared. This approach permits the effects of calcium and magnesium ions on different polymers to be compared in a quantitative manner.

The data originally reported on this test<sup>1</sup> were obtained using a Brookfield cone and plate viscometer. Additional data obtained using a Cannon four-bulb capillary viscometer and low shear rate data from a Contraves LS-30 rheometer are reported here. Details of the experimental techniques and results have been presented.<sup>8</sup>

In the divalent cation test, solutions of HPAM are prepared at constant values of ionic strength and varying ratios of divalent and monovalent cations. The viscosity of a solution with no divalent cation

is taken as a reference value, and the fraction of viscosity retained in the test solution is considered as a function of the fraction of divalent cation in the solution.

Figure 8 shows the reduction in viscosity trend observed as the fraction of calcium ion increases for solutions of 1500 mg/L Calgon 835 (HPAM-type polymer) for three values of ionic strength. The fraction of divalent ion,  $X_2$  is defined as:

$$X_2 = \frac{I_2}{I_1 + I_2}$$

where  $I_1$  = contribution of monovalent salt to total ionic strength

$I_2$  = contribution of divalent salt to total ionic strength

Figure 9 shows these same results where the viscosities are expressed as the fraction of the viscosity at  $X_2 = 0$ . In the notation used in this and subsequent figures,  $\eta_x$  is the viscosity at  $X_2 = x$ ,  $\eta_z$  is the viscosity at  $X_2 = 0$ , and the shear rate at which both of these viscosities are reported is  $100 \text{ s}^{-1}$  unless otherwise indicated. As reported previously<sup>1</sup>, these results indicate that the fraction of viscosity retained is independent of ionic strength over the range studied.

A correlation such as that shown here between fraction of divalent cation and fraction of viscosity retained which is independent of total ionic strength over a range of practical interest has great potential value. It provides a method of predicting viscosities of HPAM solutions in a variety of brines containing mixtures of ions. Only a few basic measurements are required to establish trends with increasing divalent cation concentration and with increasing total ionic strength in the absence of divalent cations. The constant ionic strength approach also provides a method for evaluating and comparing the sensitivity to divalent ions for a variety of anionic polymers.

Investigations of constant ionic strength solutions of HPAM polymers with varying degrees of hydrolysis have been conducted using other polymers in the Calgon 800 series. These polymers were selected because the molecular weights of all three polymers are approximately equivalent, and the major differences are the levels of hydrolysis. The nominal degree of hydrolysis is indicated by the last two numbers in the product designation. Results in this laboratory indicate that the percent hydrolysis (expressed as percent of free acid units) of Calgon 815 is 24.8%, 825 is 31.9% and 835 is 38.9%.<sup>1</sup>

Figure 10 shows the results of constant ionic strength tests for each of these polymers at concentrations of 1500 mg/L. As percent hydrolysis increases, it is evident that calcium ion has a greater effect on reducing viscosity of HPAM solutions. Each of the three lines shown is a composite of four ionic strengths ranging from 0.02 to 0.2.

Further divalent cation tests have been performed to investigate several variables, including the effect of polymer concentration, identity of the divalent ion and the effect of shear rate. Figures 11-18 summarize these results. Figure 11 shows the effect of changing the concentration of Calgon 835; increasing concentration decreases the fraction of viscosity retained. A comparison of the effect of calcium and magnesium ions on the viscosity retention of Calgon 815 (Figure 12) shows a somewhat greater decrease for the solutions containing calcium ion. A equimolar mixture of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  gives roughly intermediate results.

The results at differing concentrations can perhaps be understood if specific viscosities are considered. Standard definitions for relative, specific, and reduced viscosity are given in the nomenclature. The ratio of the observed viscosities is very nearly equal to the ratio of the relative viscosities since the solvent viscosities should differ only slightly. Thus,

$$\eta_x/\eta_z = \frac{\eta_{sp_x} + 1}{\eta_{sp_z} + 1}$$

where  $\eta_{sp_x}$  = specific viscosity at  $X_2 = x$

and  $\eta_{sp_z}$  = specific viscosity at  $X_2 = 0$ .

Further,

$$\eta_x/\eta_z = \frac{\eta_{sp_x}}{\eta_{sp_z} + 1} + \frac{1}{\eta_{sp_z} + 1}$$

The second term is a constant for a given set of conditions and as the polymer concentration increases, the specific viscosity at  $X_2 = 0$  also increases and the value of this constant term decreases. Therefore, higher values of  $\eta_x/\eta_z$  can be expected for lower polymer concentrations. This agrees with the observed trend.

It is therefore of interest to reanalyze the data at varying concentrations, comparing specific viscosities rather than apparent viscosities. This has been done for Calgon 825 where data were available for three different concentrations. Figure 13 illustrates the results of apparent viscosity comparisons; Figure 14 plots specific viscosity ratios for the same data. Clearly, a more useful correlation is obtained for data at varying polymer concentrations from the comparison of specific viscosities.

The data in Figures 13 and 14 are all for a single value of ionic strength. The question arises whether the independence of the retained viscosity from ionic strength observed for the ratio of apparent viscosities holds for the specific viscosity ratio as well. This question is not yet fully resolved. Figure 15 shows the specific viscosity comparison for data reported previously.<sup>1</sup> The specific viscosity ratio

shows much more scatter than was observed for the apparent viscosities. In other cases, however, fits to a single curve which were equivalent or better were obtained comparing specific viscosities as shown in Figures 16 and 17 for 1500 mg/L of Calgon 825 with magnesium as the divalent ion. It is likely that one or the other of the observed correlations is fortuitous. It is not expected that both correlations would hold, but as apparent viscosity increases, the difference between the two ratios would decrease. The data gathered so far are not sufficient to distinguish between these two possible correlations and further experiments are now underway which may help clarify this question.

The results reported in Figures 8-17 are for apparent viscosities at shear rates of 100 to 115  $s^{-1}$ . This shear rate is high compared to shear rates expected under field conditions in a polymer flood once the injected solution leaves the vicinity of the wellbore. Figure 18 shows the results obtained for solutions of Calgon 825 at 100  $s^{-1}$ . Results for these same solutions as the shear rate approached zero are shown in Figure 19. In the region of the shear rate versus viscosity curve where the viscosity becomes Newtonian at low shear rates, the correlation previously developed does not hold. This is true for both the apparent and the specific viscosity ratios. For nearly all of the solutions investigated,  $100^{-1}$  lies in the Power Law region where the log of viscosity is linearly related to the log of shear rate. Apparently, the correlation applies in this Power Law region, but not in the zero shear rate region. Perhaps further investigation will reveal more about the differences in polymer rheology in these two regions that might permit extension of the predictive ability developed in the Power Law region to the lower shear rate regime. Investigation is continuing into these interesting and potentially useful phenomena.

## 2. Thermal Stability

### a. Background

Long-term chemical stability at elevated temperatures is an extremely important consideration in evaluation of polymers for enhanced oil recovery. Processes are designed to operate over a period of years during which time the polymer solution will be required to withstand exposure to the reservoir temperature without substantial loss of solution viscosity. The purposes of this phase of the project have been to design a screening test which will predict the performance of polymers at elevated temperatures, to test representative samples of the currently available commercial polymers, and to test new products for comparison with those currently in use.

A number of factors have been considered in designing the long-term stability tests. These include temperature, dissolved oxygen, salinity, pH, and the effect of additives including formaldehyde and sodium dithionite (sodium hydrosulfite).

Temperature. Initial tests<sup>1</sup> conducted at 25°C, 43°C, 66°C and 93°C showed predictably that the rate of viscosity loss increased in a regular fashion with increasing temperature. Thus the highest and lowest temperatures were chosen for comparison in the screening tests.

Dissolved Oxygen. The effect of oxygen is evaluated by comparison of samples incubated in the presence of dissolved oxygen with those of the same composition from which oxygen has been removed by nitrogen-purge in a glove box. Oxygen levels are monitored down to 5 ppb (parts per billion) by a colorimetric test (CHEMetrics test kit). Dissolved oxygen concentration is measured for each sample to monitor possible oxygen contamination during incubation.

Salinity. Salinity has a profound effect on HPAM solution viscosity, but the effect of salinity on long-term stability is not clear. Samples have been tested in different salinity environments, but thorough characterization of long-term stability in a range of ionic environments is outside the scope of this screening procedure. HPAM and similar materials are tested at 0.01% and 1.0% NaCl, xanthan gum and other polysaccharides at 2% NaCl.

Hydrogen Ion Concentration. Since pH could have an effect on long-term stability, it is monitored in these tests. All samples are initially at a pH of 7.5 and the pH of each solution is measured at the time of sampling to determine whether significant changes have occurred.

Additives. Finally, additives are tested to determine whether and to what extent they improve the long-term viscosity stability of polymer solutions. Additives investigated in the screening test include 300 mg/L formaldehyde (in the form of formalin), and sodium dithionite, an oxygen scavenger, at a concentration of 83 mg/L.

#### b. Testing Procedure

Figure 20 shows the overall testing scheme for a given polymer at one or more values of salinity. A screening test for one polymer at one salinity consists of two batches of polymer solution, one with dissolved oxygen and one purged to less than 5 ppb dissolved oxygen. Both batches are divided according to the flow chart in Figure 20 into the untreated, formaldehyde and dithionite samples.

Aliquots of each of these six sample types are stored in sealed glass bottles along with several extra samples of untreated polymer. The latter samples are monitored following the sample preparation; viscosities and screen factors are measured, and changes in these quantities observed with

time. When the viscosity and screen factor of these preliminary samples reach steady values, the remaining samples are stored at the appropriate temperatures and the steady values are taken as the initial measurements to which all subsequent data are compared.

Sampling schedules may vary with the rate of change of screen factor and viscosity of a particular sample type. Thus, a sample which loses viscosity rapidly would be sampled more often and for a shorter total period than one for which viscosity is retained for a longer period. Purged samples are opened in a glove box and dissolved oxygen is immediately measured, followed by pH, which is also measured in an oxygen-free environment for the purged samples. Oxygen concentrations of 25 to 100 ppb are routinely observed. Samples are then removed from the glove box. Viscosity and screen factor data are measured for all samples.

### c. Results

Work during this reporting period has concentrated on improvements in the oxygen removal portion of the screening procedure. Recently this technique has been improved to the point where concentrations of 5 ppb or less are routinely achievable. Tests of both synthetic and biopolymers are now underway.

A test of Calgon 454, for comparison with the Pusher 700 results previously reported, is in progress. Figures 21 and 22 show some of the viscosity results obtained so far. Data are plotted as the fraction of viscosity retained versus time. The results of the samples with oxygen present at two temperatures, with and without formaldehyde, are reported in Figure 21 for Calgon 454 (1000 mg/L) in 0.01% NaCl. Sampling techniques probably account for some of the scatter in the early data. Despite this scatter, the trends are clear: viscosity loss in the plain samples is much greater at the higher temperature. At both temperatures the addition of formaldehyde decreases the total viscosity loss over the time period tested and it reduces the rate of loss, especially at the higher temperature. Screen factor data show similar trends. Figure 22 compares the high temperature results of the plain sample with oxygen to the high temperature data for the purged samples. Clearly, removal of oxygen to less than 5 ppb improves viscosity retention, though viscosity loss is not entirely eliminated. Other recently presented data<sup>9</sup> suggest that pH of the original polymer solution can have a substantial effect on thermal stability. Addition of formaldehyde gives the highest retained viscosities, although the initial increase in viscosity suggests that crosslinking may be one reason for the higher viscosity of these samples.

Kelco Xanflood, a representative biopolymer, is currently being tested in 2% NaCl. Results are outlined in Table 5.

Data for HPAM and XG are basically in agreement with recently presented data<sup>9,10</sup>, but our studies of purged polymer solutions tend to

indicate somewhat greater amounts of degradation. During the next year, the screening test for long-term stability outlined here will be used to begin evaluation of some of the new polymers of interest.

### 3. Microbial Degradation

An important activity of many natural populations of bacteria is the degradation of organic polymeric compounds. Polymer degradation is a result of hydrolytic or phosphorolytic enzyme activity. Polymers used to increase viscosity of oilfield flood water, e.g., polyacrylamides and xanthan polysaccharide gum, may be degraded by bacteria. Microbes may be able to affect polymer solution viscosity either by direct enzymatic degradation and subsequent utilization of the monomeric units, indirect breakdown resulting from polymer-metabolic end product (e.g., organic acids and alcohols) interaction, or by co-metabolism, a process whereby recalcitrant molecules are altered by microbial enzyme activity, but not utilized by the microbes.

Many factors affect biodegradation. These factors include the availability of oxygen or redox potential, pH, temperature, and inorganic nutrients (nitrogen, phosphorus, potassium, etc.). The conditions within an environment determine the types and functions of bacteria which can occur. Thus, stability of polymeric compounds will be affected by environmental control over the potential bacteria capable of utilizing these compounds.

Two factors must be considered in the evaluation of stability of viscosity-affecting polymers in the field application -- the types of microorganisms capable of polymer degradation, and the environmental parameters which affect the microbes.

The objective of the microbial degradation investigation of Phase 2 is to determine whether the polymers with potential use in oil recovery will remain biologically stable under field conditions.

#### a. Experimental Methods

Test procedures were developed utilizing common microorganisms, easily cultured in laboratory conditions. Laboratory strains of Bacillus megaterium, Micrococcus luteus, Pseudomonas aeruginosa and Desulfovibrio species were used. Cultures of single types of microorganisms were employed. The species of Bacillus, Micrococcus, and Pseudomonas are cultured aerobically; the Desulfovibrio was grown anaerobically.

Xanthan gum was first evaluated for bio-stability in the presence of aerobic organisms. The culture medium for the aerobic microbes consisted

of 75 ml of xanthan (1000 mg/L) in 2% NaCl sterilized under N<sub>2</sub>-atmosphere at 121°C for 12 minutes plus 25 ml of nutrient broth in 2% NaCl sterilized under normal atmosphere at 121°C for 12 minutes. In order to determine if the xanthan gum could serve as a sole carbon source for microbial growth, a duplicate set of culture flasks was prepared substituting a nutrient-salt solution (K<sub>2</sub>HPO<sub>4</sub>, 0.004g; MgSO<sub>4</sub>·7H<sub>2</sub>O, 0.04g; (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 0.04g in 25 ml 2% NaCl solution) for the nutrient broth. Postgate's medium E was used with the xanthan gum solution for growth of the anaerobic Desulfovibrio. The organic contents, except for the reducing agents, were deleted in order to determine if the gum could be metabolized by the Desulfovibrio.

All aerobic and anaerobic media were adjusted to pH 7.5 and incubated at 30°C following inoculation. The culture flasks were sampled immediately after inoculation. The aerobic cultures were sampled after 7 and 14 days; the anaerobic cultures were sampled 7 days after inoculation. Viscosities of the samples were determined with a Contraves LS-30 rheometer.

#### b. Results and Discussion

Polymer degradation is a common phenomenon among aerobic microbes. Figure 23 is indicative of the results obtained with nutrient broth containing cultures of B. megaterium and Ps. aeruginosa. Following seven days of incubation under aerobic conditions, both microbes reduced the viscosity of xanthan gum solution about 20%. In the absence of nutrient broth, the Ps. aeruginosa decreased viscosity 8.5% after 14 days incubation and the B. megaterium decreased the viscosity 24% (see Table 6). No decrease was observed for the corresponding uninoculated control. The decrease of viscosity in the presence of these microbes and aerobic conditions was not unexpected.

Following seven days incubation, no decrease in viscosity occurred with the aerobic M. luteus and the anaerobic Desulfovibrio species (see Table 6). Growth was noted by turbidity and sulfide production in the anaerobic culture of Desulfovibrio. The inability of Desulfovibrio to affect viscosity was anticipated, as these microbes require short-chain organic acids (e.g., lactic acid) for metabolism. It would be necessary for a different type of bacterium to first metabolize polymeric compounds to short chain organic acids and alcohols before the Desulfovibrio could grow.

Research dealing with microbial degradation will continue with the procedures that have been developed and will employ mixed cultures native to oilfield sites. A consortium of microbes may be more effective at polymer degradation, and the role of these microbes in anaerobic conditions will be determined.

#### 4. Surfactant-Polymer Interaction

Interaction between surfactant and polymer slugs in a micellar/polymer process can have disastrous effects on the outcome of the process. Such interactions must, therefore, be considered in designing a particular process. Trushenski<sup>11-13</sup> has shown that phase separation can take place when polymer invades the micellar slug. He therefore suggests that trapping of a viscous, high surfactant concentration phase may be responsible for the low recoveries observed in some core flooding experiments. Whether trapping is due to high interfacial tension or to high viscosity as suggested by Szabo<sup>14</sup> is an unresolved question. The physical phenomena contributing to surfactant-polymer interactions are not yet well understood. Shah and Walker<sup>15</sup> report that there may in fact be more than one mechanism of interaction operating at different ranges of salinity, but they have not yet suggested what either mechanism may be.

Pope, et al<sup>16</sup> have extensively studied the question of the effect of polymer on surfactant phase behavior. The changes are most dramatic in aqueous systems where the presence of polymer can cause phase separation at salinities above some critical electrolyte concentration (CEC). The CEC depends on the surfactant, alcohol, and temperature, but not on the type or concentration of polymer. Phase behavior tests using sodium dodecylbenzene sulfonate and Exxon PDM-337 in this laboratory have confirmed the observations found in the literature.

It thus seems clear that what is required in the area of surfactant-polymer interaction is basic research to elucidate the mechanism or perhaps mechanisms of interaction in polymer-surfactant mixtures containing salts, alcohol, and perhaps oil. Work of this nature is planned at the University of Florida and at Carnegie-Mellon University. Since the interactions observed so far seem to vary little with polymer, it does not seem likely that a useful screening test for differences in polymers can be designed at this time.

#### 5. Flow Tests in Berea Sandstone Cores

Rheological tests on polymer solutions can provide a great deal of useful information, but there are important features of polymer flooding which can be measured only by flowing the solutions through rock samples. Phenomena such as plugging tendencies, changes in permeability to water after polymer injection, polymer retention in the reservoir, and polymer degradation during flow through a porous medium are measured in this project using cores of Berea sandstone.

### a. Injectivity, Mobility Reduction, and Polymer Retention

The first step in the core flooding procedure is to test the injectivity characteristics of the polymers. Polymer solutions are filtered through a 325-mesh screen before further testing in order to remove any particulate matter or undissolved polymer. Solutions are then pumped through a small injectivity-core of Berea sandstone. The purpose of this procedure is twofold: any tendency of the solution to plug this initial core is an indication of injectivity problems, and the solution is prefiltered by rock at a fairly high flow rate in a manner similar to the actual situation in the reservoir around the wellbore.

A larger core of Berea sandstone is used to measure the reduction in mobility caused by 750 mg/L of the various commercial polymer samples in 0.1% NaCl and in 2.0% NaCl brine solutions. The pressure drop across the core is related to the flow rate, the solution viscosity, and the permeability of the rock. All tests are performed at a constant flow rate in the range of expected reservoir flow rates (1 ft/day), so that the pressure drop is a measure of the ratio of permeability to viscosity, and is thus a measure of effective viscosity. Two measurements are of particular interest: the polymer resistance factor, which compares the mobility of water to that of the polymer solution; and the residual resistance factor, which compares the mobility of water before and after polymer flooding. Higher values of polymer resistance factor correspond to greater mobility control, and higher values of residual resistance factor indicate a permanent or long-term effect on the rock permeability, probably caused by adsorption or entrapment of polymer. Concentration determinations on the effluent from the mobility core tests permit calculation of the amount of polymer retained in the core. Resistance factors and retention data are summarized in Table 7. These data are used for comparison of the commercial products with new polymers of interest.

Because of the favorable rheological behavior of Scleroglucan, flow tests were recently conducted with this polymer. Results are also presented in Table 7. The flow resistance in the injectivity core appeared to correlate with solution viscosity, but some anomalous pressure responses were observed in the mobility cores. Tests with the glucan polymer in 2% NaCl will be repeated. One area of concern regarding the use of this nonionic polymer is the extremely high level of polymer retention within the Berea core. Figures 24 and 25 compare the polymer concentrations in the core effluent for glucan to similar tests previously conducted with xanthan gum. The aqueous medium in both cases was 2% NaCl. The greater amount of retention for the glucan polymer is apparent. Similar trends were observed when the aqueous medium for the comparison was 0.1% NaCl. Additional tests are planned in which the glucan polymer will be preceded by injection of a surfactant solution. If some of the adsorption sites are satisfied by the surfactant, the level of polymer retention may be greatly reduced.

Flow tests in Berea cores were also conducted to compare the effect of N-alkyl substitution on adsorption or retention of acrylamide polymers.

These polymers were synthesized in our laboratory; details of preparations are presented in a subsequent section of this report. For these studies, flow tests utilized the homopolymer of acrylamide and the homopolymer of N-methylacrylamide. Molecular weights of the two polymers are similar. Polymer concentrations in the effluents from the cores are shown in Figures 26 and 27. These data suggest the N-alkyl substitution of acrylamide polymers reduces the amount of polymer retention. These nonionic polymers are not of direct interest for mobility control, but the effect of this substitution must be determined before similar tests with copolymers are considered. Flow tests with hydrolyzed versions of the N-methyl polymer are planned.

#### b. Mechanical Degradation

One area of difficulty with some of the mobility control polymers is the tendency of the polymer chains to break when subjected to mechanical shear. Several tests are reported in the literature for shearing the polymer and for determining the extent of damage. It is not clear that such methods as homogenizing in a blender or pumping through a single restriction at high flow rate are sufficiently similar to the stresses experienced in actual polymer injection to be of use in evaluating polymers. Therefore, the approach chosen for this study is to pass the polymer solution through a small core at varying flow rates. Experimental details are outlined in our first annual report.<sup>1</sup>

Partially hydrolyzed polyacrylamides in various aqueous solvents were subjected to mechanical degradation during flow through Berea cores. The solvents included 0.01% NaCl, 0.3% NaCl, and 3% NaCl that contains 0.3% CaCl<sub>2</sub>. The extent of mechanical degradation, as measured by loss in screen factor, increases with increasing salinity. This observation is in agreement with previous findings.<sup>1</sup> Figure 28 compares the results for 750 mg/L of Dow Pusher 700 in several solvents. The effects of mechanical degradation are clearly visible for HPAM when the screen factor of the effluent solution is compared to the original screen factor. Viscosities of the HPAM solutions show similar trends but are not as sensitive as screen factors. The degradation data from the Berea core tests are also being compared to shear studies that are being conducted in blender tests, and also in high-rate flow through screens.

In similar studies in Berea cores, a xanthan gum polymer was resistant to mechanical degradation (Table 8). A slight loss in viscosity was observed when the linear frontal advance exceeded 15,000 ft/day. Mobility control tests with the sheared XG solutions suggest only a minimal amount of mechanical degradation.

Results of these studies will provide a baseline of data for comparing new or modified polymers that become available.

## C. PHASE 3: POLYMER SYNTHESIS AND PRELIMINARY SCREENING

### 1. Objective

The objective of this laboratory work is to obtain structure-utility correlations which should be helpful in designing and making mobility control agents that are more effective than the polymers currently used in surfactant/polymer flooding.

The approach to meeting this objective has been to synthesize, characterize, and test polymers similar to poly(acrylamide-co-sodium acrylate), but with specific structural alterations. These polymers are tested uniformly in order to obtain systematic correlations of polymer performance with polymer structure. Structural alterations have included:

- (1) substitution of an alkyl group for one of the amide hydrogen atoms of each acrylamide residue,
- (2) incorporation of groups expected to stiffen the polymer chain, and
- (3) variation of the relative amounts of residues containing amide and carboxylate anion and therefore charge-to-mass ratio on the polyanion or degree of hydrolysis.

The synthetic method was also varied, which may affect the sequencing of residues in a copolymer.

### 2. Experimental Details

Synthetic work was completed in three areas during the second year of the project:

(1) Several copolymers of acrylamide and sodium acrylate with carboxyl contents significantly lower or higher than those of commercial copolymers were synthesized by free-radical copolymerization. Table 9 contains the preparative details.

(2) Poly(methacrylamide-co-sodium methacrylates) with significant reduced viscosities and a wide range of carboxyl contents were prepared both by copolymerization and by hydrolysis of amide homopolymer. Polymerization data are included in Table 10.

(3) Water-soluble, N-alkyl-substituted acrylamides and their copolymers with sodium acrylate were prepared by free-radical polymerization. Synthetic details are contained in Tables 12-16.

Some materials were synthesized for polymer systems still under investigation. Additional samples of poly(N-methylacrylamide-co-sodium acrylate) were prepared by hydrolysis of the homopolymers listed in Table 12. Synthetic particulars for the poly(N-methylmethacrylamide-co-sodium methacrylate) samples prepared to date are presented in Table 11. Tables 17-19 include details on the preparation of imidized poly(methacrylamides) and polymers containing maleimide functionalities.

Structural representation formulas of the copolymers and terpolymers mentioned above are shown in Figure 29. Structural formula IV assumes the imide resulted from homopolymer that had formed by the usual head-to-tail mechanism.

Reagent grade chemicals were used in all syntheses. Commercial monomers were redistilled before use. Water used as solvent for polymerizations was deaerated. Polymerizations were performed in nitrogen atmosphere. Polymeric products were isolated and purified by reprecipitation and/or washing.

The preliminary screening procedure<sup>1</sup> provides data on viscosity loss in aqueous NaCl brine by comparing the ratios of the specific kinematic viscosity in 2% NaCl to the specific kinematic viscosity in 0.01% NaCl. This "NaCl effect ratio" is subsequently designated  $(\eta_{sp})_2/(\eta_{sp})_{.01}$ . Shear degradation is evaluated in each brine by comparing specific kinematic viscosities before and after shearing. Shearing is accomplished via passage of the polymer solutions through a stainless steel screen in a pressurized system. The fraction of specific (or reduced) kinematic viscosity retained is used with other data in order to infer potential structure-utility relationships for polymers with respect to enhanced oil recovery.<sup>17</sup> All polymers are then compared using data obtained at essentially the same test conditions. These potential relationships are used for guidance in synthesizing improved polymer types.

Characterization of polymers includes identity, viscosity in solutions (as indicated above), copolymer composition and, therefore, charge-to-mass ratio of polyanion in salt form, and acid strength as indicated by  $pK_a$  as a function of ionization of comonomer residues. An iterative data-treatment method (see Appendix A), which has been developed and tested as part of this project, has been used to determine copolymer composition and acid strength from potentiometric titration data. The percentage of volatile material is determined so that concentrations, copolymer compositions, and reduced viscosities are based on dry weights.

The lack of suitable methods for determining molecular weights of many of these materials makes interpretation somewhat less quantitative than desired. Methods are being investigated to obtain this information by a procedure consistent with a relatively rapid preliminary screening procedure.

In order to screen a large number of polymers within a reasonable time, some experimental uncertainty has been tolerated. Thus, very small experimental differences or differences between poorly matched samples may

not be significant. However, this preliminary screening procedure is designed to search for gross effects; selected samples are subjected later to more rigorous testing. In some of the comparisons between groups of polymers, statistical analysis (see Appendix B) has indicated statistically significant differences between polymer groups.

### 3. Presentation of Screening Data

Preliminary screening test results, grouped according to polymer type and arranged within each polymer type according to increasing charge-to-mass ratio of polyanion, are presented in Tables 21 and 23. Table 21 presents screening results in 1.6% (v/v) ethylene glycol (aqueous), and Table 23 reports screening results of selected polymer types dissolved in water. Polymer types synthesized by emulsion copolymerization, or suspected of being hydrolyzed under screening conditions, or not yet fully screened are omitted from Table 23. Table 20 is a key to the sample numbers given in Table 21. Likewise, Table 22 is a key to the sample numbers used in Table 23.

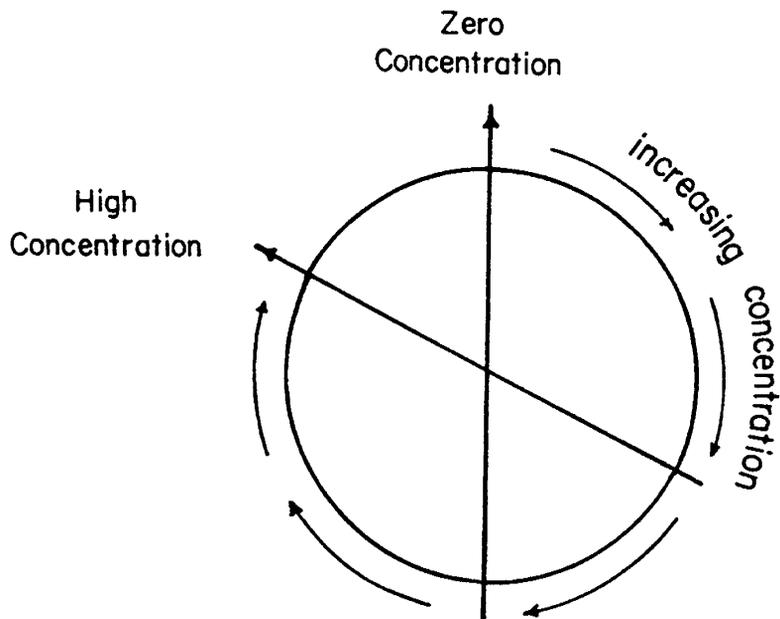
Screening results are also shown in Figures 30 through 51. The effect of shear on specific kinematic viscosity is displayed in Figures 30 through 35. Smoothed data for all of the polymer samples listed in Tables 22 and 23 are plotted in three dimensions in Figures 30 and 31. These plots are for polymers dissolved in 0.01% NaCl and 2% NaCl, respectively. The reduced viscosity in 2% NaCl is plotted as the y-coordinate in both figures, since this is believed to be more reliable as an indicator of relative molecular weight than is the reduced viscosity in 0.01% NaCl. The general appearance of both figures is similar, which indicates that the shear resistance in 0.01% NaCl is similar to that in 2% NaCl. The cliff appearing near the right-hand side of each of these figures indicates a sharp increase in sensitivity to shear at a reduced viscosity (measured in 2% NaCl) of 27 to 39 dL/g. This same effect is also shown in Figures 32 through 34. In Figure 35, the specific viscosity fraction surviving the induced shear in 2% NaCl is plotted against that in 0.01% NaCl. Again, a fair degree of correlation is seen in the effect of shear in 2% NaCl and that in 0.01% NaCl. The early demise of poly(acrylamide) samples (the + symbols) and one poly(ethylene oxide) sample (one of the ◊ symbols) in Figure 32 is attributed to the choice of abscissa. In such a low salt concentration, much of the reduced viscosity of polyanions is due to a polyelectrolyte effect. Thus, if poly(acrylamide-co-sodium acrylate) reaches its region of high sensitivity to shear at approximately the same molecular weight as poly(acrylamide) and poly(ethylene oxide), the copolymer would exhibit a much higher reduced viscosity in fresh water in this region than would the two uncharged homopolymers.

In Figures 32 through 37, different symbols represent different polymer types. These are listed in Table 24. Since the residues of salts of weak acids do not have the same formula weight for every polymer, the charge-to-mass ratio cannot be plotted on the same axis as percent

hydrolysis. Further, the meaning of percent hydrolysis is not clear for xanthan gum, which is omitted from Figure 36. Hence, Figures 36 and 37 are presented as separate plots.

Figures 36 through 51 depict the effect of NaCl on the specific kinematic viscosity of aqueous polymer solutions. Of these figures, only Figure 51 is for a series of solutions that also contain 1.6% (v/v) ethylene glycol.

Figures 38 through 51 show  $(\eta_{sp})_2/(\eta_{sp})_{.01}$  for different polymer types as a function of charge-to-mass ratio of polyanion, reduced viscosity in 2% NaCl, and concentration. To facilitate comparison, identical scales are used for all of these figures. As shown below, all four variables are represented in each of these plots. The horizontal coordinate of the center of each circle represents the charge-to-mass ratio of the polyanion. The vertical coordinate represents  $(\eta_{sp})_2/(\eta_{sp})_{.01}$ . The radius of the circle is proportional to the reduced viscosity of the unsheread polymer in 2% NaCl. Concentration of the polymer is indicated by the direction of the arrow; concentration is zero at the 12:00 direction and increases clockwise up to the 10:00 direction.



## 4. Structure-Utility Relationships

### a. N-Alkyl Substitution

One structural variation has been the substitution of an alkyl group for one of the amide hydrogen atoms of each acrylamide residue of poly(acrylamide) and poly(acrylamide-co-sodium acrylate). Comparisons of  $(\eta_{sp})_2/(\eta_{sp})_{.01}$  without considering differences in synthetic methods indicated that poly(N-methylacrylamide-co-sodium acrylate) samples exhibited consistently higher  $(\eta_{sp})_2/(\eta_{sp})_{.01}$  values than poly(acrylamide-co-sodium acrylate). Differences can be seen in Figures 36 and 37 and by comparing Figures 38 through 40 with Figures 41 through 43. Statistical tests were performed both on the raw or untransformed data and on the same data transformed to reduce the effect of differences in charge-to-mass ratio. This transformation and a discussion of the modified Mann-Whitney statistic are presented in Appendix B. Differences equal to or greater than the observed differences in the modified Mann-Whitney statistic would occur only 0.028% of the time for untransformed data and only 0.12% of the time for transformed data if the rankings were completely random. These very small values indicate that it is highly unlikely that these differences have occurred only by random chance. Therefore, a real difference very likely exists between the NaCl sensitivities of the two polymer groups.

Poly(N-isopropylacrylamide-co-sodium acrylate) samples (Figures 44-46) consistently exhibited higher  $(\eta_{sp})_2/(\eta_{sp})_{.01}$  values than poly(acrylamide-co-sodium acrylate) when differences in synthetic methods were disregarded. Differences equal to or greater than the observed differences in the modified Mann-Whitney statistic would occur only 2.16% of the time for untransformed data and only 0.31% of the time for transformed data if the rankings were completely random. Again, these small values indicate that there is likely a real difference between the NaCl sensitivities of the two polymer groups. Although these statistically-significant differences have been observed, another structural variation--sequencing--may be largely responsible for these differences. The importance of sequencing is discussed later in this report.

### b. Chain Stiffening

Another structural variation has been the incorporation of groups expected to stiffen the polymer backbone. Polymers containing methacrylamide, sodium methacrylate, and imide residues have been synthesized to accomplish this. Some of the backbone carbon atoms of the polymer are included in the imide rings. Aqueous solutions containing excess alkali were used initially for dissolution of these polymers. However, the apparent ease of ring-opening hydrolysis of imide residues in

alkaline solution hampered initial attempts to screen this polymer type under standard conditions. Salt resistance of selected polymers containing sodium methacrylate is presented graphically in Figures 47 through 50.

Meaningful results were obtained by dissolving imidized methacrylamide homopolymer in a small quantity of ethylene glycol and then adding limited amounts of sodium hydroxide dissolved in ethylene glycol. Sufficient water was added so that the final solutions contained 1.6% (v/v) ethylene glycol. Marked improvement--approximately doubling--of  $(\eta_{sp})_2/(\eta_{sp})_{.01}$  was seen for imidized polymers when compared with a poly(acrylamide-co-sodium acrylate) sample that had been purified from a commercial product (Dow Pusher 700) and dissolved identically. The comparative screening results for these systems containing 1.6% ethylene glycol in the final solutions are presented in Table 21, in which  $(\eta_{sp})_2/(\eta_{sp})_{.01}$  is given as C/A. NaCl resistance is plotted in Figure 51.

Recent synthetic work has involved monomers, such as maleimide and N-methylmaleimide, which are expected to stiffen the polymer backbone.

### c. Charge-to-Mass Ratio of Polyanion

For each extensively-studied polymer type, the copolymer composition has been varied in order to have polymers whose anions have varying charge-to-mass ratios or degrees of hydrolysis. This structural variation is very important when considering  $(\eta_{sp})_2/(\eta_{sp})_{.01}$ .

The most outstanding structure-utility effects exhibited include the very rapid onset of NaCl sensitivity (low value for  $(\eta_{sp})_2/(\eta_{sp})_{.01}$ ) when viewed as a function of charge-to-mass ratio of the polymer anion. Nonionic polymers exhibit little or no sensitivity to NaCl. However, many solutions of ionic polymers lose more than 90% of their specific viscosity when NaCl concentration is increased from 0.01% to 2%. When comparing partially hydrolyzed poly(acrylamides) and analogous N-alkyl substituted poly(acrylamides) that are very similar except for charge-to-mass ratio, the polymers with higher charge-to-mass ratios tend to exhibit greater viscosities and greater sensitivity to NaCl. For both partially hydrolyzed poly(acrylamides) and substituted poly(acrylamides), there is a very rapid decrease in  $(\eta_{sp})_2/(\eta_{sp})_{.01}$  with increasing charge-to-mass ratio at very small charge-to-mass ratios. However, at relatively large charge-to-mass ratios, the charge-to-mass ratio seems to have little further effect on  $(\eta_{sp})_2/(\eta_{sp})_{.01}$ , which seems to approach an asymptotic value of approximately 0.07 under typical screening conditions. This effect can be seen especially in Figures 37, 38, 41, 42, and 44, in which  $(\eta_{sp})_2/(\eta_{sp})_{.01}$  is plotted as the vertical coordinate.

#### d. Effects of Possible Sequence Variation

A structural variation may result when different synthetic methods are used. Most of the N-alkyl substituted copolymers were synthesized by copolymerization. Recently, some poly(N-methylacrylamide-co-sodium acrylate) samples have been synthesized by partial hydrolysis of poly(N-methylacrylamide). Although both synthetic methods should produce essentially random copolymers, the copolymers synthesized by one method may have an increased number of like-monomer sequences (more nearly like block copolymers), and the copolymers prepared by the other method may be more nearly like alternating copolymers.

The samples synthesized by partial hydrolysis tend to lose a larger fraction of their viscosity when subjected to increased NaCl than do samples of the same polymer type synthesized by copolymerization (see Table 23 and Figures 41 and 42). Calculation of the modified Mann-Whitney statistic shows this difference to be statistically significant. Differences in the modified Mann-Whitney statistic equal to or greater than the observed differences would occur only 2.5% of the time if the rankings are completely random. This two-tailed significance level is the same for transformed and untransformed data. This could indicate that differences in sequencing may affect salt sensitivity.

Many of the poly(acrylamide-co-sodium acrylate) samples tested have been purified (and in some cases, sheared) industrial samples, which were synthesized by partial hydrolysis. Thus, although poly(N-alkylacrylamide-co-sodium acrylate) samples in which the alkyl group equals methyl or isopropyl have shown statistically significant improvement in  $(\eta_{sp})_2/(\eta_{sp})_{.01}$  when compared with poly(acrylamide-co-sodium acrylate) samples, the identity of the structural variation responsible for this improvement remains uncertain. At least in the case of N-methyl substitution, it seems reasonable tentatively to credit differences in sequencing, rather than N-alkyl substitution, for the improved viscosity retention in NaCl brine. (See Table 23 and Figures 41 and 42.) Further studies are planned in order to test this hypothesis.

A small number of poly(N-n-butylacrylamide-co-sodium acrylate) samples exhibiting sufficiently high viscosity have been synthesized. They seem to exhibit a small improvement in viscosity retention in NaCl brine, compared with what would be expected from other copolymers having similar weight percent sodium acrylate residues. Because of the water insolubility of N-n-butylacrylamide, these samples were synthesized by an emulsion polymerization method, rather than the solution polymerization method used for other polymer types. Also, all of these poly(N-n-butylacrylamide-co-sodium acrylate) samples have higher percentages of sodium acrylate residues than most of the other samples being compared. Therefore, it is not possible at this point to attribute the apparent improvement to any one factor. Since data for a suitable control (e.g., the same polymer type synthesized by solution polymerization or partial hydrolysis) have not been obtained, results for this polymer type are not included in Table 23. Copolymers made by emulsion polymerization will be studied further.

## 5. Additional Correlations

### a. Molecular Weight

A striking feature in the behavior of the polymer solutions observed in the screening tests is the rapid onset of high sensitivity to shear above a certain reduced viscosity. This behavior can be seen very clearly as the dominant feature in Figures 30 through 34. This behavior is consistent with the theory<sup>18,19</sup> that under a given set of conditions, including shear stress and polymer type, there is a certain critical molecular weight above which a polymer is increasingly susceptible to shear degradation.

### b. NaCl Concentration

It has been observed that relatively high NaCl concentration imparts what might be called a "leveling" effect. For example, viscosities are quite similar over a rather wide pH range in 2% NaCl. Moreover, the reduced viscosities of a given polymer series do not vary over such a wide range in 2% NaCl as they do in 0.01% NaCl. This observation suggests that the increased NaCl sensitivities exhibited at higher charge-to-mass ratios of poly(acrylamide-co-sodium acrylate) and N-substituted analogs are due most likely to higher reduced viscosities being produced at higher charge-to-mass ratios in 0.01% NaCl solutions.

### c. Strength of Acid Moieties of Polymers

There is no obvious correlation between a copolymer's  $pK_a$  at 100% neutralization and  $(\eta_{sp})_2/(\eta_{sp})_{.01}$  in NaCl brine. This indicates that productive results would not be expected from varying the acid strength of comonomer residues in order to improve viscosity retention in NaCl brine.

## 6. Screening of Commercial Products

A number of commercial samples, some of which represent other classes of polymers, also have been screened. Xanthan gum retains a much higher fraction of its specific viscosity in the presence of increased NaCl than do partially hydrolyzed poly(acrylamides) and N-substituted poly(acrylamides) having similar charge-to-mass ratios. Xanthan gum exhibits only slight shear degradation under the conditions of this screening procedure. Nonionic polymers, such as poly(ethylene oxide),

hydroxyethylcellulose, and poly(vinyl alcohol) also exhibit little or no NaCl sensitivity. The trends observed with the commercial materials, although commonly known to people experienced in the use of polymers for mobility control, were included in the interest of completeness, and to provide a confirmation of the validity of the screening procedure. Scleroglucan (trade name, JETCO Actigum CS-11-L) exhibits little NaCl or shear sensitivity. (See Table 23.) Since this biopolymer is not ionic, such behavior is expected.

## 7. Conclusions and Recommendations

A method<sup>20</sup> described in Appendix A has been derived for obtaining accurate percentages of weak acid residues from potentiometric titration data for systems in which the acid strength varies linearly with percent neutralization. Commonly-used methods for determining equivalence points in such systems can lead to errors of several percent in the weak acid residues calculated. Reliable structure-utility correlations depend on the accuracy in determining copolymer composition. This is especially true for investigation of the relationship between the fraction of acidic residues and salt sensitivity. Thus, this method is an important contribution to accurate characterization and data analysis.

A statistical procedure to aid in assessing the significance of apparent differences between groups of polymers has been developed and is presented in Appendix B. A novel modification of the Mann-Whitney statistic<sup>21</sup> has enabled comparison and calculation of statistical significance of differences of two main groups, each divided into subgroups to restrict comparisons to otherwise-similar samples. Neither rejecting an actual difference nor accepting random deviation as though it were an actual difference in polymer groups is desirable. Therefore, this statistical method, by providing a means to judge the probable significance of differences, is an important phase of assessing data and inferring structure-utility correlations.

A very large number of polymers, representing a wide variety of polymer types, have been synthesized and subjected to the preliminary screening procedure. Although efforts have concentrated on many polymer types similar to partially hydrolyzed poly(acrylamide), a considerable number of other polymer types have also been tested. Polymers with straight-chain backbones and polymers with rings in their backbones have been synthesized and screened. Polymers with nitrogen or oxygen atoms in addition to carbon atoms in the polymer backbones, as well as polymers with all-carbon backbones, have been tested. Degrees of hydrolysis have ranged from 0% to 100%.

In addition to polymers synthesized internally, a number of commercially available polymers have been purified and tested. These include both synthetic polymers and biopolymers. Data from this wide variety of polymers have been obtained under a standard set of test

conditions to facilitate comparison. From the large data bank that has been assembled from the results of these tests, important structure-utility relationships have been inferred. These relationships are very important, since they are used for guidance in determining structural modifications likely to lead to improved performance.

One of the most promising structure-utility relationships indicates that incorporating imide rings in the polymer backbones of selected polyanions increases the fraction of viscosity retained when the polymers are subjected to a higher NaCl concentration. Imidization and partial hydrolysis of poly(methacrylamide) lead to a product believed to be essentially poly(methacrylamide-co-sodium methacrylate-ter-1,3-dimethylglutarimide-diyl). This product exhibits an average  $(\eta_{sp})_2/(\eta_{sp})_{.01}$  value in 1.6% (v/v) ethylene glycol (aq) more than twice that of a poly(acrylamide-co-sodium acrylate) sample in the same solvent system. However, not all ring structures may be effective in increasing viscosity retention in brine. Further research on the effect of backbone-stiffening structures is recommended and planned.

For a given polymer type at a given degree of hydrolysis, there is a rapid onset of high sensitivity to shear above a certain reduced viscosity. This observation is consistent with the theory<sup>18,19</sup> that there is a critical molecular weight, above which the polymer is increasingly susceptible to shear degradation. In general, the fraction of specific viscosity surviving shear for a polymer in 2% NaCl is similar to the corresponding fraction for that same polymer in 0.01% NaCl. These data indicate that going to extra high molecular weights in order to attain higher viscosity would introduce more instability to shear in both 0.01% NaCl and 2% NaCl.

Several correlations involving ionic effects have been observed. Polymers with higher charge-to-mass ratios tend to exhibit greater viscosities in 0.01% NaCl. However, these polymers also tend to exhibit greater sensitivity to increasing NaCl concentration. Thus, the advantage in fresh water is largely lost in the presence of high salt. The viscosity exhibited by a given polymer remains relatively constant over a rather wide pH range in 2% NaCl but varies more with pH in 0.01% NaCl. The reduced viscosities of a given polymer series do not vary over such a wide range in 2% NaCl as they do in 0.01% NaCl. There is no obvious correlation between a copolymer's  $pK_a$  at 100% neutralization and  $(\eta_{sp})_2/(\eta_{sp})_{.01}$  in NaCl brines. The onset of high sensitivity to shear occurs at nearly the same reduced viscosity in 2% NaCl for both anionic and uncharged polymers. This observation is also true for the onset of high sensitivity to shear in 0.01% NaCl if reduced viscosity in 2% NaCl is plotted as the abscissa.

For poly(N-methylacrylamide-co-sodium acrylate), there is a correlation between the synthetic method and viscosity retention in brine. This effect is presently believed to be due to sequencing. Further research on sequencing effects is recommended, and work is proceeding in that direction.

The results of polymer testing and synthesis experience during the first two years of the project will all be applied toward development of improved candidates for mobility control during the next year.

## V. NOMENCLATURE

$C$	= concentration of polymer in effluent from Berea core, mg/L
$C_0$	= initial concentration of polymer, mg/L
$I_1$	= contribution of monovalent salt to total ionic strength
$I_2$	= contribution of divalent salt to total ionic strength
$K$	= Consistency Index, $\text{mPa}\cdot\text{s}^n$
$n$	= Flow Behavior Index, dimensionless
$X_2$	= divalent ion content, fraction
$W_{xy}$	= Mann-Whitney statistic
$\alpha$	= degree of ionization
$\dot{\gamma}$	= rate of shear, $\text{sec}^{-1}$
$\eta_r$	= relative viscosity (apparent viscosity of polymer solution divided by solvent viscosity), dimensionless
$\eta_{sp}$	= specific viscosity ( $\eta_r - 1$ ), dimensionless
$(\eta_{sp})_2$	= specific viscosity in 2% NaCl
$(\eta_{sp})_{.01}$	= specific viscosity in 0.01% NaCl
$(\eta_{sp})_2 / (\eta_{sp})_{.01}$	= NaCl Effect Ratio, dimensionless
$\eta_{spx}$	= specific viscosity of a polymer solution that contains a fraction of divalent ion equal to $x$ , dimensionless
$\eta_{spz}$	= specific viscosity of a polymer solution that contains no divalent ion, dimensionless
$\eta_{sp}/c$	= reduced viscosity (specific viscosity of the polymer solution divided by the polymer concentration in grams of polymer per 100 ml of solvent), $\text{dL/g}$
$\eta_x$	= apparent viscosity of polymer solution that contains a divalent ion fraction equal to $x$ , $\text{mPa}\cdot\text{s}$
$\eta_z$	= apparent viscosity of polymer solution that contains no divalent ion, $\text{mPa}\cdot\text{s}$
$\mu$	= apparent viscosity of a polymer solution measured at a given rate of shear and temperature, $\text{mPa}\cdot\text{s}$

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TABLE 1

## Commercial Products Tested

Partially Hydrolyzed Polyacrylamides

Allied Colloids Alcoflood 800  
Allied Colloids Alcoflood 900  
Allied Colloids Alcoflood 900L  
Allied Colloids Alcoflood 1100  
Allied Colloids Alcoflood 1100L  
Allied Colloids Alcoflood 1200  
Allied Colloids Alcoflood 1200L  
Amoco Sweepaid 103  
Betz HiVis  
Calgon Polymer 340  
Calgon Polymer 454  
Calgon Polymer 815  
Calgon Polymer 825  
Calgon Polymer 835  
Cort N-Hance 315  
Cort N-Hance 330  
Cort N-Hance 335  
Cyanamid 960S  
Dow Pusher 500  
Dow Pusher 700  
Dow Pusher 1000  
Nalco Nal-flo

Polysaccharides

Abbott Xanthan Broth  
Henkle Galactosol  
Hercules Natrosol 250 HHR  
Jetco Actigum CS-11-L  
Kelco Xanflood  
Pfizer Biopolymer 1035  
Stauffer Colloid XH0  
Stauffer Colloid XHX  
Stauffer Colloid XH1  
Stauffer Colloid XH2  
Stauffer Colloid XH3

TABLE 2

Effect of Salinity on Power Law Parameters

Jetco Actigum CS-11-L

750 mg/l Polymer, 25°C

Percent salt	K	n
0.01% NaCl	142.5	0.337
0.1% NaCl	142.5	0.337
1.0% NaCl	140.0	0.334
10.0% NaCl	159.0	0.349
0.01% CaCl <sub>2</sub>	120.0	0.356
0.1% CaCl <sub>2</sub>	130.5	0.333
1.0% CaCl <sub>2</sub>	145.0	0.331
2.0% CaCl <sub>2</sub>	145.0	0.359

TABLE 3

Effect of Salinity on Polymer Screen Factors

Jetco Actigum CS-11-L

750 mg/1 Polymer, Room Temperature

<u>Percent NaCl</u>	<u>Screen Factor</u>
0.01	3.0
0.1	2.8
1.0	3.1

<u>Percent CaCl<sub>2</sub></u>	<u>Screen Factor</u>
0.01	2.9
0.1	3.7
1.0	3.6

TABLE 4

## Rheology of AMPS Homopolymer

750 mg/l, pH = 7.5, 25°C

Lot No. OS#40641A

Salt Solution	Screen Factor	$\mu @ 6 \text{ sec}^{-1}$	K	n	$\eta_0$
0.01% NaCl	19.54	46.2	151	0.370	>1340
0.1 % NaCl	23.5	18.7	36.6	0.623	68.5
0.3 % NaCl	19.34	9.40	14.6	0.744	14.9
2.0 % NaCl	20.05	4.56	6.01	0.847	5.30
10.0 % NaCl	20.65	3.67	4.43	0.897	3.85
0.01% CaCl <sub>2</sub>	19.75	35.2	91.3	0.470	>450
0.1 % CaCl <sub>2</sub>	18.1	5.00	7.00	0.827	5.65
0.3 % CaCl <sub>2</sub>	20.28	3.45	4.24	0.889	3.67
2.0 % CaCl <sub>2</sub>	20.21	2.65	3.23	0.906	2.67

Notes: Units of viscosity are mPa·sec (centipoise).

No cloudiness or precipitation was observed in any of the solutions.

Polymer mixtures in both 0.01% salt solutions were pseudoplastic even at very low shear rates; thus, accurate estimates of zero shear viscosities could not be determined in these two waters.

TABLE 5

## Long-Term Thermal Stability of Xanthan Gum

Polymer: 1000 mg/L Kelco Xanflood in 2% NaCl, Oxygen Present, pH 7.5

Time, days	<u>Loss of Viscosity (6 sec<sup>-1</sup>) @ 25°C, Percent</u>			
	<u>1</u>	<u>10</u>	<u>25</u>	<u>35</u>
No Additive	0	0	0	0
83 mg/L Dithionite	7	4	10	4
300 mg/L Formaldehyde	5	4	4	3

Time, days	<u>Loss of Viscosity (6 sec<sup>-1</sup>) @ 93°C, Percent</u>			
	<u>1</u>	<u>10</u>	<u>25</u>	<u>35</u>
No additive	29	94	96	96
83 mg/L Dithionite	63	17	95	95
300 mg/L Formaldehyde	10	93	48	72

TABLE 6

## Microbial Degradation of Xanthan Gum (750 mg/L)

<u>Aerobic Cultures</u>	<u>Fraction of Original Viscosity @ 6 sec<sup>-1</sup></u>
<u>Nutrient Broth Medium</u>	<u>After 7 days</u>
Control	0.97
Bacillus megaterium	0.79
Pseudomonas aeruginosa	0.81
Micrococcus luteus	0.99
<u>Salt Broth Medium</u>	<u>After 14 days</u>
Control	1.04
Bacillus megaterium	0.72
Pseudomonas aeruginosa	0.90
Micrococcus luteus	0.96
<u>Anaerobic Cultures</u>	<u>Fraction of Original Viscosity @ 6 sec<sup>-1</sup></u>
<u>Postgate's Medium E</u>	<u>After 7 days</u>
Desulfovibrio with 2% NaCl	1.02
Desulfovibrio without Organics	0.97

TABLE 7

## Resistance Factors and Polymer Retention in Berea Sandstone

750 mg/L, Room Temperature, 1 ft/day

Polymer	Supplier	Polymer Resistance Factor		Residual Resistance Factor		Polymer Retention, lbs/ac.ft.	
		0.1% NaCl	2% NaCl	0.1% NaCl	2% NaCl	0.1% NaCl	2% NaCl
Sweepaid 103	Amoco	19.0	3.5	2.6	1.1	99	147
Hi Vis	Betz	19.5	3.9	2.1	1.3	68	130
Cyanatrol 960S	Cyanamid	40.6	10.8	14.8	3.9	103	155
Pusher 500	Dow	12.5	3.4	2.7	1.4	65	125
Pusher 700	Dow	14.2	7.1	3.3	1.1	70	135
Pusher 1000	Dow	34.1	6.4	4.2	1.5	107	160
Nal-flo	Nalco	24.4	6.1	2.2	3.2	95	149
Xanthan Broth	Abbott	19.5	20.5	1.2	1.2	36	77
Xanflood	Kelco	13.5	11.6	5.3	6.7	48	75
Biopolymer 1035	Pfizer	14.6	13.6	3.2	2.3	41	46
Colloid XHO	Stauffer	6.1	3.4	1.9	1.3	33	200
Actigum CS-11-L	Jetco	51.5	19.4	21.2	4.2	532	666

Initial permeability to water for Berea cores: 350-550 md.

TABLE 8

## Mechanical Degradation of Xanthan Gum

Polymer: 750 mg/L Abbott XG Broth in 0.3% NaCl  
 Permeability of Shear Core Plug:  $k_w = 444$  md  
 Permeability of Mobility Core:  $k_w = 476$  md

<u>Frontal Advance Rate in Shear Plug, ft/day</u>	<u>Loss of Viscosity @ 7.3 sec<sup>-1</sup>, Percent</u>	<u>Loss of Resistance Factor in Mobility Core, Percent*</u>
10	0	0
100	0	0
500	0	2.1
1,000	1.3	3.0
2,500	0	0.8
5,000	0	1.1
10,000	0	6.9
15,000	2.0	7.0
17,300	3.3	9.4

\* Based on Resistance Factor of 16.0 for Polymer Injected through the Shear Plug at 1 ft/day.

TABLE 9

## Poly(acrylamide-co-sodium acrylate)

## Synthesis Details

Sample Number	$\eta_{sp}/c$ dL/g	Acrylamide grams	Acrylic Acid grams	Water ml	Initiator grams	Time min	Temperature °C
40 (a)	64.02	1.80	2.88	36	$K_2S_2O_8$ 0.0368	105	20
53	4.87	30.13	1.54	395	2.1466	10	25
84	26.58	14.87	0.80	420	0.5007	60	25
85	14.78	24.95	0.53	430	1.0374	30	25

Reduced viscosities measured in 0.01% NaCl

All reactions performed in a  $CO_2$  or  $N_2$  atmosphere

(a) 0.0037 g  $Na_2S_2O_5$  added as an activator

TABLE 10

## Poly(methacrylamide-co-sodium methacrylate)

## Synthesis Details

Sample Number	$\eta_{sp}/c$ dL/g	Methacryl- amide grams	Methacrylic Acid grams	Sodium Hydroxide grams	Water ml	Initiator grams $K_2S_2O_8$	Time hrs	Temperature $^{\circ}C$
96	44.59	10.09	10.62	5.00	180	0.1326	24	25
97	25.22	15.33	5.31	2.50	180	0.1121	24	25
98	15.40	19.26	1.06	0.50	190	0.1031	24	25
152 (a) (b)	107.77	30.22	--	--	570	0.1076	120	20
154 (b)	20.08	29.63	--	--	570	0.1253	120	20
170	42.72	5.11	15.93	7.55	185	0.1064	48	25

Reduced viscosities measured in 0.01% NaCl

(a) 0.0003 g N,N-methylenebisacrylamide added in an attempt to increase molecular weight

(b) poly(methacrylamides) hydrolyzed with N/2 aqueous NaOH; t = 48 - 72 hrs

TABLE 11

## Poly(N-methylmethacrylamide-co-sodium methacrylate)

## Synthesis Details

Sample Number	$\eta_{sp}/c$ dL/g	N-methyl- methacrylamide grams	Initiator grams $K_2S_2O_8$	Water ml	Time hrs	Temperature $^{\circ}C$
153	11.20	9.80	0.0175	150	80	27
172	11.63	4.90	0.0529	20	120	25
176	24.69					
173	16.91	4.90	0.0048	20	120	25
175	29.68					
177	26.19					

Reduced viscosities measured in 0.01% NaCl

Samples hydrolyzed in N/20 to N/2 aqueous NaOH

TABLE 12

Poly(N-methylacrylamide) and Poly(N-methylacrylamide-co-sodium acrylate)  
 Synthesis Details

Sample Number	$\eta_{sp}/c$ dL/g	N-methyl- acrylamide grams	Acrylic Acid grams	Initiator grams $K_2S_2O_8$	Activator grams	Water ml	Time min	Temperature $^{\circ}C$
134	5.76	3.00	--	0.0150	--	6	10	28
45	113.12	2.36	2.00	0.0238	--	26	45	25
46	103.85	2.36	2.00	0.0400	0.0200	35	20	22 - 25
72	68.58	1.02	2.02	0.0303	0.0152	30	60	16 - 18
73	27.13	1.36	1.73	0.0309	0.0154	25	90	18
74	81.20	1.70	1.44	0.0140	0.0157	25	60	18
75	102.73	2.04	1.15	0.0319	0.0160	15	40	16 - 18
76	76.66	2.38	0.86	0.0324	0.0162	15	45	16 - 17
78	74.94	3.06	0.29	0.0335	0.0167	14	30	16
79	35.69	3.23	0.14	0.0338	0.0169	14	30	16 - 17
80	111.09	0.68	2.30	0.0298	0.0149	10	70	14 - 15
81	76.09	0.34	2.59	0.0293	0.0146	12	55	15 - 16
122	63.46	2.72	0.58	0.0066	--	15	60	4
124	24.96	2.72	0.58	0.0066	--	12	30	-7
127	6.75	0.68	2.30	0.0059	--	10	20	-4

TABLE 12 (cont.)

Poly(N-methylacrylamide) and Poly(N-methylacrylamide-co-sodium acrylate)  
Synthesis Details

Sample Number	$\eta_{sp}/c$ dL/g	N-methyl- acrylamide grams	Acrylic Acid grams	Initiator grams $K_2S_2O_8$	Activator grams	Water ml	Time min	Temperature $^{\circ}C$
121	36.49	2.38	0.86	0.0324	0.0162	16	5	13 - 16
B1	8.04	2.00	--	0.0020	0.0020	4	155	25
B2	9.42	2.54	--	0.0025	0.0025	20	1080	4
B3	9.36	2.52	--	0.0012	0.0012	10	60	25
B4	14.53	2.00	--	0.0010	0.0010	8	18000	0

Reduced viscosities measured in 0.01% NaCl

TABLE 13

## Poly(N-isopropylacrylamide) and Poly(N-isopropylacrylamide-co-sodium acrylate)

## Synthesis Details

Sample Number	$\eta_{sp}/c$ dl./g	N-isopropyl- acrylamide grams	Acrylic Acid grams	Initiator grams K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	Activator grams Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub>	Water ml	Time min	Temperature °C
62	1.38	3.00	--	0.0280	0.0150	15	45	26
135	0.74	4.00	--	0.0120	0.0060	8	60	28
56	223.04	2.26	1.44	0.0370	0.0185	30	50	20 - 22
48	83.62	2.71	1.15	0.0370	0.0185	30	60	20 - 21
60	7.57	2.71	1.15	0.0370	0.0185	30	60	20 - 21
58	71.64	3.62	0.58	0.0370	0.0185	30	60	18 - 20
69	16.13	3.62	0.58	0.0370	0.0185	30	60	20 - 23
65	14.52	4.06	0.14	0.0370	0.0185	30	40	16 - 18
64	27.59	1.81	1.73	0.0353	0.0177	15	60	16 - 17
70	45.88	1.36	2.02	0.0337	0.0168	15	60	14 - 16
71	43.10	0.90	2.30	0.0321	0.0160	10	840	15 - 30
68	24.81	0.90	2.30	ABIN (a) 0.0320	--	--	30	30

Reduced viscosities measured in 0.01% NaCl

(a) 2,2'-azobisisobutyronitrile

TABLE 14

Poly(N-t-butylacrylamide-co-sodium acrylate)  
Synthesis Details

Sample Number	$\eta_{sp}/c$ dL/g	N-t-butyl- acrylamide grams	Acrylic Acid grams	Initiator grams K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	Activator grams Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub>	Solvent mL	Time min	Temperature °C
101	24.48	1.27	0.72	0.0199	0.0099	6.0 (a) DMF	60	22
102	8.76	1.27	0.72	0.0199	0.0099	8.0 DMF 2.0 H <sub>2</sub> O	180	15 - 31
111	6.51	0.76	1.01	0.0177	0.0040	6.5 DMF 2.0 H <sub>2</sub> O	90	16
103	5.12	1.02	0.85	0.0188	0.0094	8.0 DMF 2.0 H <sub>2</sub> O	120	15

Reduced viscosities measured in 0.01% NaCl

(a) N,N-dimethylformamide

TABLE 15

## Poly(N-n-butylacrylamide-co-sodium acrylate)

## Synthesis Details

Sample Code	$\eta_{sp}/c$ dL/g	N-n-butyl- acrylamide grams	Acrylic Acid grams	Initiator grams	Activator grams	Water ml	Time min	Temperature $^{\circ}\text{C}$
B5	28.41	2.54	1.44	$\text{K}_2\text{S}_2\text{O}_8$ 0.0398	$\text{Na}_2\text{S}_2\text{O}_5$ 0.0020	10.0	10	25
B6	48.73	2.03	1.73	0.0370	0.0188	10.0	8	25

Reduced viscosities measured in 0.01% NaCl

0.10 g sodium dodecyl sulfate added to each polymerization mixture as an emulsifier

TABLE 16

## Poly(N-octylacrylamide-co-sodium acrylate)

## Synthesis Details

Sample Code	$\eta_{sp}/c$	N-octyl- acrylamide grams	Acrylic Acid grams	Initiator grams	Activator grams	Solvent ml	Time min	Temperature $^{\circ}\text{C}$
B7	---	2.93	1.08	$\text{K}_2\text{S}_2\text{O}_8$ 0.0401	$\text{Na}_2\text{S}_2\text{O}_5$ 0.0200	5.0 DMF	5	25
B8	---	2.93	1.08	0.0401	0.0200	2.5 dioxane 2.0 $\text{H}_2\text{O}$	60	26
B9	---	1.46	0.52	BP (a) 0.0200	--	bulk	35	45 - 80
B10	---	1.46	0.52	0.0200	--	bulk	250	40 - 80
B11	---	4.10	0.65	0.0400	--	bulk	170	45 - 78

Reduced viscosities measured in 0.01% NaCl

(a) benzoyl peroxide

Poly(N-methylmaleimide-co-sodium acrylate or methacrylate)  
 Synthesis Details

Sample Number	$\eta_{sp}/c$ dL/g	N-methyl- maleimide grams	Acrylic Acid grams	Methacrylic Acid grams	Initiator grams $K_2S_2O_8$	Activator grams $Na_2S_2O_5$	Water ml	Time hrs	Temp. $^{\circ}C$
162	67.34	0.2775	--	0.65	0.0023	0.0012	2.6	6.00	28
165	38.00	0.5550	1.08	--	0.0041	0.0020	2.0	1.75	25

Reduced viscosities measured in 0.01% NaCl

TABLE 18

Poly(maleimide-co-sodium acrylate and/or acrylamide)  
 Synthesis Details

Sample Number	$\eta_{sp}/c$ dL/g	Maleimide grams	Acrylic Acid grams	Acrylamide grams	Initiator grams $K_2S_2O_8$	Activator grams $Na_2S_2O_5$	Water ml	Time hrs	Temp. $^{\circ}C$
136	10.78	0.345	--	1.095	0.0144	0.0072	8	1	24
137	19.55	1.940	4.32	--	0.0063	0.0032	24	5	28
138	17.29	1.940	--	2.380	0.0058	0.0029	28	26	27 - 28
161	31.79	1.035	3.87 (a)	--	0.0049	0.0025	22	1.5	28

Reduced viscosities measured in 0.01% NaCl

(a) methacrylic acid

TABLE 19

## Poly(methacrylamides) - imidized

## Synthesis Details

Sample Number	$\eta_{sp}/c$ dL/g	Methacryl- amide grams	Initiator grams	Water ml	Methanol ml	Time hrs	Temperature °C
E6	14.42	43.40	$K_2S_2O_8$ 0.1875	240	--	120	25
E3	20.79	20.05	0.1056	170	10.0	168	20
E4	28.07	29.63	0.1253	570	--	120	25
E1	36.93						
E2	35.28	30.22	0.1076	570	--	120	25
E5	23.95						

Reduced viscosities measured in 0.01% NaCl

Imidization was achieved by heating a 4-8% solution of the homopolymer in 6 N HCl at 65-85°C for 168 hrs.

Dissolution was effected in a 50x weight excess of ethylene glycol; limited hydrolysis (necessary for water solubility) was also carried out in the same medium.

TABLE 20

Key to Polymer Sample Numbers Used in Table 21

Sample no.	Polymer	a Sample code	b Source	c Concentration (g/dL)
E1	Poly(methacrylamide-co-sodium methacrylate), imide	PMAAm #13-B -- imide	JS	0.0136
E2	Poly(methacrylamide-co-sodium methacrylate), imide	PMAAm #13-C -- imide	JS	0.0139
E3	Poly(methacrylamide-co-sodium methacrylate), imide	PMAAm #9 -- imide	JS	0.0171
E4	Poly(methacrylamide-co-sodium methacrylate), imide	PMAAm #12 -- imide	JS	0.0125
E5	Poly(methacrylamide-co-sodium methacrylate), imide	PMAAm #13-E -- imide	JS	0.0136
E6	Poly(methacrylamide-co-sodium methacrylate), imide	PMAAm #5A -- imide	JS	0.0150
E7	Poly(acrylamide-co-sodium acrylate)	Pusher P-700 clean	Dow; modified by JS	0.0146

(a) The commercial sample was re-precipitated to isolate polymer from the composition.

(b) JS = Joel Shepitka of our research group

(c) Uncertainties in polymer concentrations are estimated at 4% of the stated values.

TABLE 21

Results of Preliminary Screening Laboratory Tests of  
Polymers Dissolved in 1.6% (v/v) Ethylene Glycol

Sam- ple no.	Polymer conc. (g/dL)	Charge- to-mass ratio of anion	Weight percent acid residues (salt form)	Reduced kinematic viscosities			Specific kinematic viscosities			$\eta_{sp}$ divided by $\eta_{sp}$ of unsheared polymer in 0.01% NaCl(aq) solution				
				in 0.01% NaCl(aq)	in 2% NaCl(aq)	U* S*	in 0.01% NaCl(aq)	in 2% NaCl(aq)	U* S*	in 0.01% NaCl(aq)	in 2% NaCl(aq)	U* S*		
E7	0.0146	0.00494	41.7	49.06	48.86	4.40	3.95	0.718	0.715	0.064	0.058	0.996	0.090	0.080
				Poly(acrylamide-co-sodium acrylate)										
				Poly(methacrylamide-co-sodium methacrylate), imide										
E1	0.0136	0.00310	31.2	34.60	32.59	8.05	7.85	0.469	0.442	0.109	0.106	0.942	0.233	0.227
E6	0.0150	0.00408	40.3	13.22	12.17	1.89	1.51	0.198	0.183	0.028	0.023	0.921	0.143	0.114
E5	0.0136	0.00448	43.9	21.88	19.03	4.28	3.90	0.297	0.238	0.058	0.033	0.870	0.195	0.178
E2	0.0139	0.00455	44.6	32.19	31.57	8.23	7.00	0.448	0.439	0.115	0.097	0.981	0.256	0.217
E3	0.0171	0.00598	56.8	18.35	18.26	3.63	3.59	0.314	0.312	0.062	0.061	0.995	0.198	0.196
E4	0.0125	0.00671	62.9	24.43	22.13	4.44	4.34	0.306	0.277	0.056	0.034	0.906	0.182	0.178

\* U = unsheared; S = sheared

Uncertainties in polymer concentrations, charge-to-mass ratios, weight % acid values, and reduced kinematic viscosities are estimated at 4% to 6% of the stated values. Estimated uncertainties in specific kinematic viscosities are usually approximately 1% of the stated values. If the specific kinematic viscosity is less than 0.2, its percent uncertainty may be estimated by dividing 0.2 by the specific kinematic viscosity. Uncertainties of values in the last three columns may be estimated at the greater of 0.01 and 0.002 divided by the specific kinematic viscosity of unsheared solution in 0.01% NaCl.

TABLE 22

## Key to Polymer Sample Numbers Used in Table 23

Sample no.	Polymer	Sample code <sup>a</sup>	Source <sup>b</sup>	Concentration (g/dL) <sup>c</sup>
2	Poly(N-methylacrylamide)	P22	GK	0.0599
3	Poly(N-methylacrylamide-co-sodium acrylate)	M11	GK	0.0604
4	Poly(acrylamide)	M.W. 5--6,000,000 (av)	Polysciences, Inc.	0.0653
6	Poly(acrylamide-co-sodium acrylate)	#2	JS	0.0608
7	Poly(acrylamide-co-sodium acrylate)	#3	JS	0.0086
8	Poly(acrylamide)	2.E6 MW	JS	0.0562
9	Poly(acrylamide)	1.2E6 MW	JS	0.0575
10	Poly(acrylamide)	A2	GK	0.2539
11	Poly(acrylamide)	A3	GK	0.2566
12	Poly(N-isopropylacrylamide-co-sodium acrylate)	M15	GK	0.0574
13	Poly(N-isopropylacrylamide-co-sodium acrylate)	M16	GK	0.0081
14	Poly(acrylamide)	A4	GK	0.1212
15	Poly(N-isopropylacrylamide)	A8	GK	0.0601
16	Poly(acrylamide-co-sodium acrylate)	Pusher P-500 degraded 25 minutes	Dow; modified by JS	0.0069
17	Poly(acrylamide-co-sodium acrylate)	Pusher P-500 degraded 12 minutes	Dow; modified by JS	0.0030
18	Poly(acrylamide-co-sodium acrylate)	Pusher P-1000 degraded 15 minutes	Dow; modified by JS	0.0139
19	Poly(acrylamide-co-sodium acrylate)	Pusher P-1000 degraded 30 minutes	Dow; modified by JS	0.0149
20	Poly(acrylamide)	#4, N-bar-sub-V = 3.3E6	JS	0.0591
21	Poly(acrylamide)	#5, N-bar-sub-V = 2.5E6	JS	0.0874
22	Poly(N-methylacrylamide)	F1	GK	0.0902
23	Poly(N-methylacrylamide)	F2	GK	0.0579
24	Poly(acrylamide-co-sodium acrylate)	Pusher P-500 reprecipitated -- clean	Dow; modified by JS	0.0120
25	Poly(acrylamide-co-sodium acrylate)	Pusher P-1000 reprecipitated -- clean	Dow; modified by JS	0.0116
26	Poly(acrylamide)	A9	GK	0.1255
27	Poly(acrylamide)	A11	GK	0.1966
28	Poly(acrylamide-co-sodium acrylate)	Pusher P-500 degraded 12 minutes	Dow; modified by JS	0.0134
29	Poly(acrylamide-co-sodium acrylate)	Pusher P-700 clean	Dow; modified by JS	0.0106
30	Poly(acrylamide-co-sodium acrylate)	Pusher P-500 reprecipitated -- clean	Dow; modified by JS	0.0126
31	Poly(acrylamide)	A10	GK	0.2457
32	Poly(acrylamide-co-sodium acrylate)	Calgon 835 clean	Calgon; modified by JS	0.0143
33	Poly(acrylamide-co-sodium acrylate)	Calgon 835 clean	Calgon; modified by JS	0.0029
34	Poly(acrylamide-co-sodium acrylate)	Calgon 815 clean	Calgon; modified by JS	0.0101
35	Poly(acrylamide-co-sodium acrylate)	Pusher P-700 clean	Dow; modified by JS	0.0043
36	Poly(acrylamide-co-sodium acrylate)	Pusher P-500 degraded 35 minutes B	Dow; modified by JS	0.0109
37	Poly(acrylamide-co-sodium acrylate)	Pusher P-500 degraded 35 minutes C	Dow; modified by JS	0.0166
38	Poly(N-methylacrylamide)	F4	GK	0.0566
39	Poly(N-methylacrylamide)	F6	GK	0.0799
40	Poly(acrylamide-co-sodium acrylate)	A6	GK	0.0126
41	Poly(acrylamide-co-sodium acrylate)	Pusher P-1000 degraded 35 minutes B	Dow; modified by JS	0.0134
42	Poly(acrylamide-co-sodium acrylate)	Pusher P-1000 degraded 35 minutes C	Dow; modified by JS	0.0099
43	Poly(N-isopropylacrylamide-co-sodium acrylate)	M16-R	GK	0.0125
44	Poly(N-methylacrylamide-co-sodium acrylate)	GK1	GK	0.0152
45	Poly(N-methylacrylamide-co-sodium acrylate)	GK2	GK	0.0151
46	Poly(N-methylacrylamide-co-sodium acrylate)	GK7	GK	0.0714
47	Poly(N-isopropylacrylamide-co-sodium acrylate)	GK8	GK	0.0720
48	Poly(N-isopropylacrylamide-co-sodium acrylate)	#4	JS	0.0135
53	Poly(acrylamide-co-sodium acrylate)	GK7	GK	0.0152
56	Poly(N-isopropylacrylamide-co-sodium acrylate)	GK8	GK	0.0153
57	Poly(N-isopropylacrylamide-co-sodium acrylate)	GK10	GK	0.0169
58	Poly(N-isopropylacrylamide-co-sodium acrylate)	GK9	GK	0.0155
60	Poly(N-isopropylacrylamide-co-sodium acrylate)	GK15	GK	0.0154
61	Poly(N-isopropylacrylamide-co-sodium acrylate)	GK5	GK	0.0788
62	Poly(N-isopropylacrylamide)	GK6	GK	0.0721
63	Poly(N-methylacrylamide)	GK14	GK	0.0163
64	Poly(N-isopropylacrylamide-co-sodium acrylate)	GK12	GK	0.0367
65	Poly(N-isopropylacrylamide-co-sodium acrylate)	GK19	GK	0.0182
68	Poly(N-isopropylacrylamide-co-sodium acrylate)	GK11	GK	0.0151
69	Poly(N-isopropylacrylamide-co-sodium acrylate)	GK16	GK	0.0152
70	Poly(N-isopropylacrylamide-co-sodium acrylate)	GK18	GK	0.0188
71	Poly(N-isopropylacrylamide-co-sodium acrylate)	AD1	GK	0.0141
72	Poly(N-methylacrylamide-co-sodium acrylate)	AD2	GK	0.0146
73	Poly(N-methylacrylamide-co-sodium acrylate)			

TABLE 22 (cont.)

Key to Polymer Sample Numbers Used in Table 23

74	Poly(N-methylacrylamide-co-sodium acrylate)	AD3	GK	0.0141
75	Poly(N-methylacrylamide-co-sodium acrylate)	AD4	GK	0.0149
76	Poly(H-methylacrylamide-co-sodium acrylate)	AD5	GK	0.0147
78	Poly(H-methylacrylamide-co-sodium acrylate)	AD7	GK	0.0151
79	Poly(H-methylacrylamide-co-sodium acrylate)	AD8	GK	0.0151
80	Poly(H-methylacrylamide-co-sodium acrylate)	AD9	GK	0.0176
81	Poly(H-methylacrylamide-co-sodium acrylate)	AD10	GK	0.0169
82	Poly(N-isopropylacrylamide-co-sodium acrylate)	GK20	GK	0.0178
84	Poly(acrylamide-co-sodium acrylate)	#7	JS	0.0172
85	Poly(acrylamide-co-sodium acrylate)	#9	JS	0.0133
86	Poly(methacrylamide-co-sodium methacrylate)	P(HAAM/NaMA) #6	JS	0.0153
97	Poly(methacrylamide-co-sodium methacrylate)	P(HAAM/NaMA) #7	JS	0.0159
98	Poly(methacrylamide-co-sodium methacrylate)	P(HAAM/NaMA) #8	JS	0.0161
101	Poly(N-tert-butylacrylamide-co-sodium acrylate)	TBA5 #1	GK	0.0175
102	Poly(H-tert-butylacrylamide-co-sodium acrylate)	TBA5 #2	GK	0.0183
103	Poly(H-tert-butylacrylamide-co-sodium acrylate)	TBA6	GK	0.0173
108	Poly(ethylene oxide)	H.W. 5,000,000	Polysciences, Inc.	0.0783
109	Hydroxyethylcellulose	High viscosity	Polysciences, Inc.	0.0799
110	Xanthan gum	XANFLOOD	Kelco	0.0114
111	Poly(H-tert-butylacrylamide-co-sodium acrylate)	TBA7	GK	0.0175
118	Scleroglucan	Actigum CS-11-L	Jetco Chemicals, Inc.	0.0167
119	Poly(sodium acrylate)	"HW 250,000"; Catalog no. 3312	Polysciences, Inc.	0.0210
121	Poly(H-methylacrylamide-co-sodium acrylate)	GK-3-127	GK	0.0157
122	Poly(H-methylacrylamide-co-sodium acrylate)	GK-3-131	GK	0.0160
124	Poly(H-methylacrylamide-co-sodium acrylate)	GK-3-139	GK	0.0169
127	Poly(H-methylacrylamide-co-sodium acrylate)	GK-3-146	GK	0.0164
129	Poly(vinyl alcohol)	99.0 - 99.8 mole % hyd.; Cat. # 2815	Polysciences, Inc.	0.0752
130	Poly(vinyl alcohol)	87.2 - 89.2 mole % hyd.; Cat. # 4398	Polysciences, Inc.	0.0780
131	Poly(acrylamide-co-sodium acrylate)	Pusher P-700 clean	Dow; modified by JS	0.0173
132	Poly(acrylamide-co-sodium acrylate)	Pusher P-700 clean	Dow; modified by JS	0.0173
133	Poly(acrylamide-co-sodium acrylate)	Pusher P-700 clean	Dow; modified by JS	0.0130
134	Poly(H-methylacrylamide)	Pusher P-700 clean	GK	0.0729
135	Poly(H-isopropylacrylamide)	GK-4-16	GK	0.0758
139	Xanthan gum (high carboxyl)	GK-4-17	GK	0.0127
143	Poly(ethylene oxide)	Flocon Biopolymer 4800	Pfizer Inc.	0.0127
144	Poly(ethylene oxide)	Polyox WSRN 750; Blend 66	Union Carbide Corp.	0.0799
145	Poly(acrylamide-co-sodium acrylate)	Polyox WSRN-10; Blend 218	Union Carbide Corp.	0.0823
147	Poly(H-methylacrylamide-co-sodium acrylate)	Pusher P-700 clean	Dow; modified by JS	0.0104
152	Poly(methacrylamide-co-sodium methacrylate)	GK-4-32 (synthesized by hydrolysis)	GK	0.0149
153	Poly(H-methylmethacrylamide-co-Ha methacrylate)	PHAM #13	JS	0.0179
160	Poly(H-methylacrylamide-co-sodium acrylate)	P(H-NeMAAm) #1	JS	0.0166
164	Poly(H-methylacrylamide-co-sodium acrylate)	GK-4-48 (synthesized by hydrolysis)	GK	0.0147
166	Poly(H-methylacrylamide-co-sodium acrylate)	GK-4-58 (synthesized by hydrolysis)	GK	0.0129
167	Poly(H-methylacrylamide-co-sodium acrylate)	GK-4-65 (synthesized by hydrolysis)	GK	0.0117
168	Poly(sodium methacrylate)	GK-4-68 (synthesized by hydrolysis)	GK	0.0132
169	Poly(H-methylacrylamide-co-sodium acrylate)	Catalog no. 0576	Polysciences, Inc.	0.0187
170	Poly(methacrylamide-co-sodium methacrylate)	GK-4-74 (synthesized by hydrolysis)	GK	0.0127
172	Poly(H-methylmethacrylamide-co-Ha methacrylate)	P(HAAM/NaMA) #9A	JS	0.0124
173	Poly(H-methylmethacrylamide-co-Ha methacrylate)	P(N-NeMAAm) #4-1	JS	0.0166
175	Poly(H-methylmethacrylamide-co-Ha methacrylate)	P(H-NeMAAm) #5-1	JS	0.0146
176	Poly(H-methylmethacrylamide-co-Ha methacrylate)	P(N-NeMAAm) #5-2	JS	0.0128
177	Poly(H-methylmethacrylamide-co-Ha methacrylate)	P(N-NeMAAm) #4-3	JS	0.0141
178	Poly(acrylamide-co-sodium acrylate)	P(N-NeMAAm) #5-3	JS	0.0154
179	Poly(H-methylacrylamide-co-sodium acrylate)	Pusher P-700 clean	Dow; modified by JS	0.0146
		GK-4-73 (synthesized by hydrolysis)	GK	0.0125

(a) Each commercial sample was re-precipitated to isolate polymer from the composition.

(b) GK = Gajendra Khune of our research group

JB = John Bower of our research group

JS = Joel Shepitka of our research group

(c) Uncertainties in polymer concentrations are estimated at 4% of the stated values.

TABLE 23

Results of Preliminary Screening Laboratory Tests of Polymers Dissolved in Water

Sam- ple no.	Polymer conc. (g/dL)	Charge- to-mass ratio of anion	Weight percent acid residues (salt form)	Reduced kinematic viscosities			Specific kinematic viscosities			$\eta_{sp}$ divided by $\eta_{sp}$ of unsheared polymer in 0.01% NaCl(aq) solution									
				U*	S*	U*	in 0.01% NaCl(aq)	in 2% NaCl(aq)	U*	S*	U*	in 0.01% NaCl(aq)	in 2% NaCl(aq)	S*	U*	S*	B/A	C/A	D/A
Poly(acrylamide-co-sodium acrylate)																			
85	0.0133	0.00065	6.0	14.78	14.23	4.87	4.75	0.197	0.189	0.065	0.063	0.963	0.329	0.321					
53	0.0135	0.00099	9.1	4.87	4.67	1.11	1.06	0.066	0.063	0.015	0.014	0.959	0.224	0.218					
84	0.0172	0.00103	9.4	26.58	24.84	4.66	4.32	0.456	0.426	0.080	0.074	0.934	0.175	0.162					
6	0.0608	0.00218	19.6	103.92	98.21	9.07	8.47	6.321	5.974	0.552	0.515	0.945	0.087	0.081					
34	0.0101	0.00333	29.1	115.61	97.58	12.58	9.81	1.167	0.985	0.127	0.099	0.844	0.109	0.085					
25	0.0116	0.00358	31.1	164.78	109.17	18.25	14.12	1.914	1.268	0.212	0.164	0.662	0.111	0.086					
19	0.0149	0.00361	31.3	123.25	118.36	13.28	11.88	1.837	1.764	0.198	0.177	0.960	0.108	0.096					
42	0.0099	0.00362	31.4	124.51	109.01	10.94	9.83	1.229	1.076	0.108	0.097	0.876	0.088	0.079					
41	0.0134	0.00364	31.5	145.31	130.70	17.08	13.33	1.940	1.745	0.228	0.178	0.899	0.118	0.092					
18	0.0139	0.00402	34.6	118.49	106.87	15.88	13.06	1.642	1.481	0.220	0.181	0.902	0.134	0.110					
17	0.0030	0.00481	40.7	117.84	101.43	15.10	12.14	0.359	0.309	0.046	0.037	0.861	0.128	0.103					
28	0.0134	0.00481	40.7	130.43	115.47	13.39	10.94	1.753	1.552	0.180	0.147	0.885	0.103	0.084					
29	0.0106	0.00494	41.7	148.63	111.75	17.97	13.92	1.580	1.188	0.191	0.148	0.752	0.121	0.094					
35	0.0043	0.00494	41.7	93.60	87.95	17.40	11.99	0.398	0.374	0.074	0.051	0.940	0.186	0.128					
131	0.0173	0.00494	41.7	138.63	120.16	14.01	10.68	2.398	2.078	0.242	0.185	0.867	0.101	0.077					
132	0.0173	0.00494	41.7	115.57	106.74	10.46	9.50	1.999	1.846	0.181	0.164	0.924	0.090	0.082					
133	0.0130	0.00494	41.7	115.67	110.80	12.40	11.40	1.501	1.438	0.163	0.123	0.958	0.107	0.099					
145	0.0104	0.00494	41.7	100.26	94.62	11.81	9.89	1.041	0.982	0.121	0.103	0.944	0.118	0.099					
178	0.0146	0.00494	41.7	103.71	105.38	11.11	10.53	1.517	1.541	0.162	0.154	1.016	0.107	0.102					
32	0.0143	0.00496	41.9	209.36	140.41	18.52	15.08	2.985	2.002	0.264	0.215	0.671	0.088	0.072					
33	0.0029	0.00496	41.9	96.79	96.09	15.43	12.62	0.276	0.244	0.044	0.036	0.993	0.159	0.130					
24	0.0120	0.00499	42.1	117.12	109.91	11.53	10.36	1.402	1.208	0.138	0.124	0.862	0.098	0.088					
30	0.0126	0.00499	42.1	141.23	120.53	17.12	11.78	1.774	1.514	0.215	0.148	0.853	0.121	0.083					
16	0.0069	0.00510	43.0	151.33	145.23	16.41	15.39	1.042	1.000	0.113	0.106	0.960	0.108	0.102					
37	0.0166	0.00523	43.9	291.78	153.59	8.61	9.27	4.848	2.552	0.143	0.154	0.526	0.029	0.032					
36	0.0109	0.00558	46.5	125.42	102.12	15.51	12.39	1.367	1.113	0.169	0.135	0.814	0.124	0.099					
7	0.0086	0.00617	50.8	143.86	129.85	13.66	11.21	1.232	1.112	0.117	0.096	0.903	0.095	0.078					
40	0.0126	0.00646	52.9	64.02	60.37	4.93	4.69	0.805	0.759	0.062	0.059	0.943	0.077	0.073					
Poly(N-methylacrylamide-co-sodium acrylate), synthesized by copolymerization																			
79	0.0151	0.00103	9.5	35.69	28.80	12.97	10.63	0.540	0.436	0.196	0.161	0.807	0.363	0.298					
78	0.0151	0.00179	16.1	74.94	56.31	13.17	10.77	1.129	0.848	0.198	0.162	0.751	0.176	0.144					
122	0.0160	0.00275	24.3	63.46	57.01	10.00	8.23	1.018	0.915	0.161	0.132	0.898	0.158	0.130					
76	0.0147	0.00324	28.4	76.66	68.30	10.11	9.16	1.129	1.005	0.149	0.135	0.891	0.132	0.119					
124	0.0169	0.00366	31.8	24.96	23.13	4.30	3.93	0.421	0.390	0.073	0.066	0.926	0.172	0.157					
74	0.0141	0.00422	36.2	81.20	73.91	9.89	8.62	1.146	1.043	0.140	0.122	0.910	0.122	0.106					
75	0.0149	0.00425	36.4	102.73	82.63	13.00	10.78	1.533	1.233	0.194	0.161	0.804	0.127	0.105					
121	0.0157	0.00430	36.8	36.49	30.41	5.38	4.75	0.574	0.479	0.085	0.075	0.834	0.148	0.130					
46	0.0151	0.00507	42.7	103.85	83.08	13.04	9.40	1.570	1.256	0.197	0.142	0.800	0.126	0.091					
45	0.0152	0.00559	46.6	113.12	82.90	14.79	10.50	1.723	1.263	0.225	0.160	0.733	0.131	0.093					
73	0.0146	0.00575	47.8	27.13	26.28	2.71	2.61	0.395	0.383	0.039	0.038	0.969	0.100	0.096					
72	0.0141	0.00761	60.9	68.58	62.80	7.47	6.94	0.965	0.884	0.105	0.098	0.916	0.109	0.101					
3	0.0604	0.00972	74.7	36.15	35.50	3.11	3.02	2.182	2.143	0.188	0.182	0.982	0.086	0.083					
80	0.0176	0.01050	79.6	111.09	107.85	10.09	9.66	1.954	1.897	0.177	0.170	0.971	0.091	0.087					
127	0.0164	0.01083	81.6	6.75	5.95	0.70	0.51	0.111	0.098	0.012	0.008	0.882	0.104	0.076					
81	0.0169	0.01102	82.7	76.09	71.62	6.30	6.07	1.288	1.213	0.107	0.103	0.941	0.083	0.080					

TABLE 23 (cont.)

Results of Preliminary Screening Laboratory Tests of  
Polymers Dissolved in Water

160	0.0147	0.00091	Poly(N-methylacrylamide-co-sodium acrylate), synthesized by hydrolysis										0.429	0.418
147	0.0149	0.00122	8.4	8.13	7.74	3.48	3.40	0.120	0.114	0.051	0.050	0.952	0.429	0.418
166	0.0117	0.00230	11.1	4.84	4.43	3.31	3.12	0.072	0.066	0.049	0.046	0.914	0.684	0.644
164	0.0129	0.00251	20.5	85.90	83.13	10.36	9.64	1.007	0.974	0.121	0.113	0.968	0.121	0.112
167	0.0132	0.00280	22.3	40.58	40.39	3.66	3.59	0.523	0.521	0.047	0.046	0.995	0.090	0.088
189	0.0127	0.00351	24.7	85.65	83.25	10.02	9.23	1.126	1.095	0.132	0.121	0.972	0.117	0.108
179	0.0125	0.00491	30.6	94.81	93.32	10.72	10.13	1.200	1.181	0.136	0.128	0.984	0.113	0.107
			41.5	87.05	84.61	9.10	8.47	1.090	1.059	0.114	0.106	0.972	0.104	0.097
			Poly(N-isopropylacrylamide-co-sodium acrylate)											
65	0.0367	0.00120	11.0	14.52	13.15	2.81	2.72	0.533	0.483	0.103	0.100	0.905	0.193	0.187
69	0.0151	0.00195	17.6	16.13	15.75	2.27	2.27	0.244	0.238	0.034	0.034	0.976	0.141	0.140
60	0.0155	0.00281	24.8	7.57	7.03	0.89	0.80	0.117	0.109	0.014	0.012	0.929	0.118	0.106
58	0.0169	0.00331	28.9	71.64	63.77	12.25	9.68	1.212	1.078	0.207	0.164	0.890	0.171	0.135
43	0.0125	0.00363	31.5	40.58	36.33	4.81	4.09	0.506	0.453	0.060	0.051	0.895	0.119	0.101
48	0.0720	0.00381	33.0	83.62	74.26	7.71	6.74	6.018	5.344	0.555	0.485	0.888	0.092	0.081
57	0.0153	0.00381	33.0	48.87	46.65	6.19	5.60	0.746	0.712	0.094	0.085	0.955	0.127	0.115
47	0.0714	0.00542	45.3	223.04	195.32	14.88	11.83	15.930	13.950	1.062	0.845	0.876	0.067	0.053
56	0.0152	0.00542	45.3	85.96	79.09	11.64	9.89	1.306	1.201	0.177	0.150	0.920	0.135	0.115
61	0.0154	0.00562	46.8	88.83	78.27	11.27	9.57	1.365	1.203	0.173	0.147	0.881	0.127	0.108
13	0.0081	0.00624	51.3	85.54	73.16	12.38	8.91	0.691	0.591	0.100	0.072	0.855	0.145	0.104
64	0.0163	0.00702	56.9	27.59	26.90	2.47	2.45	0.451	0.439	0.040	0.040	0.975	0.090	0.089
70	0.0152	0.00767	61.3	45.88	45.05	4.07	4.04	0.698	0.686	0.062	0.061	0.982	0.089	0.088
12	0.0574	0.00787	62.7	77.97	75.32	8.09	7.62	4.474	4.322	0.464	0.437	0.966	0.104	0.098
68	0.0182	0.00975	74.9	24.81	20.82	2.17	2.18	0.451	0.379	0.039	0.040	0.839	0.088	0.088
71	0.0188	0.00999	76.4	43.10	41.57	4.19	4.07	0.811	0.782	0.079	0.077	0.964	0.097	0.094
82	0.0178	0.01138	84.8	143.70	134.71	19.50	15.11	2.563	2.403	0.348	0.270	0.937	0.136	0.105
			Poly(methacrylamide-co-sodium methacrylate)											
98	0.0161	0.00054	5.7	13.38	13.81	3.44	3.56	0.247	0.222	0.055	0.057	0.898	0.224	0.231
97	0.0159	0.00220	22.6	25.16	23.38	3.73	3.32	0.401	0.372	0.059	0.053	0.929	0.148	0.132
132	0.0179	0.00490	47.6	94.52	88.72	10.81	10.05	1.692	1.588	0.193	0.180	0.939	0.114	0.106
96	0.0153	0.00540	51.9	45.70	43.20	4.04	3.88	0.700	0.662	0.062	0.059	0.945	0.088	0.085
170	0.0124	0.00840	76.1	41.88	41.49	4.91	3.90	0.520	0.515	0.061	0.048	0.991	0.117	0.093
			Poly(acrylamide)											
4	0.0653	0.00000	0.0	13.99	7.86	12.15	6.66	0.913	0.513	0.793	0.435	0.562	0.869	0.476
8	0.0562	0.00000	0.0	5.98	5.60	5.28	4.98	0.336	0.315	0.297	0.280	0.938	0.884	0.833
9	0.0575	0.00000	0.0	6.12	5.10	6.49	5.37	0.352	0.293	0.373	0.309	0.832	1.060	0.878
10	0.2539	0.00000	0.0	0.75	0.74	0.79	0.78	0.191	0.188	0.200	0.198	0.984	1.047	1.037
11	0.2566	0.00000	0.0	1.50	1.49	1.58	1.55	0.386	0.383	0.405	0.398	0.992	1.048	1.031
14	0.1212	0.00000	0.0	1.74	1.69	1.83	1.76	0.211	0.205	0.222	0.213	0.972	1.052	1.009
20	0.0591	0.00000	0.0	15.32	10.23	16.34	10.87	0.905	0.604	0.965	0.642	0.667	1.066	0.709
21	0.0874	0.00000	0.0	32.15	14.47	33.59	16.67	2.811	1.265	2.937	1.458	0.450	1.045	0.519
26	0.1255	0.00000	0.0	1.12	1.10	1.16	1.12	0.141	0.138	0.145	0.141	0.979	1.028	1.000
27	0.1966	0.00000	0.0	2.87	2.73	3.01	2.96	0.565	0.537	0.591	0.582	0.950	1.046	1.030
31	0.2457	0.00000	0.0	1.77	1.75	1.92	1.82	0.436	0.431	0.472	0.446	0.989	1.083	1.023
			Poly(N-methylacrylamide)											
2	0.0599	0.00000	0.0	2.05	2.05	2.15	2.10	0.123	0.123	0.129	0.126	1.000	1.049	1.024
22	0.0902	0.00000	0.0	2.91	3.12	2.95	2.90	0.263	0.282	0.266	0.262	1.072	1.011	0.996
23	0.0579	0.00000	0.0	4.77	4.70	4.61	4.60	0.276	0.272	0.267	0.266	0.986	0.967	0.964
38	0.0566	0.00000	0.0	4.22	4.19	4.43	4.31	0.239	0.237	0.251	0.244	0.992	1.050	1.021
39	0.0799	0.00000	0.0	3.25	3.20	3.37	3.28	0.260	0.256	0.269	0.262	0.985	1.035	1.008
63	0.0721	0.00000	0.0	0.91	0.93	0.90	0.90	0.066	0.067	0.065	0.065	1.016	0.986	0.990
134	0.0729	0.00000	0.0	5.76	5.56	5.59	5.49	0.420	0.406	0.408	0.400	0.967	0.971	0.953



TABLE 24

Key to symbols used in Figures 32 through 37

Plot symbol	Polymer type
◇	Poly(acrylamide-co-sodium acrylate)
▽	Poly(N-methylacrylamide-co-sodium acrylate), copolymerized
⊠	Poly(N-methylacrylamide-co-sodium acrylate), hydrolyzed
▷	Poly(N-isopropylacrylamide-co-sodium acrylate)
⊕	Poly(N-tert-butylacrylamide-co-sodium acrylate)
+	Poly(acrylamide)
×	Poly(N-methylacrylamide)
△	Poly(sodium acrylate)
□	Poly(N-isopropylacrylamide)
◁	Other polymer types

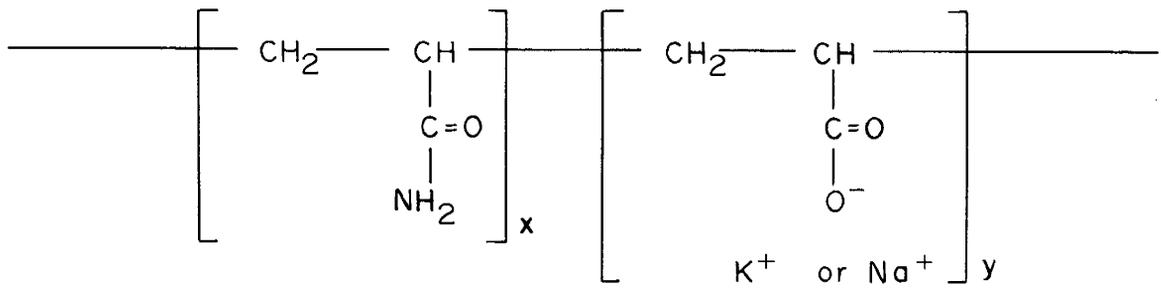


FIGURE 1

Molecular Structure of Partially Hydrolyzed Polyacrylamides

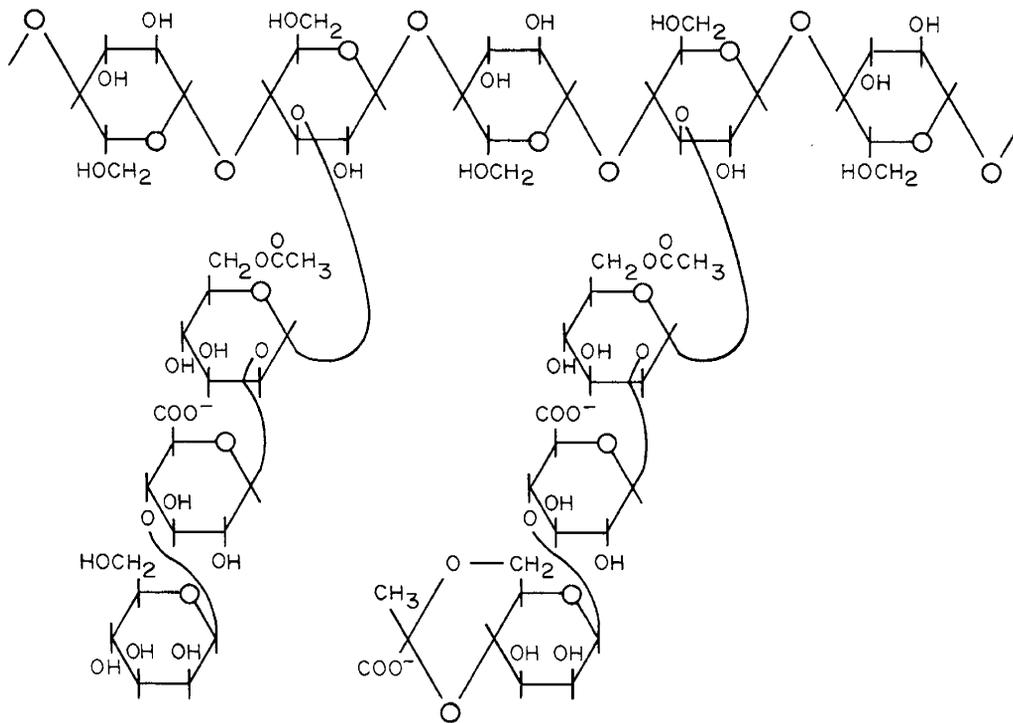
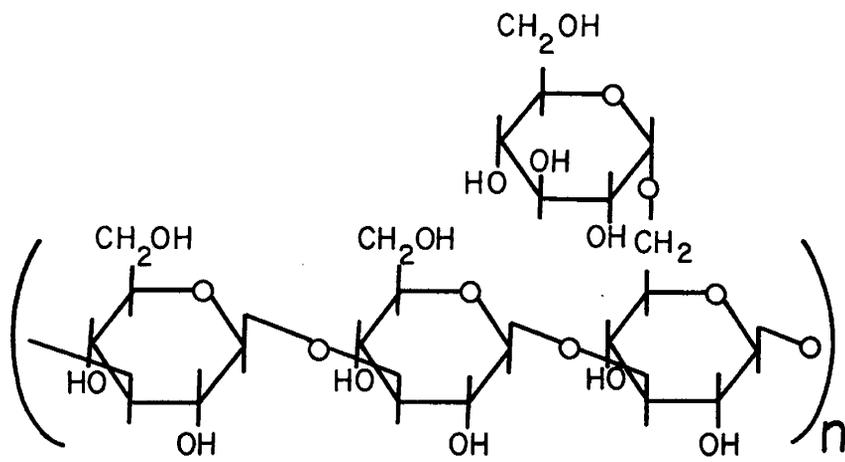


FIGURE 2

Structure of Extracellular Polysaccharide of *Xanthomonas campestris*, According to Jansson et al. (1975).



STRUCTURE OF SCLEROGLUCAN

FIGURE 3

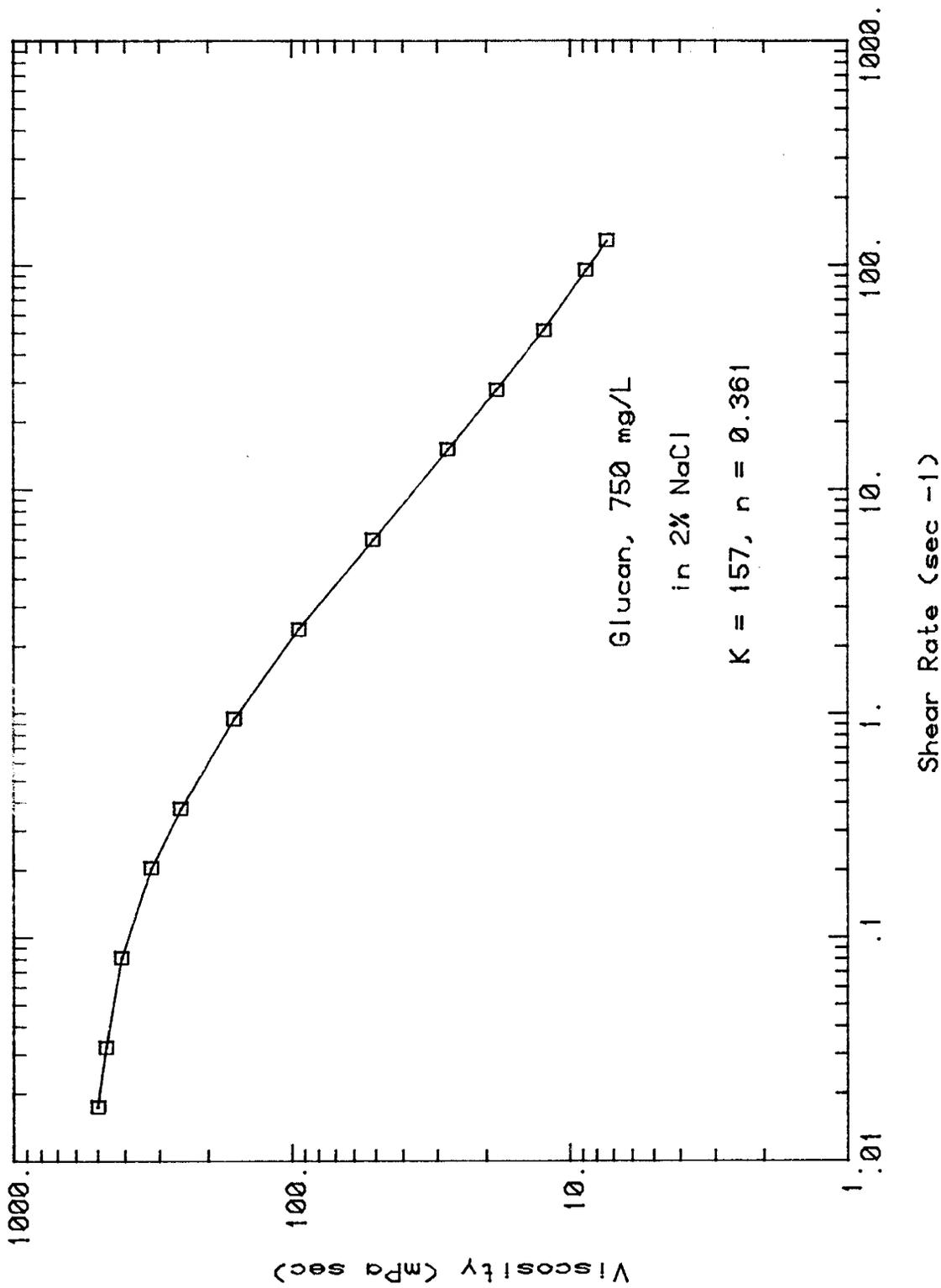


Figure 4. Rheogram of Glucan Polymer in 2% NaCl

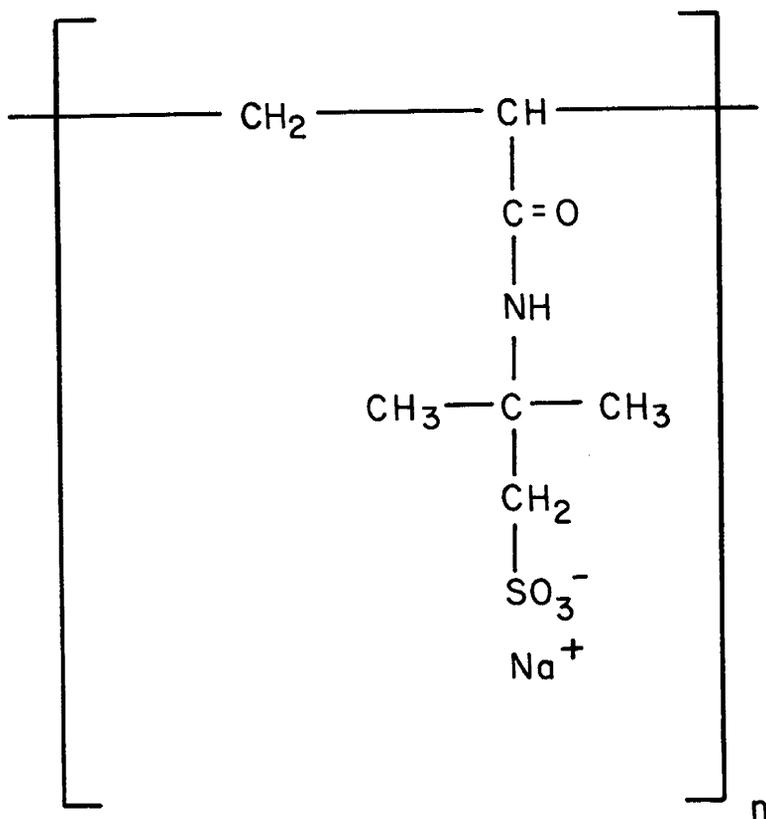


FIGURE 5

STRUCTURE OF AMPS HOMOPOLYMER [ SODIUM SALT OF  
 POLY ( 2-ACRYLAMIDO-2 METHYLPROPANE SULFONATE ) ]

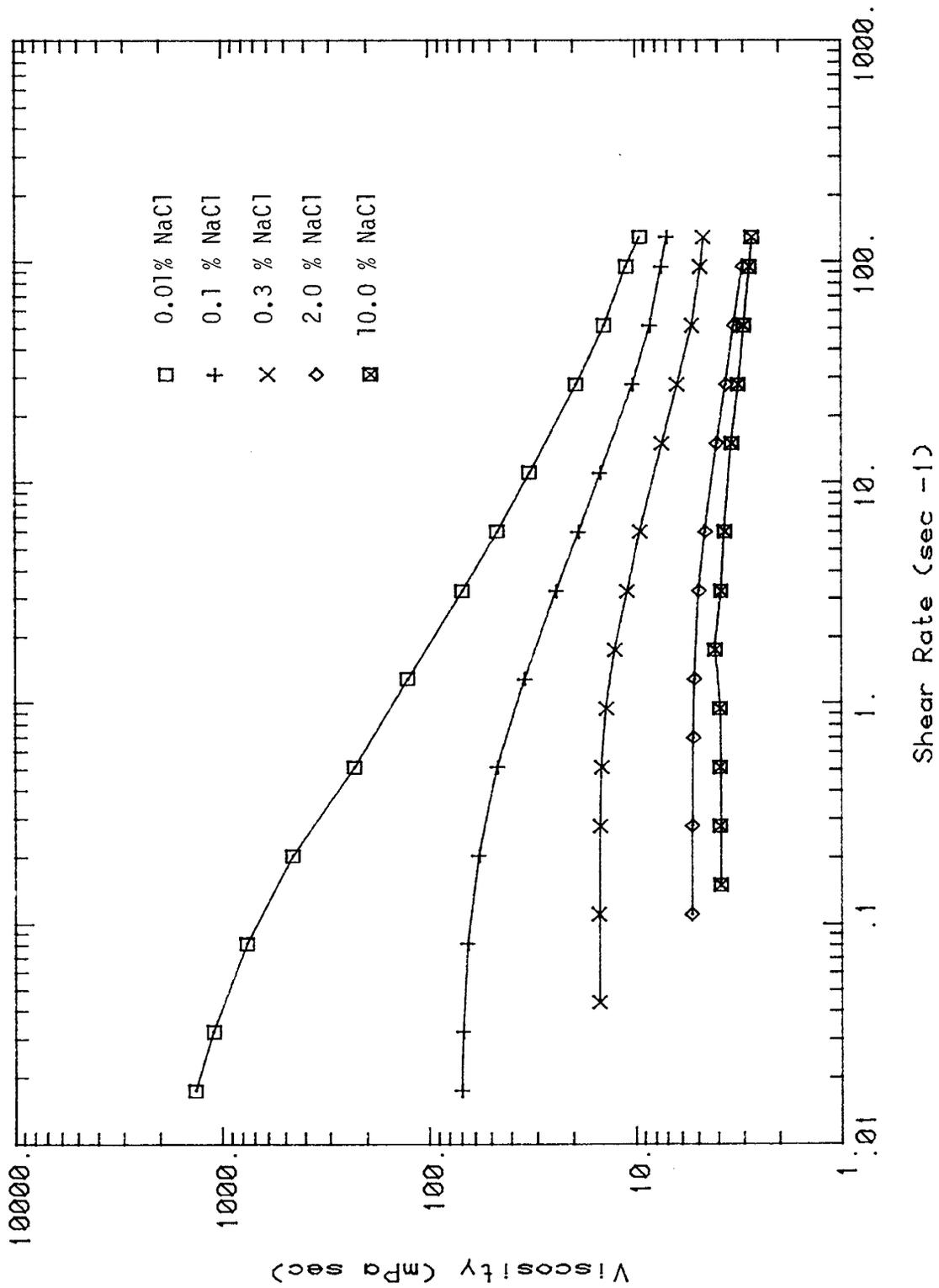


Figure 6. Rheograms of AMPS Homopolymer in NaCl Brines

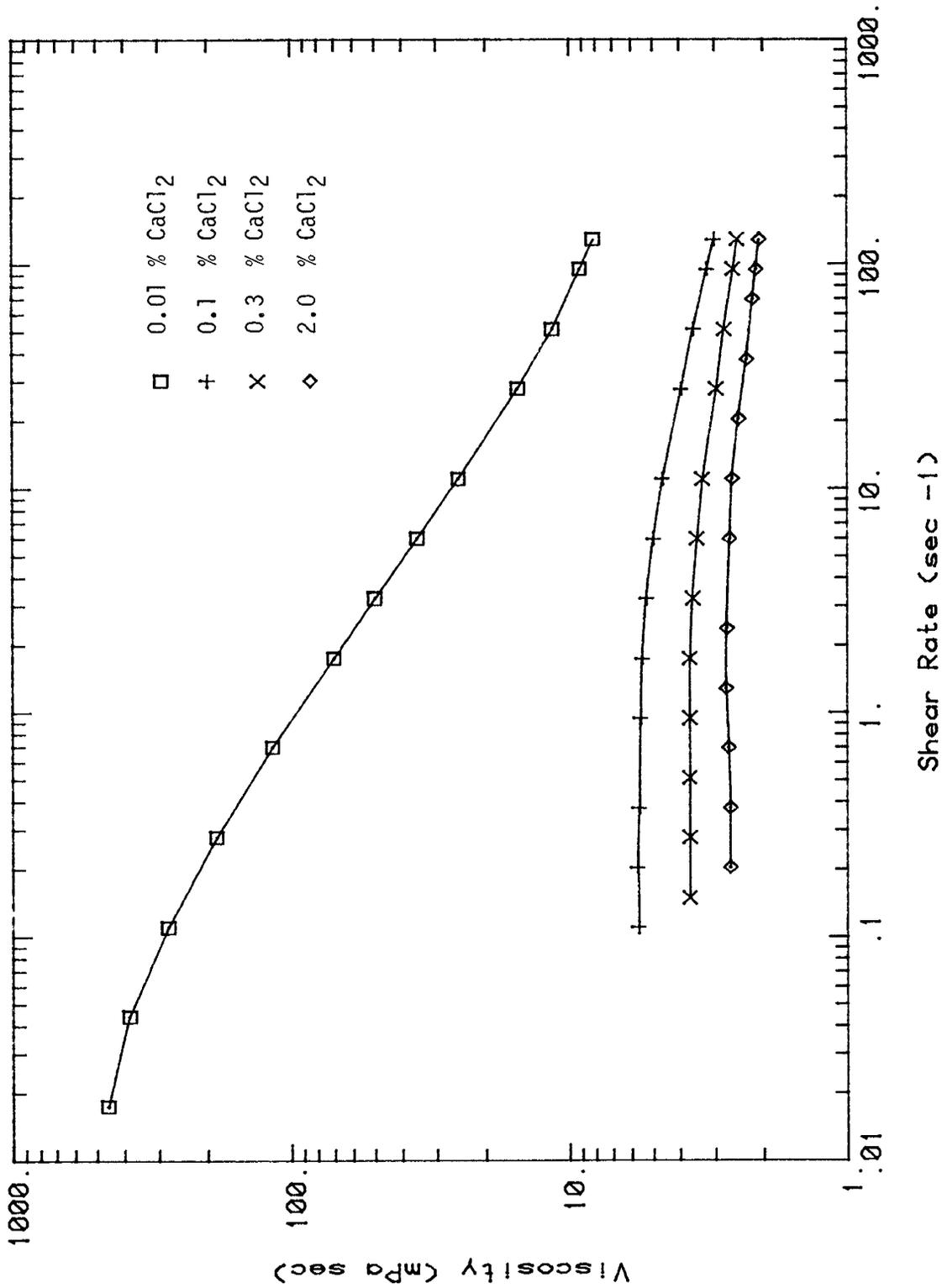


Figure 7. Rheograms of AMPS Homopolymer in CaCl<sub>2</sub> Brines

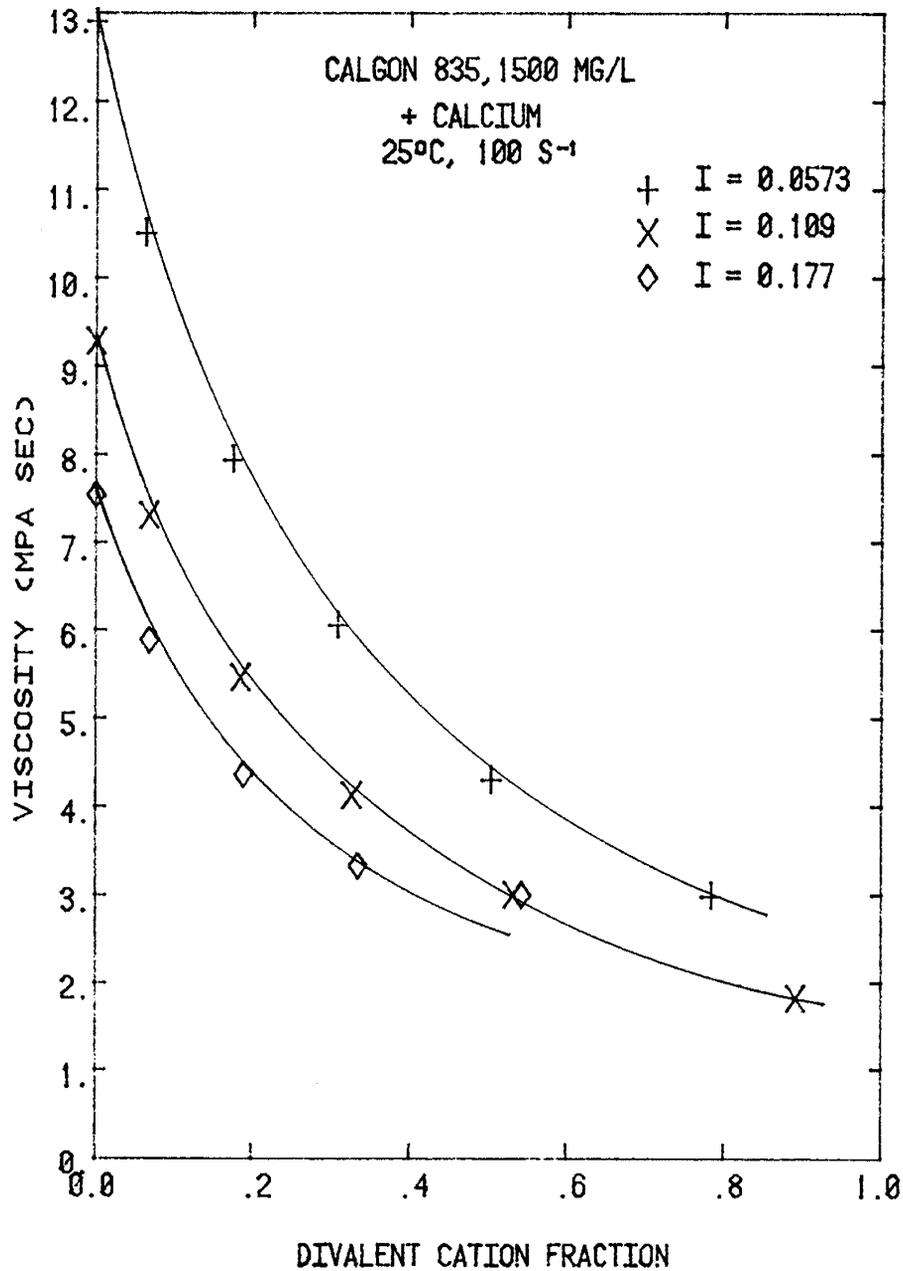


Figure 8. Comparison of Viscosity Reduction as a Function of Fraction of Calcium Ion at Different Ionic Strengths for Calgon 835

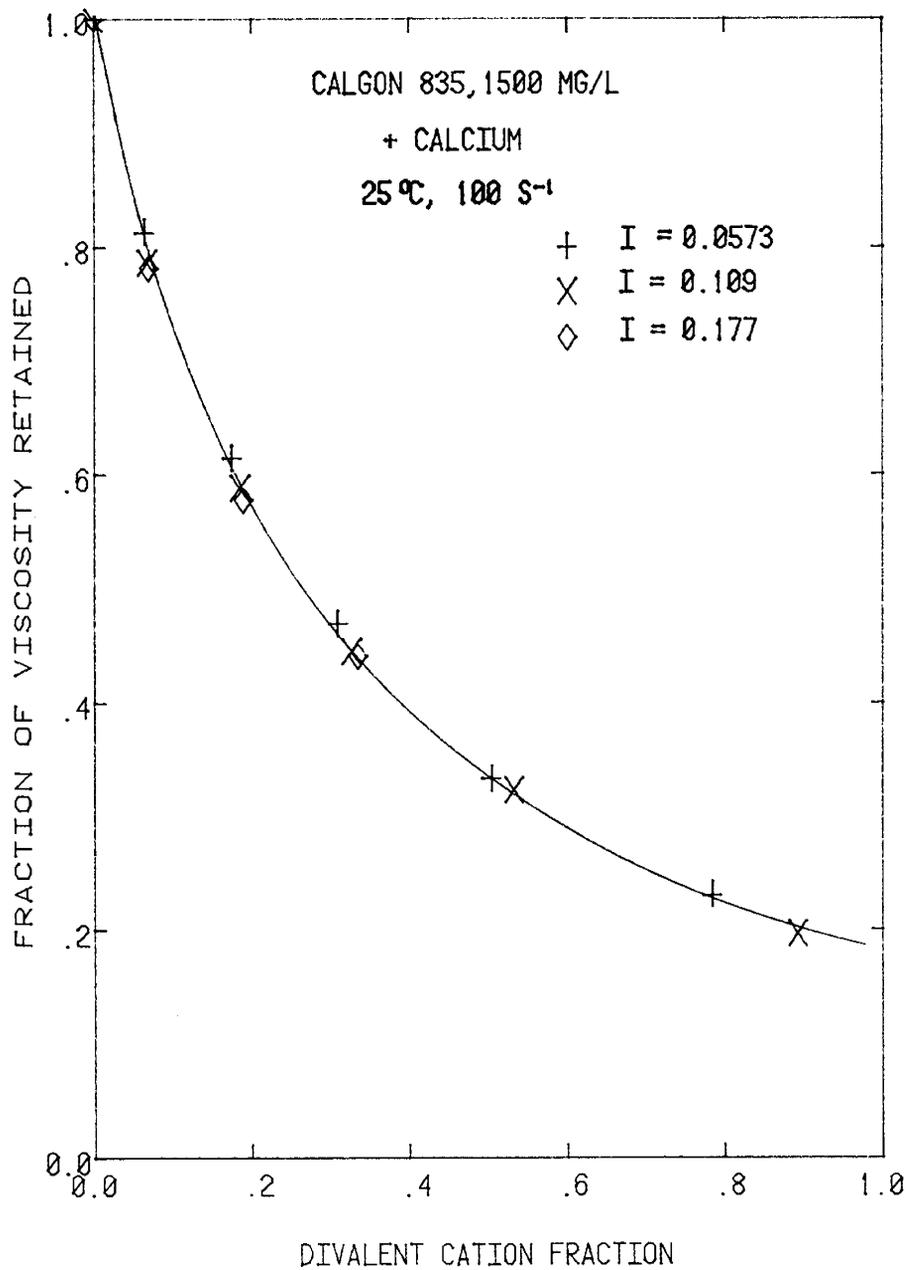


Figure 9. Fraction of Viscosity Retained as a Fraction of Calcium Ion for Calgon 835

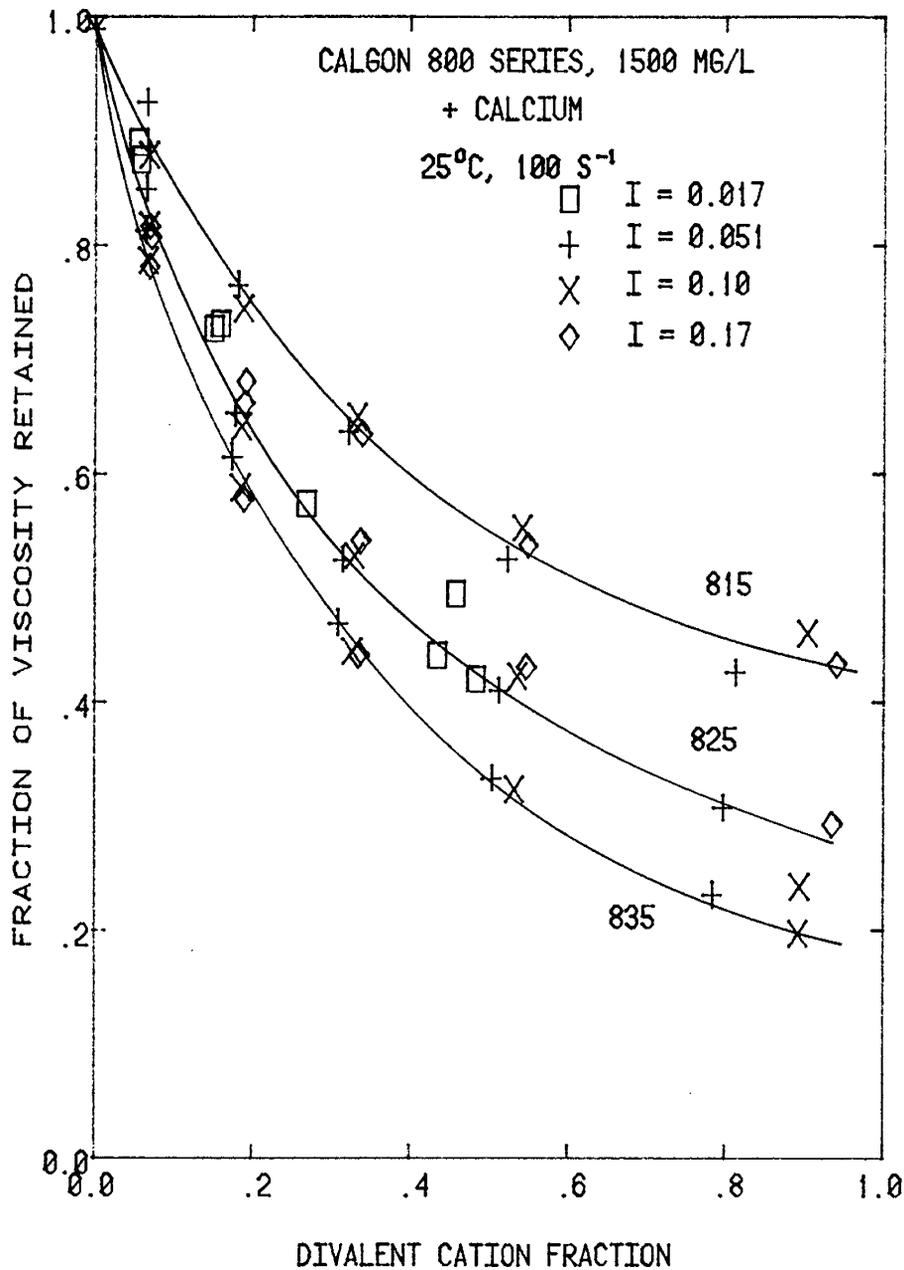


Figure 10. Effect of Degree of Hydrolysis on Fraction of Viscosity Retained for 1500 mg/L of HPAM Polymers with Sodium and Calcium Ions

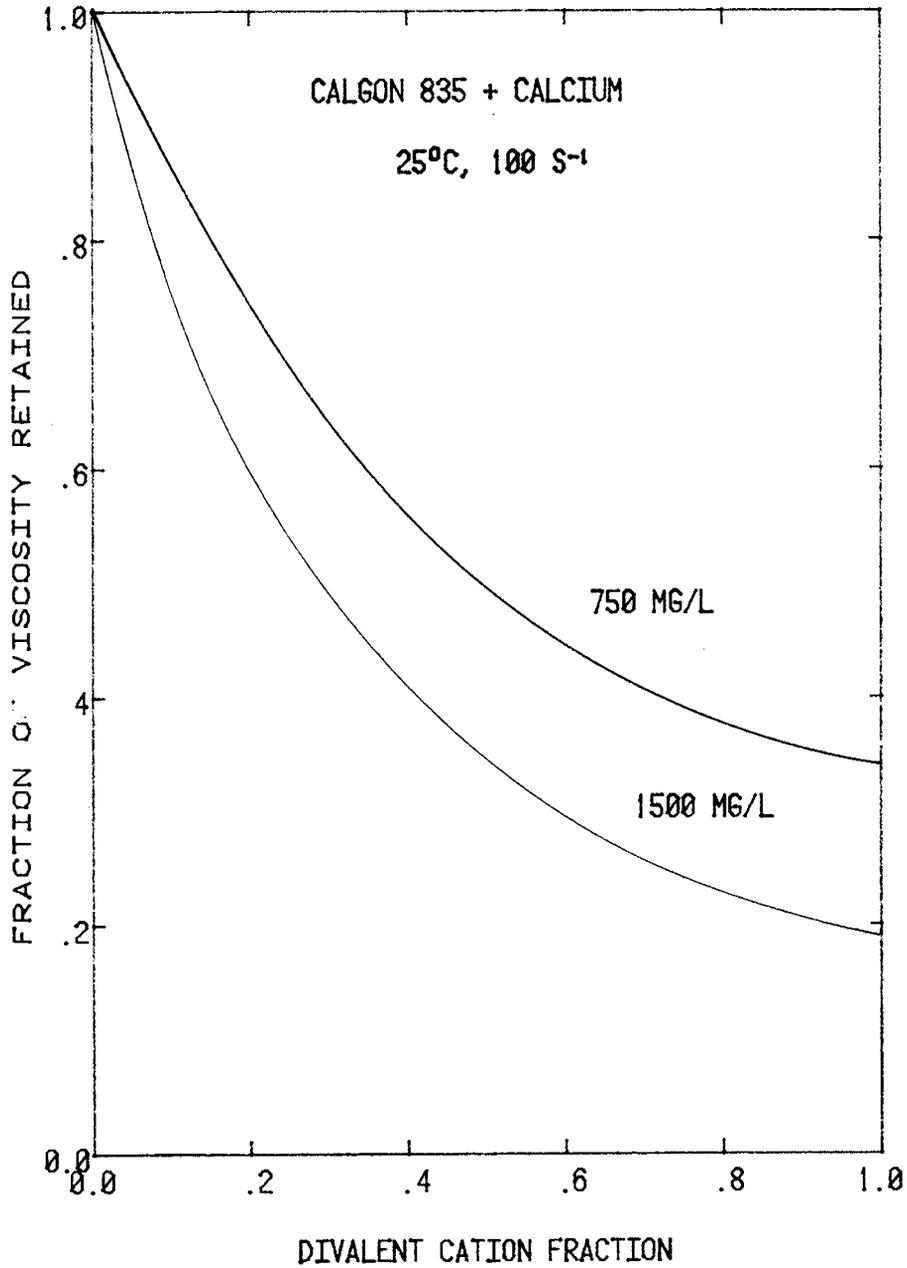


Figure 11. Effect of Polymer Concentration on Fraction of Viscosity Retained for Calgon 835 with Sodium and Calcium Ions

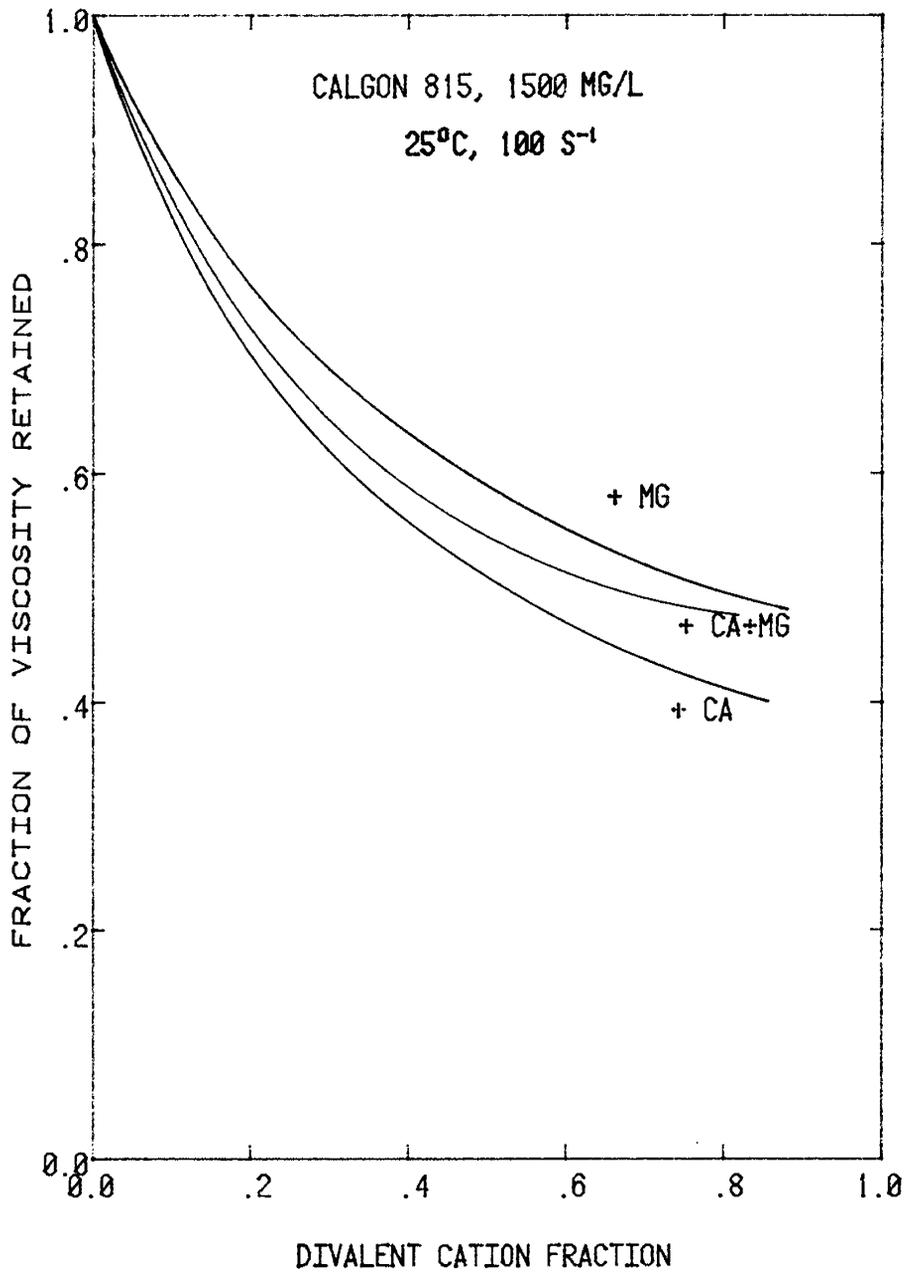


Figure 12. Comparison of the Effects of Calcium and Magnesium on Fraction of Viscosity Retained for Calgon 815

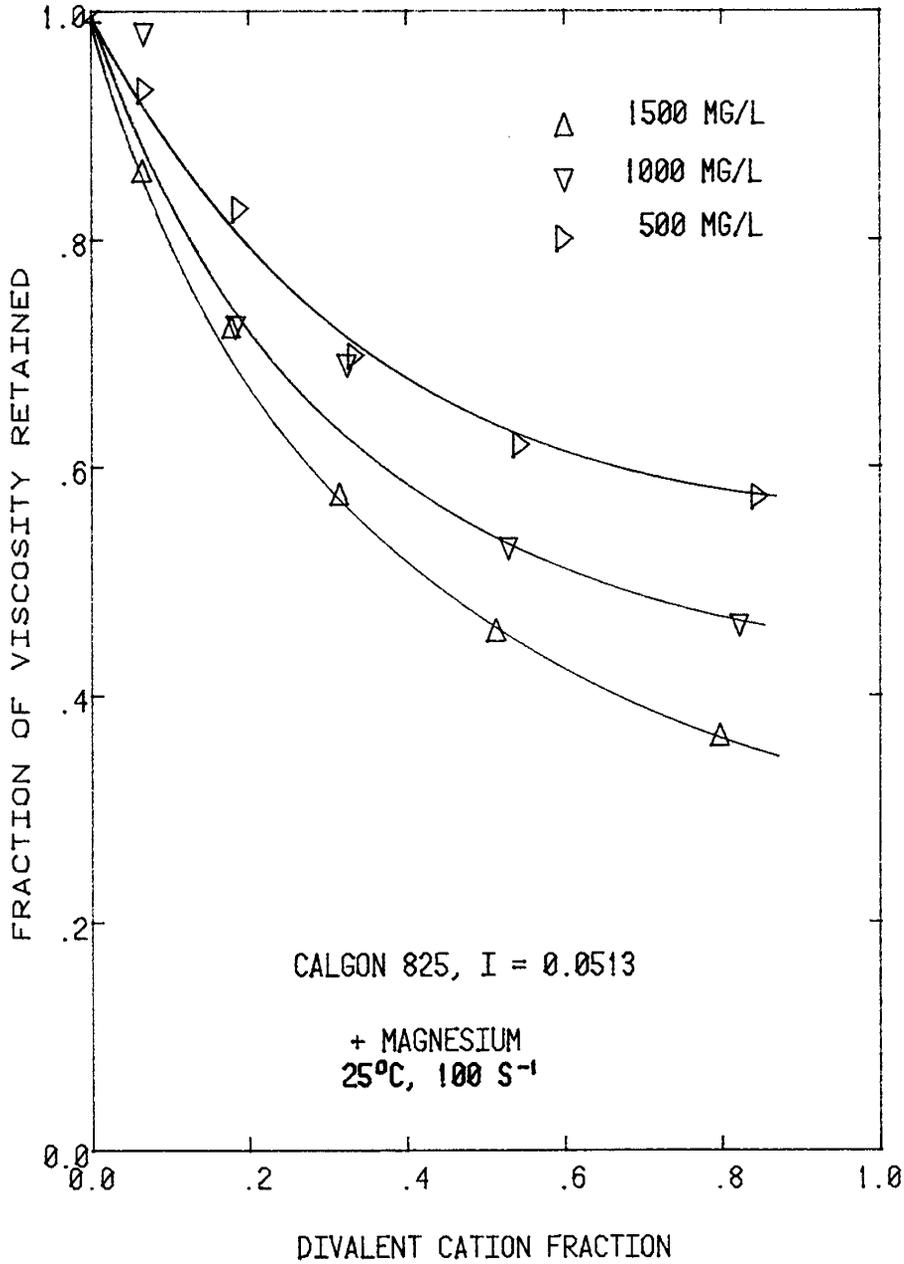


Figure 13. Effect of Polymer Concentration on Fraction of Viscosity Retained for Calgon 825 with Sodium and Magnesium Ions

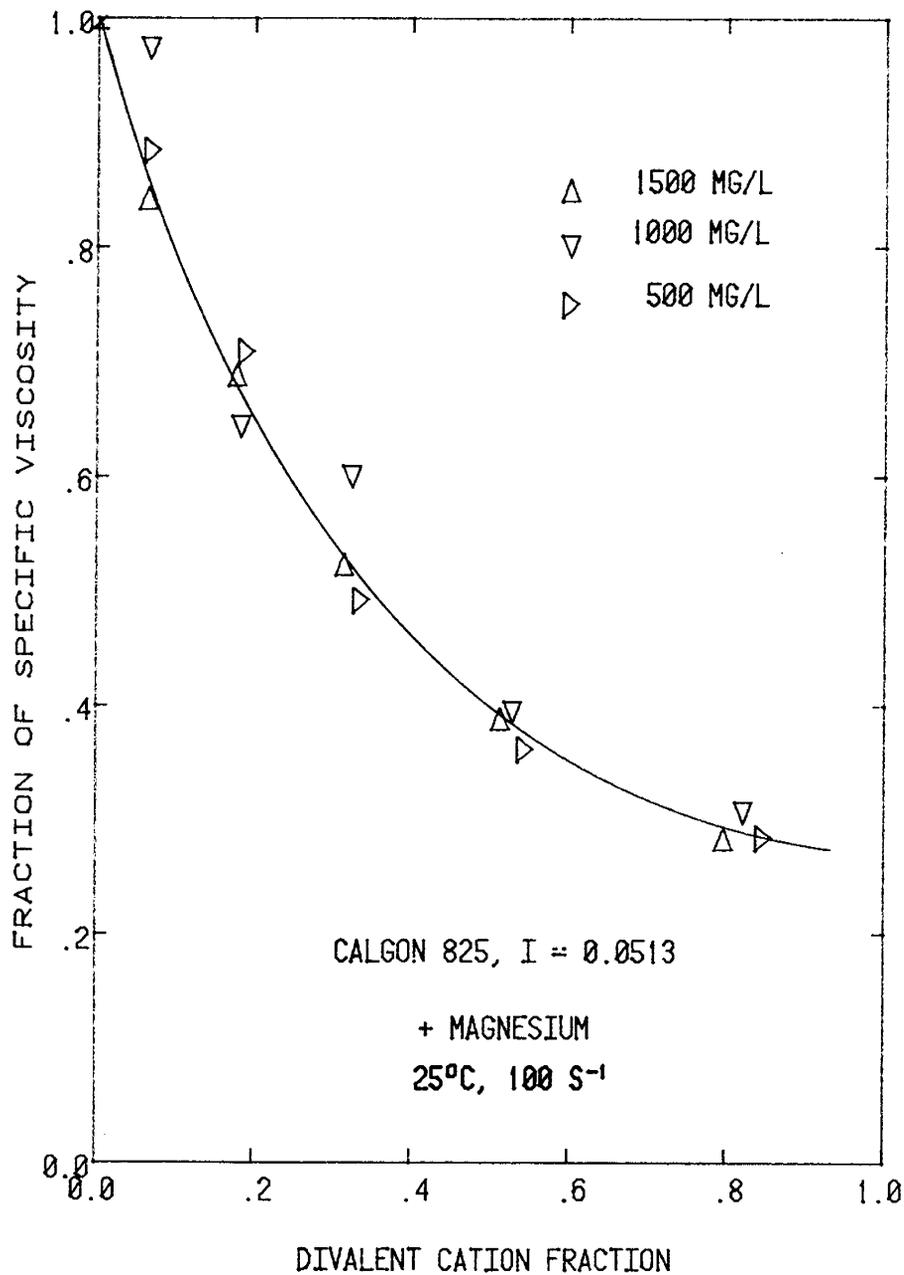


Figure 14. Fraction of Specific Viscosity Retained as a Function of Magnesium Ion Content with Calgon 825

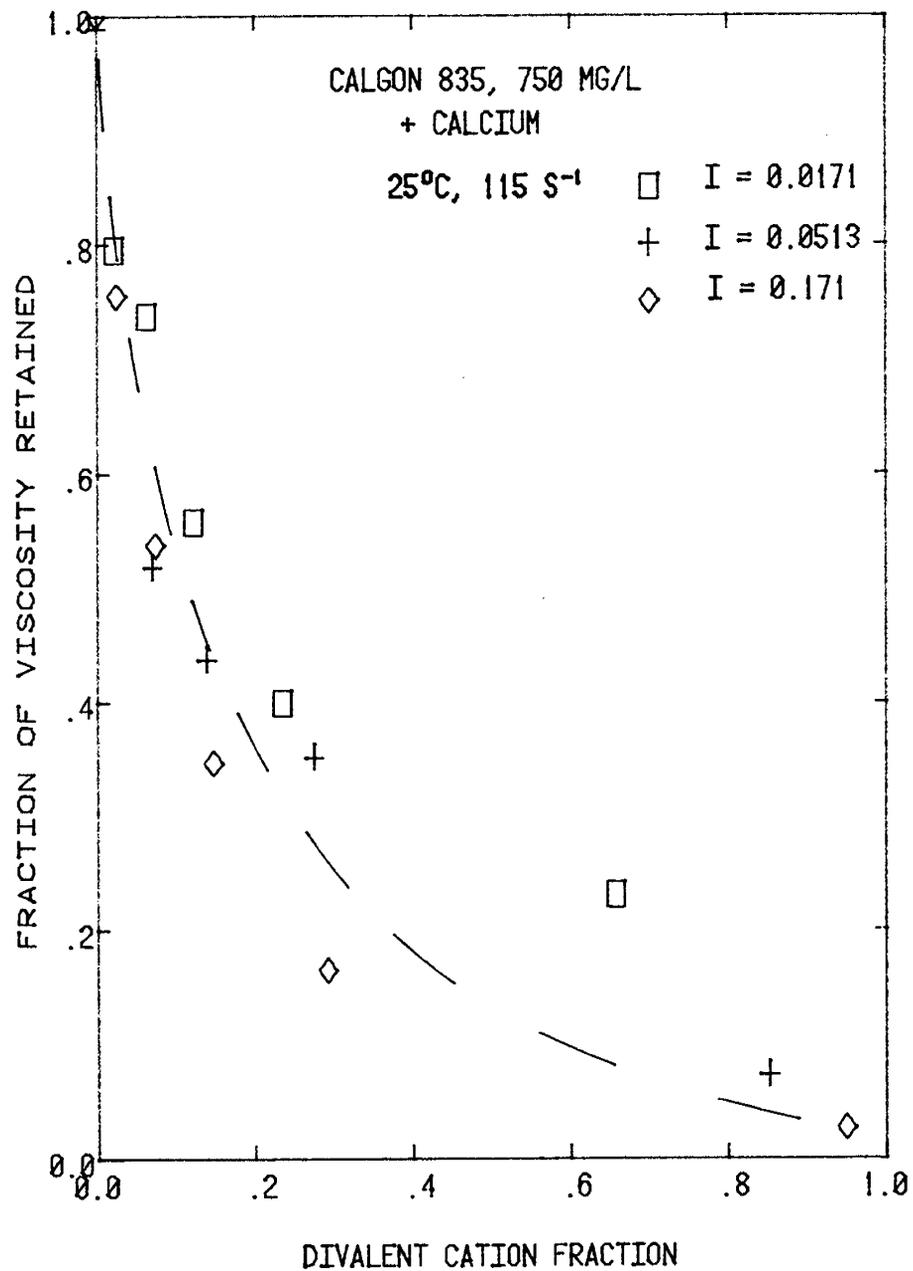


Figure 15. Fraction of Specific Viscosity Retained as a Function of Calcium Ion Content with Calgon 835

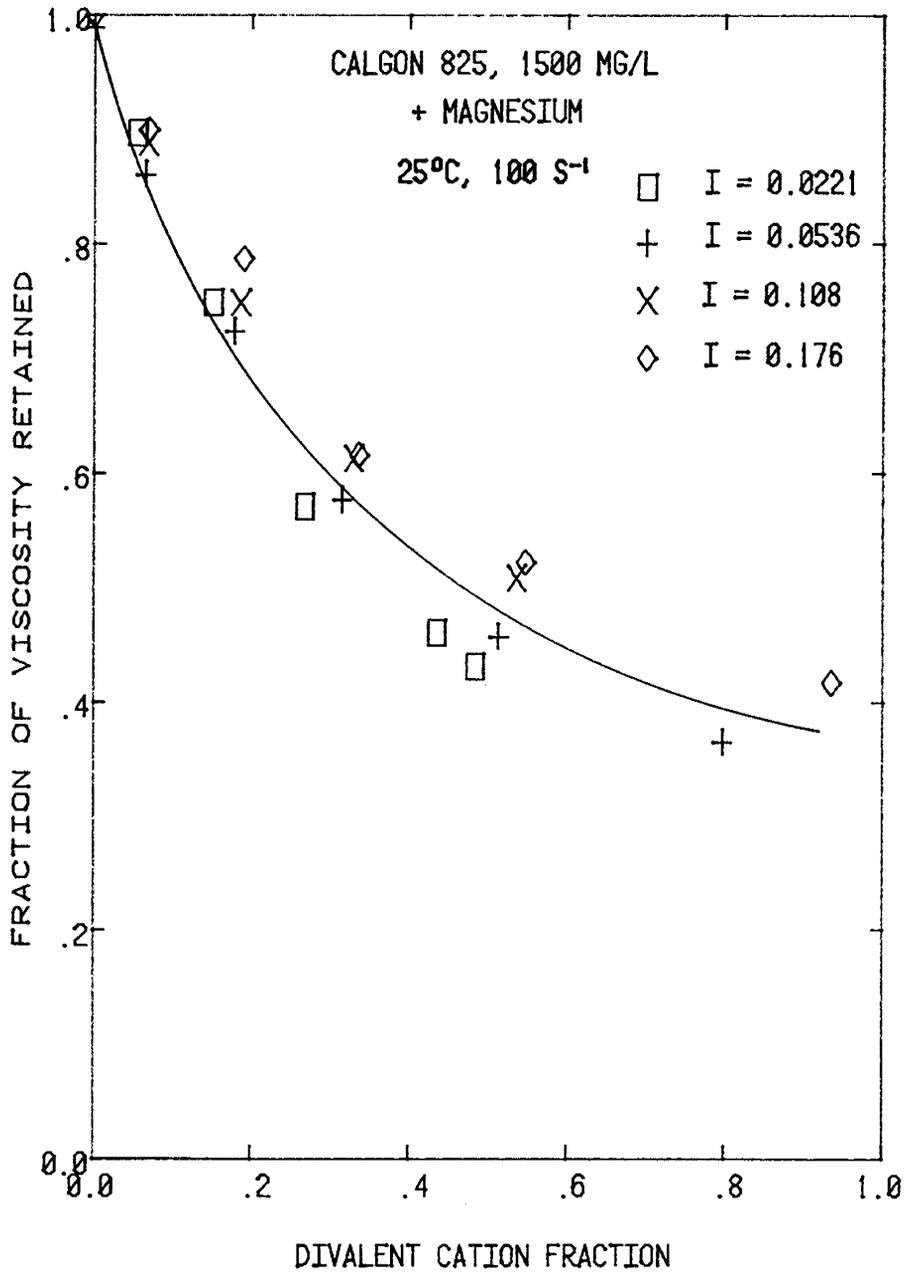


Figure 16. Effect of Magnesium Ion on the Apparent Viscosity Retention of Calgon 825 at Various Ionic Strengths

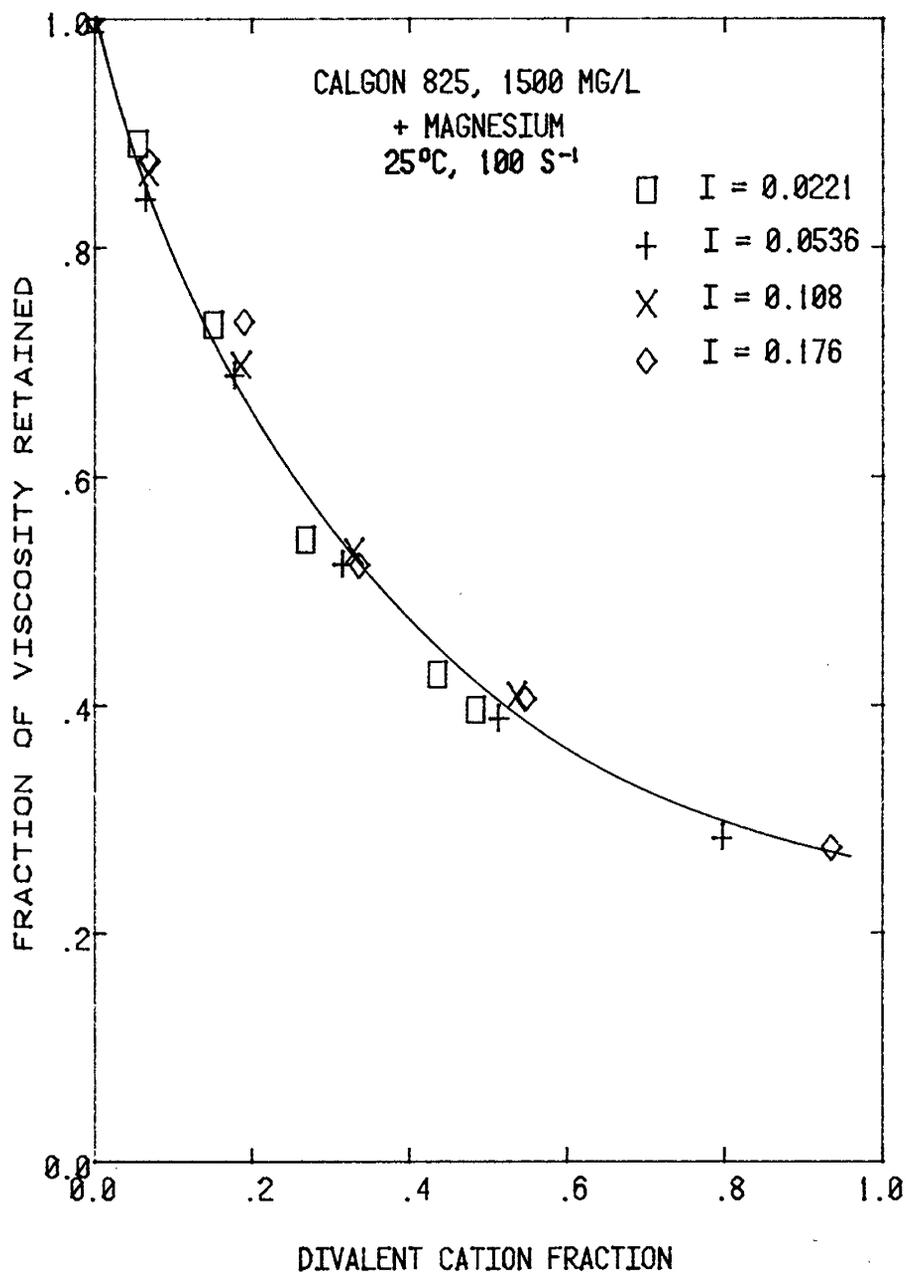


Figure 17. Effect of Magnesium Ion on the Retention of Specific Viscosity of Calgon 825 at Various Ionic Strengths

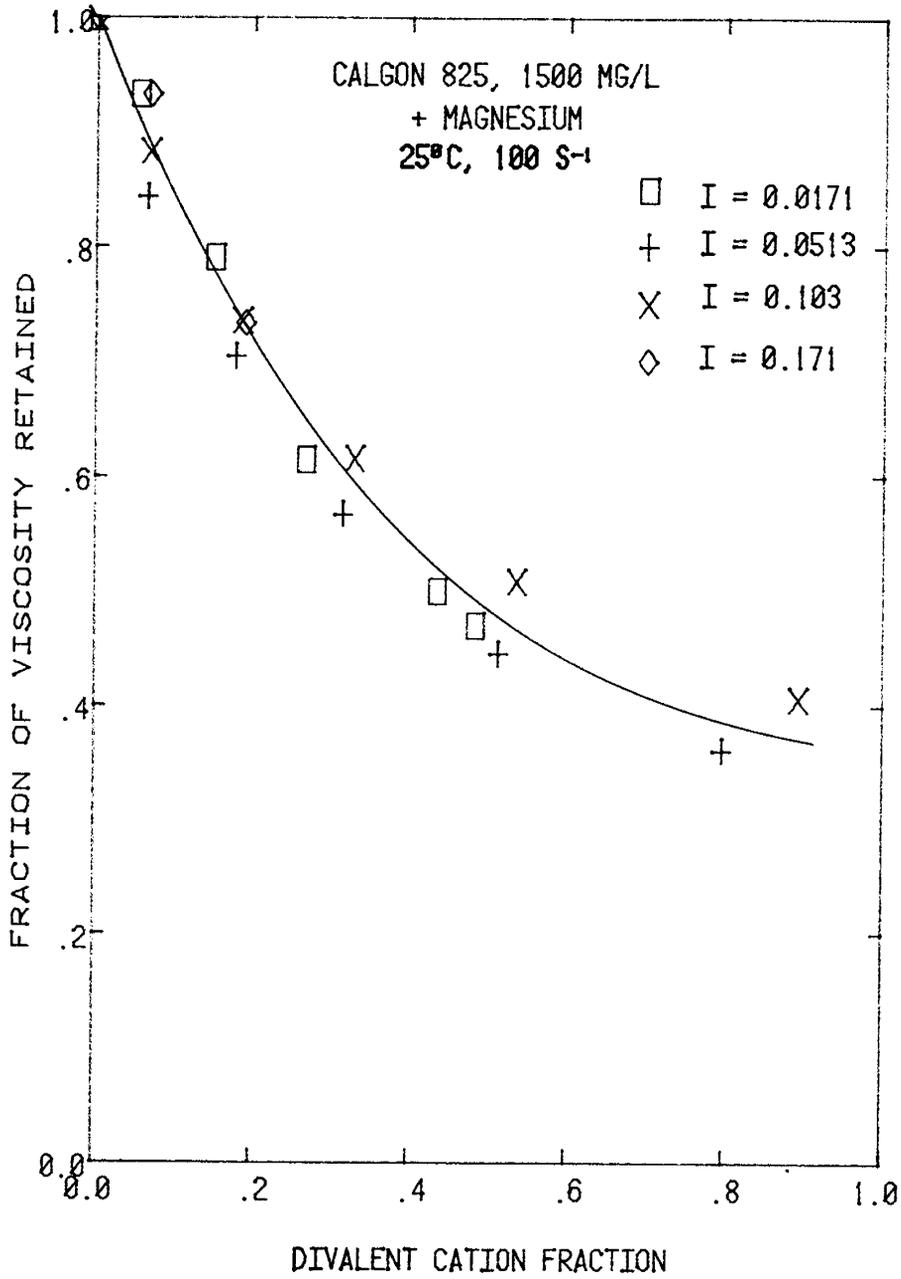


Figure 18. Data from Contraves Rheometer  
Showing the Effect of Magnesium Ion  
on Polymer 825 Viscosities at 100 sec<sup>-1</sup>

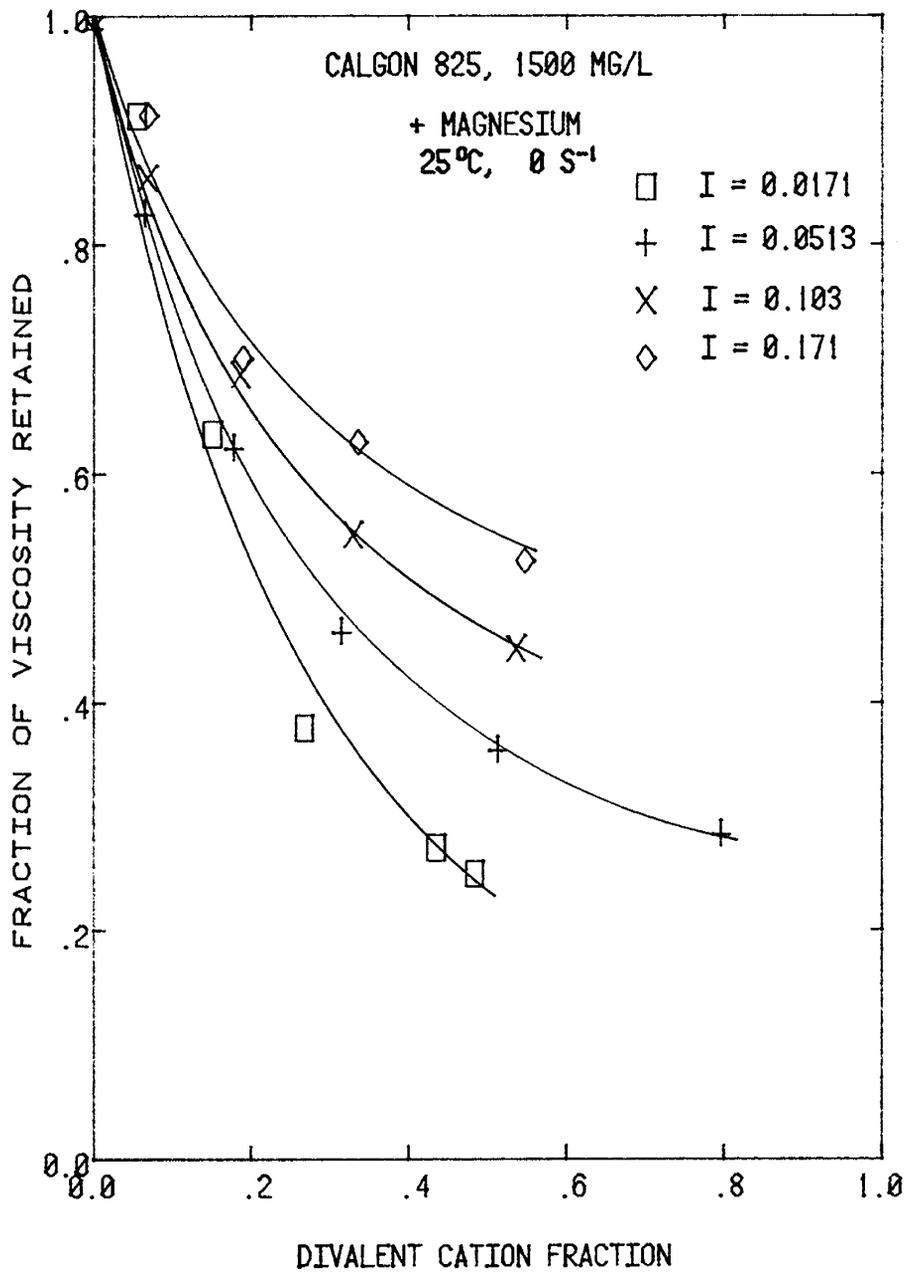
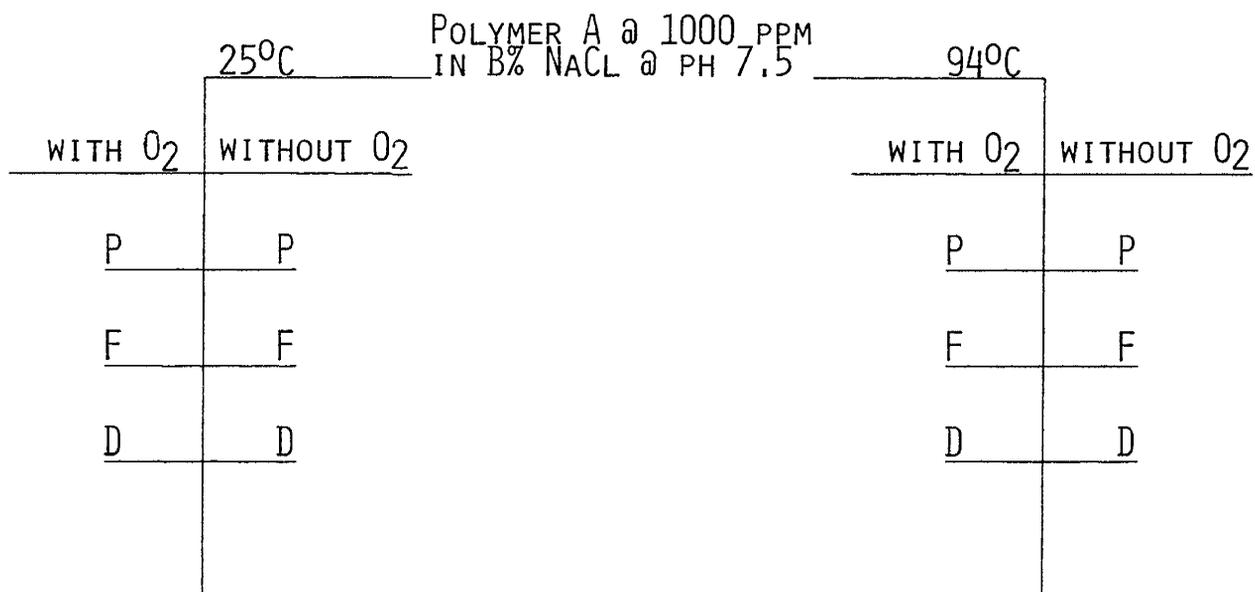


Figure 19. Data from Contraves Rheometer  
 Showing the Effect of Magnesium Ion  
 on Polymer 825 Viscosities at Zero Shear Rate

## POLYMER TESTING FLOWCHART



P = PLAIN POLYMER SOLUTION - NO ADDITIVES

F = POLYMER SOLUTION WITH 300 PPM HCHO

D = POLYMER SOLUTION WITH 0.5 ML OF 1% Na<sub>2</sub> S<sub>2</sub> O<sub>4</sub> SOLN.

Figure 20. Polymer Testing Flowchart

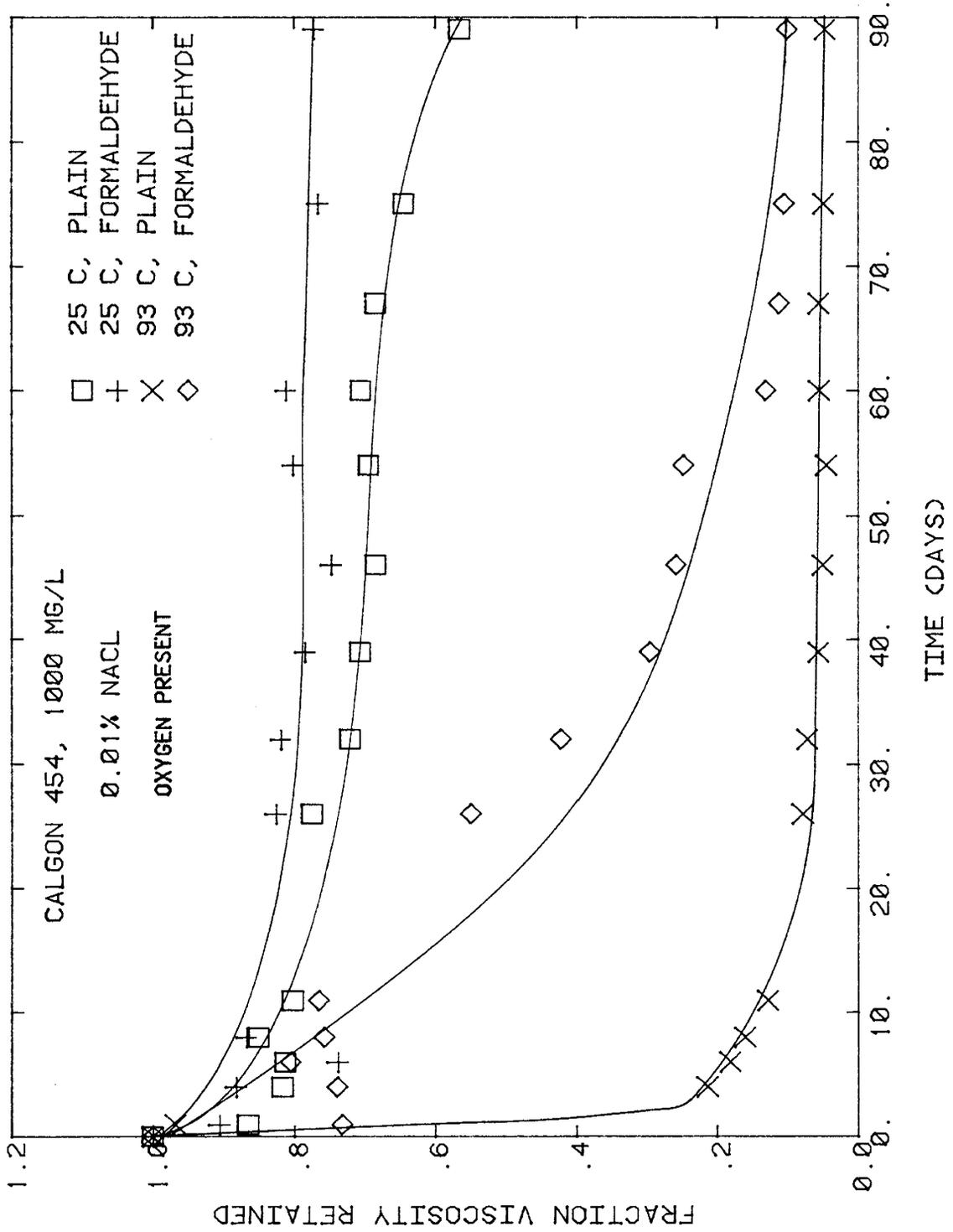


Figure 21. Effects of Temperature and Formaldehyde on the Long-Term Viscosity Stability of HPAM

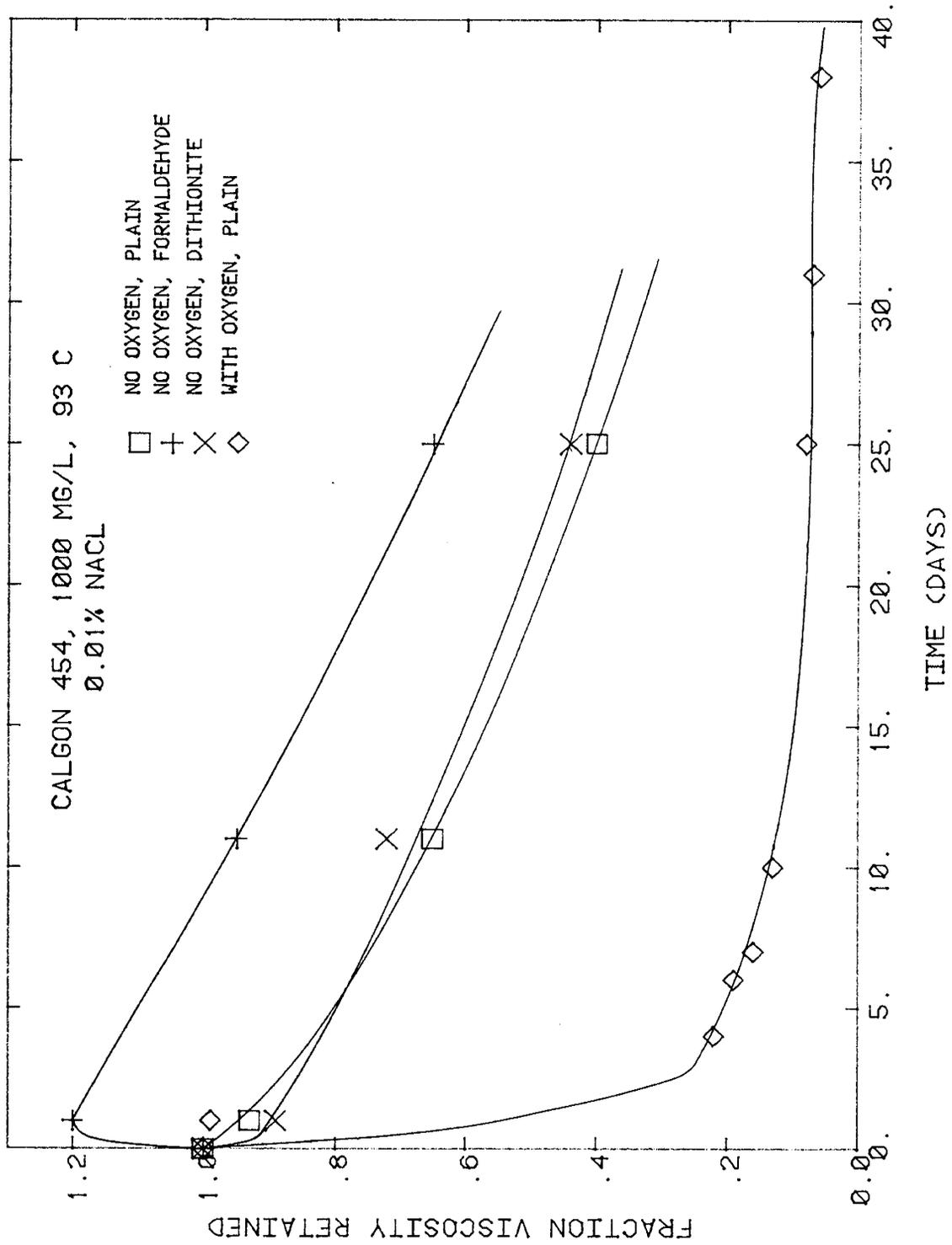


Figure 22. Effect of Oxygen and Additives on the Long-Term Stability of HPAM

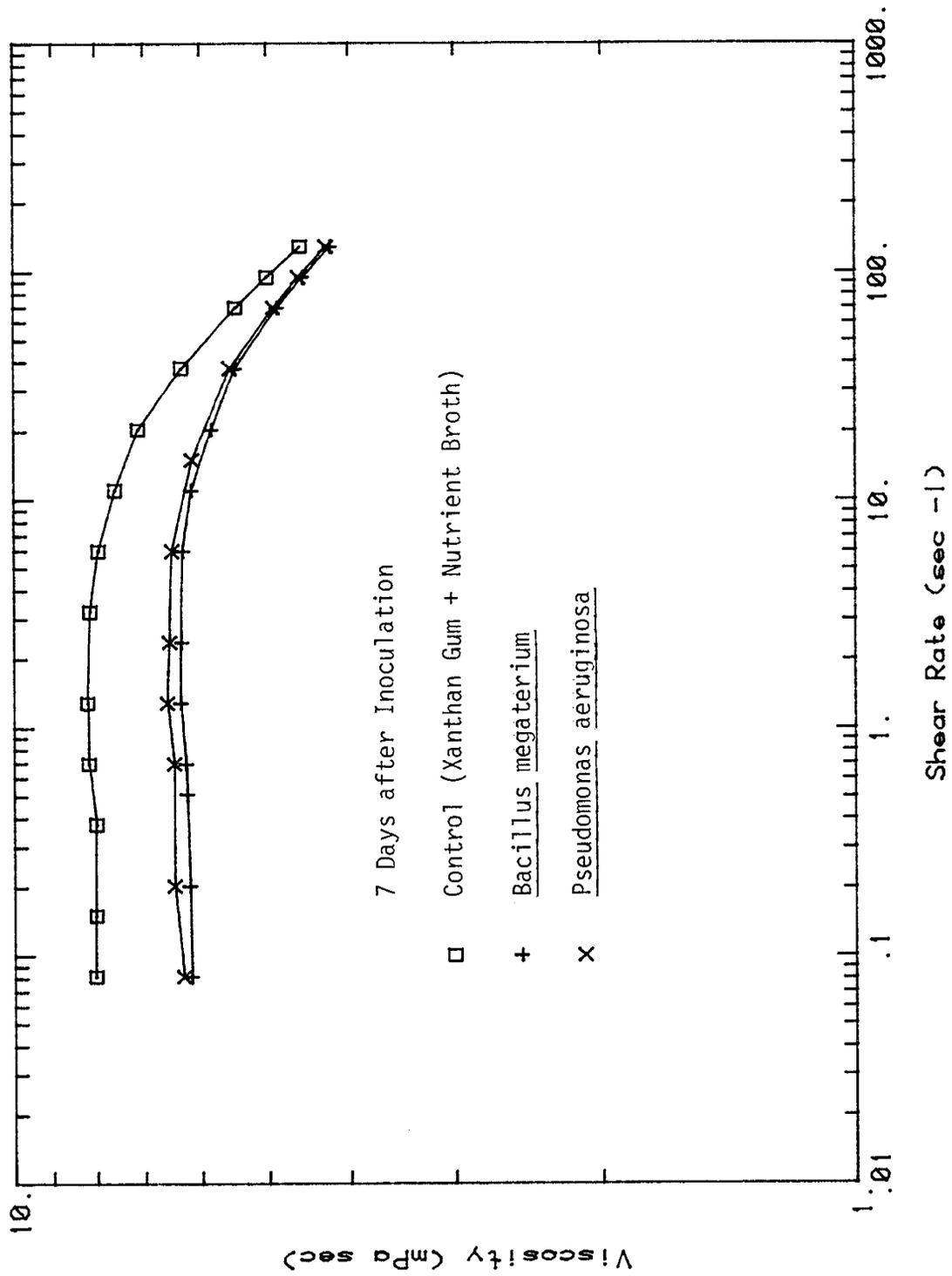


Figure 23. Effect of Some Aerobic Microbes on Viscosity of Xanthan Gum Solutions

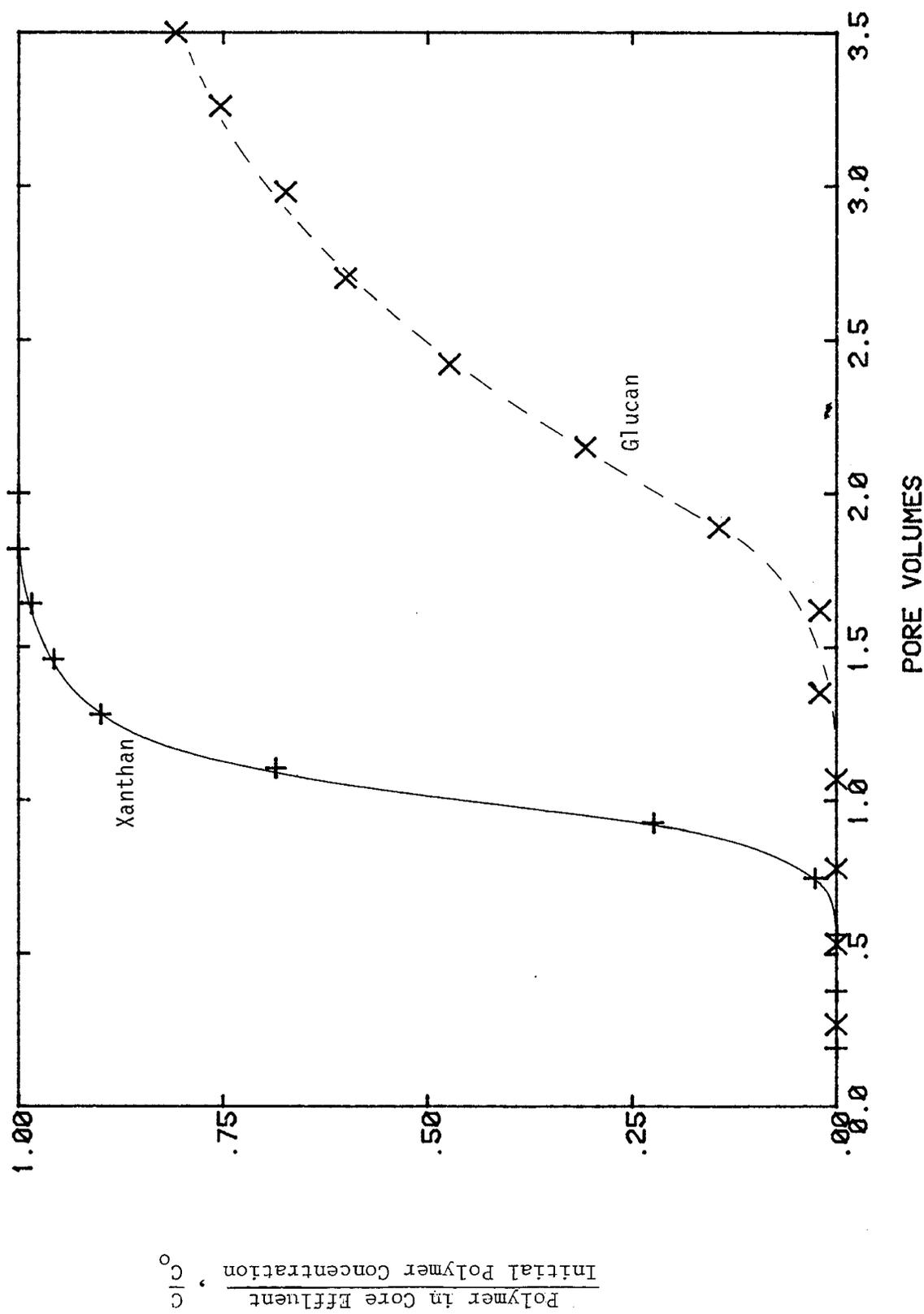


Figure 24. Comparison of Polymer Breakthrough Curves for Xanthan Gum and Scleroglucan

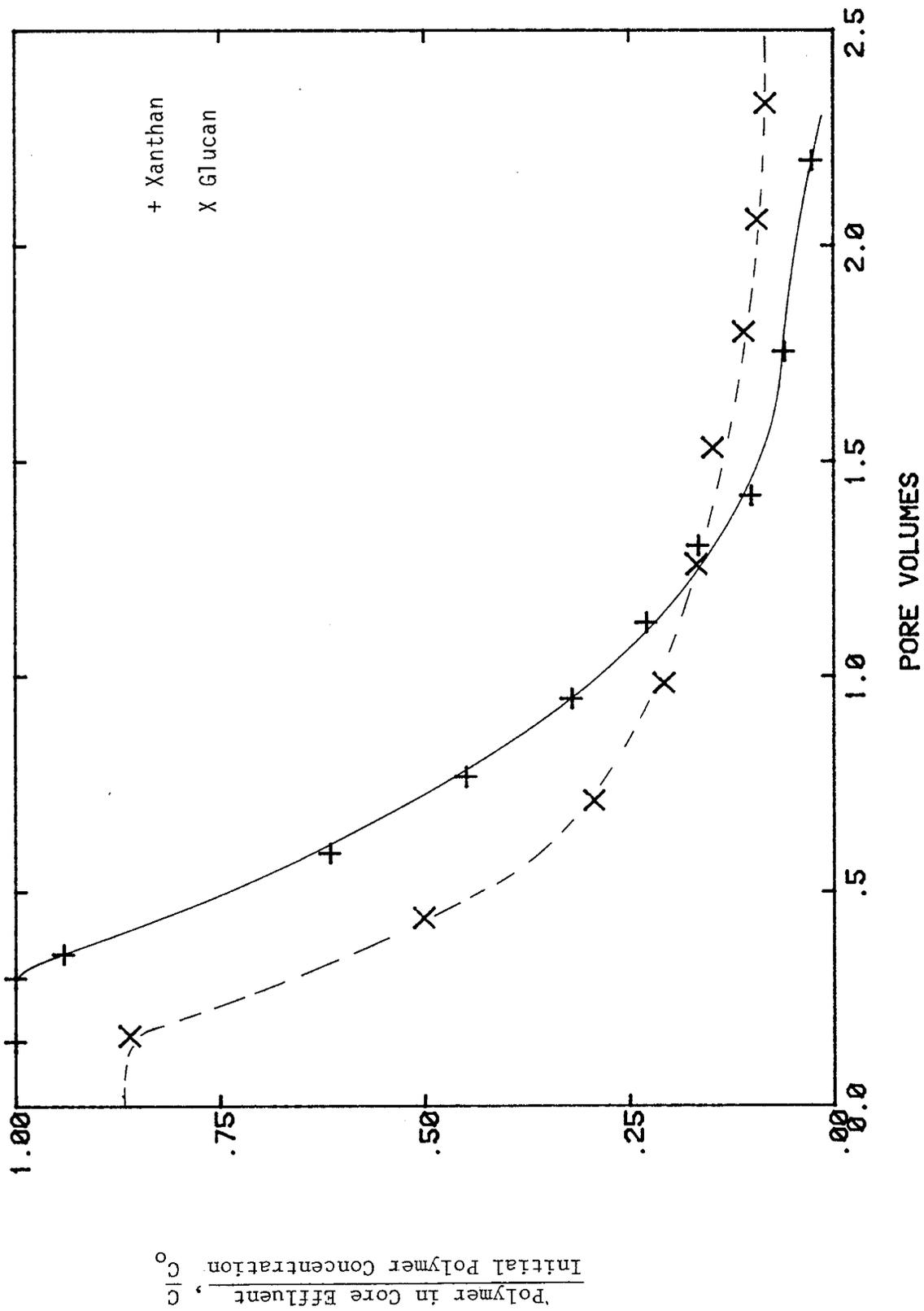


Figure 25. Displacement of Xanthan Gum and Scleroglucan Polymers from Berea Cores by Brine

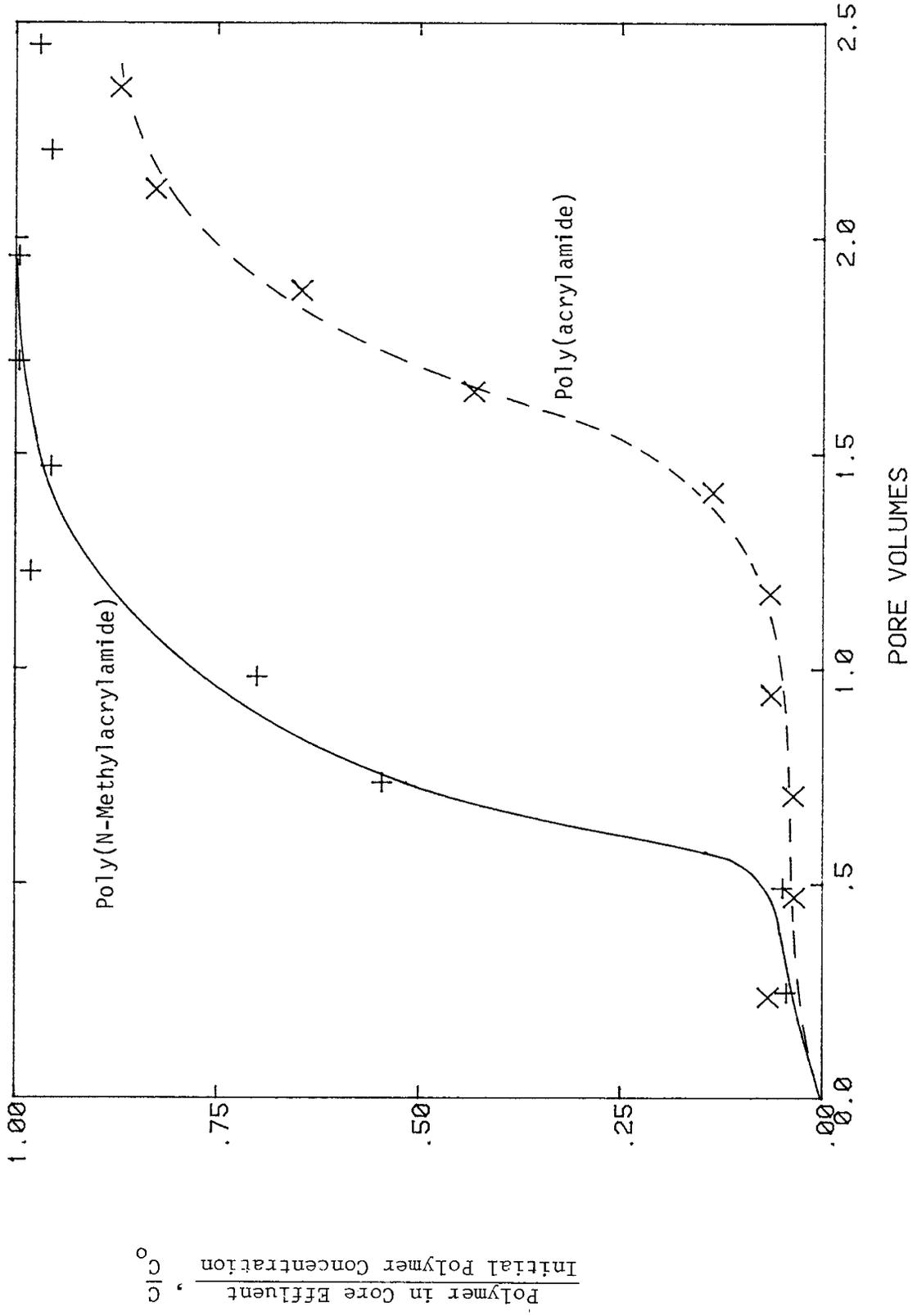


Figure 26. Comparison of Polymer Breakthrough Curves for Poly(acrylamide) and Poly(N-methylacrylamide)

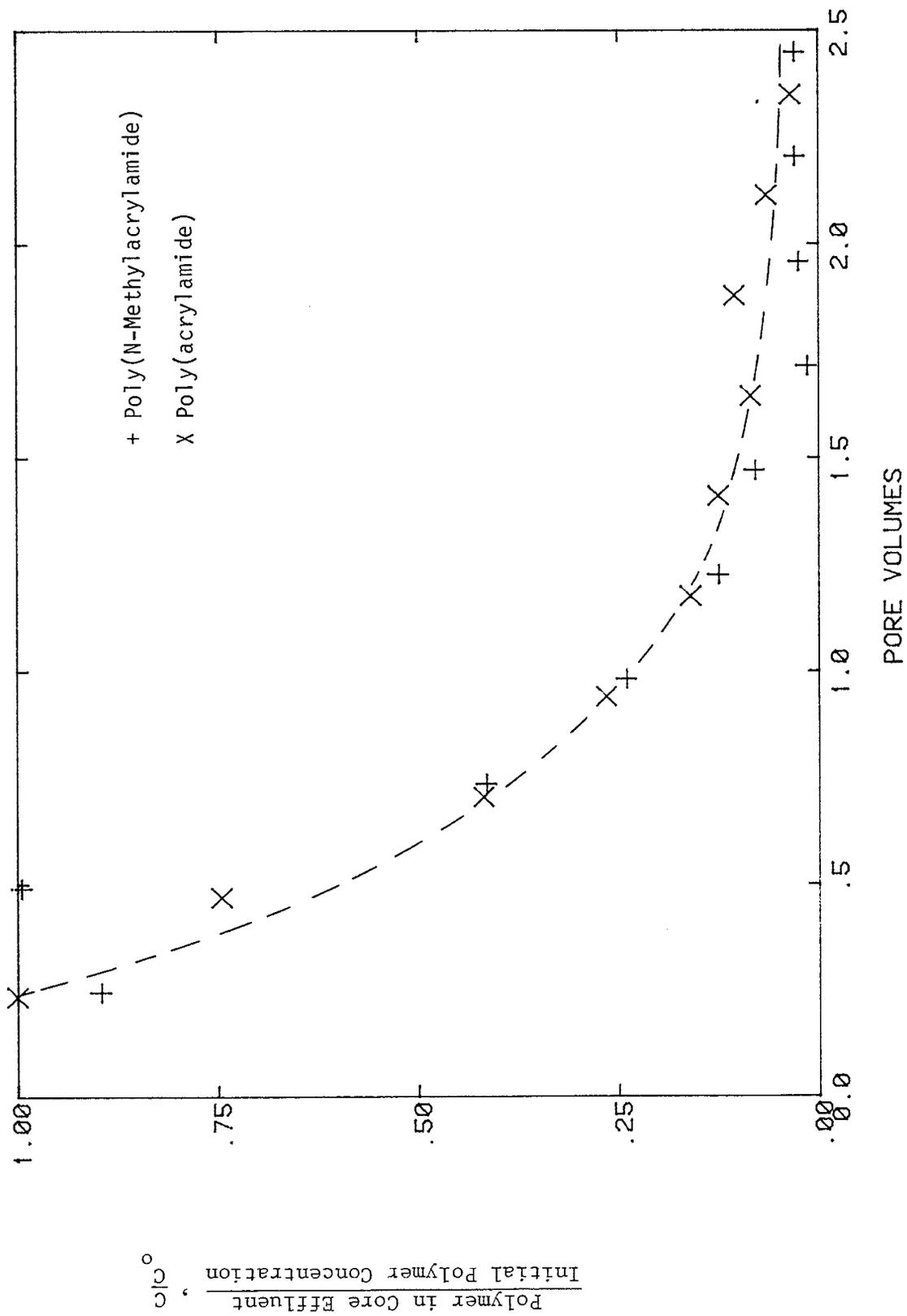


Figure 27. Displacement of Poly(acrylamide) and Poly(N-methylacrylamide) from Berea Cores by Brine

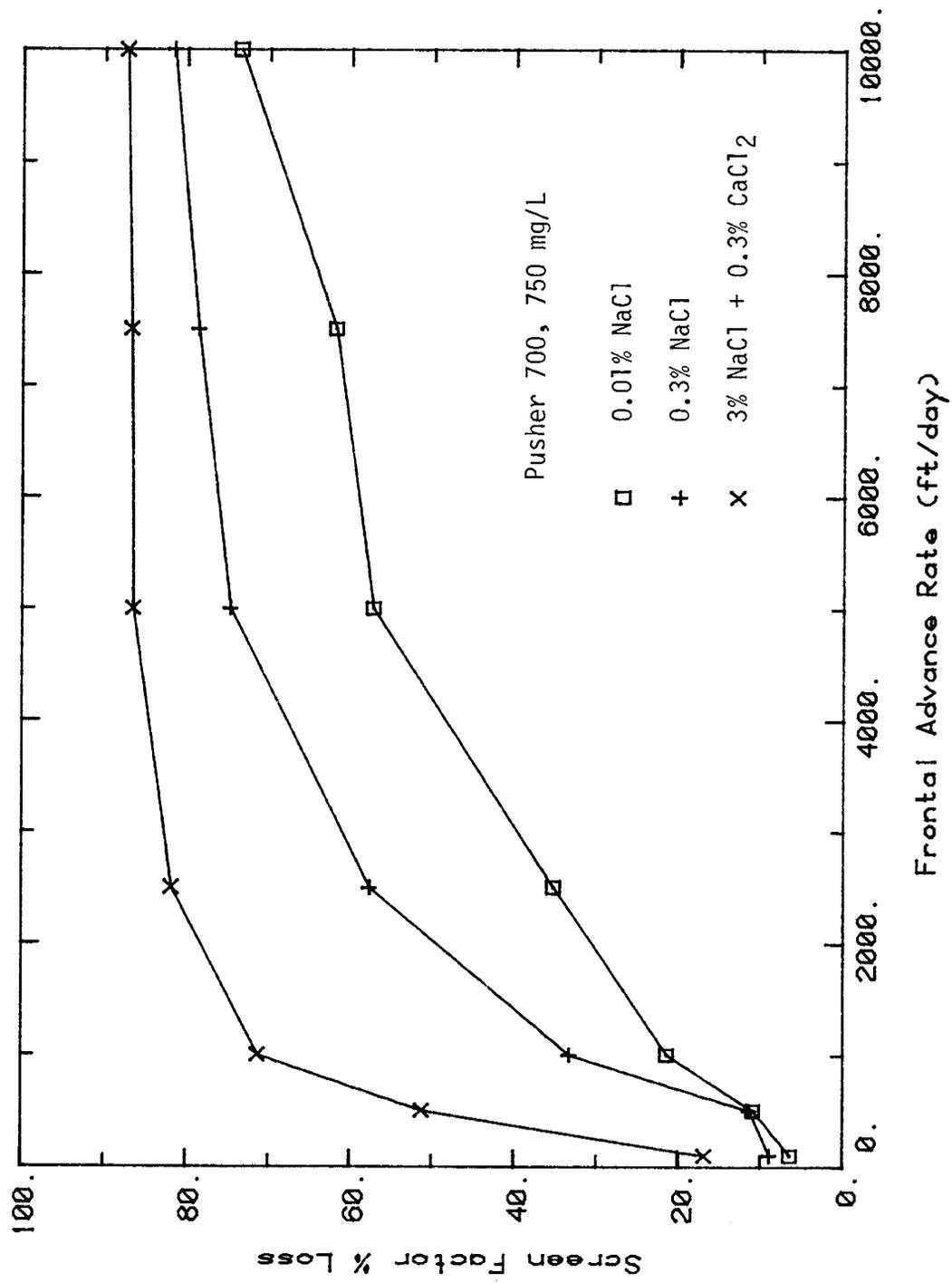
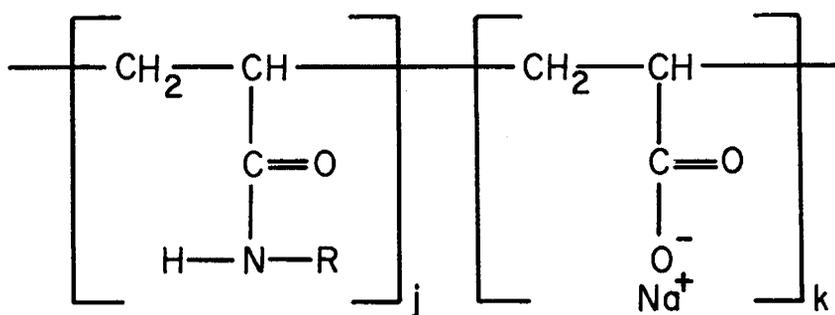
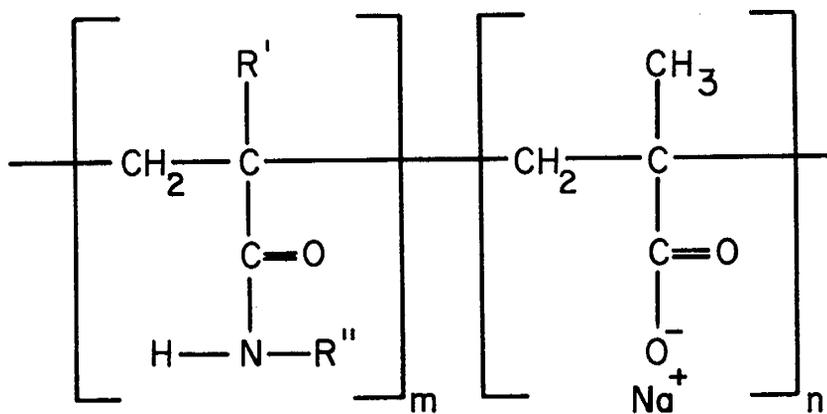


Figure 28. Effect of Salinity on Mechanical Degradation of HPAM



(I) R = H or ALKYL

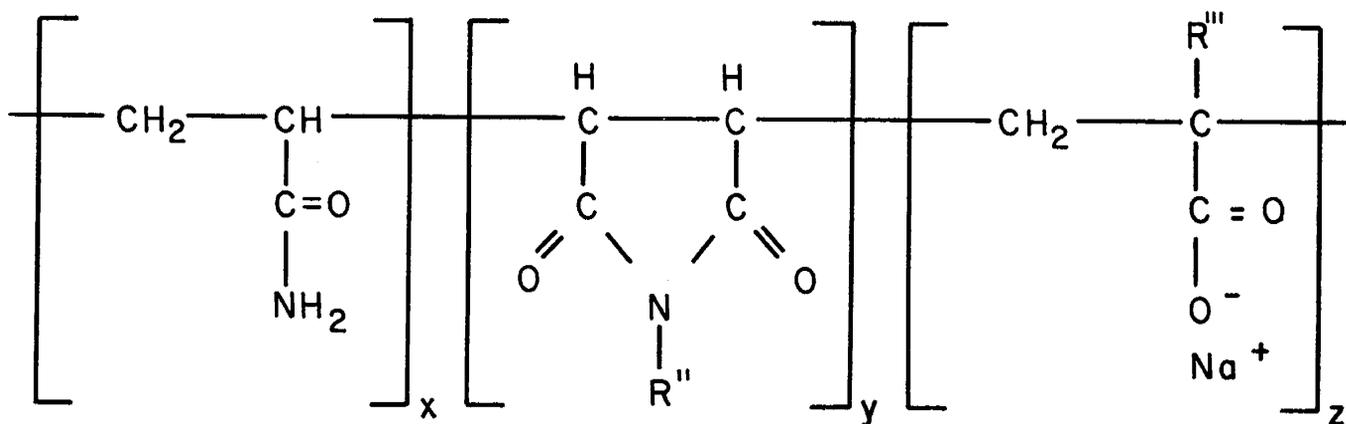


(II) R', R'' = H or CH<sub>3</sub>

FIGURE 29

STRUCTURES OF COPOLYMERS

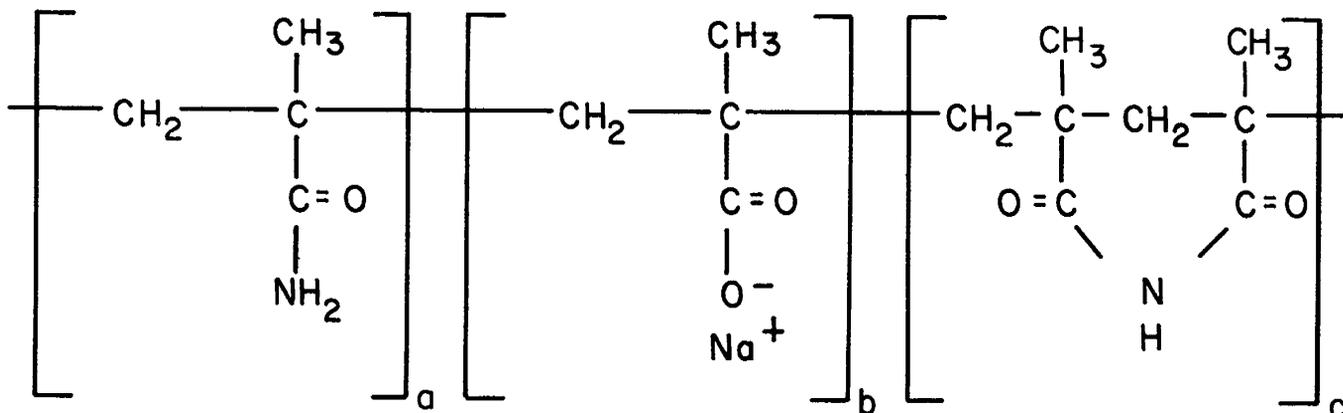
AND TERPOLYMERS SYNTHESIZED



(III) IF  $X > 0$ ,  $\text{R}'' = \text{H}$  AND  $\text{R}''' = \text{H}$

IF  $X = 0$ ,  $\text{R}'' = \text{H}$  OR  $\text{CH}_3$

AND  $\text{R}''' = \text{H}$  OR  $\text{CH}_3$



(IV)

FIGURE 29  
(CONT.)

STRUCTURES OF COPOLYMERS  
AND TERPOLYMERS SYNTHESIZED

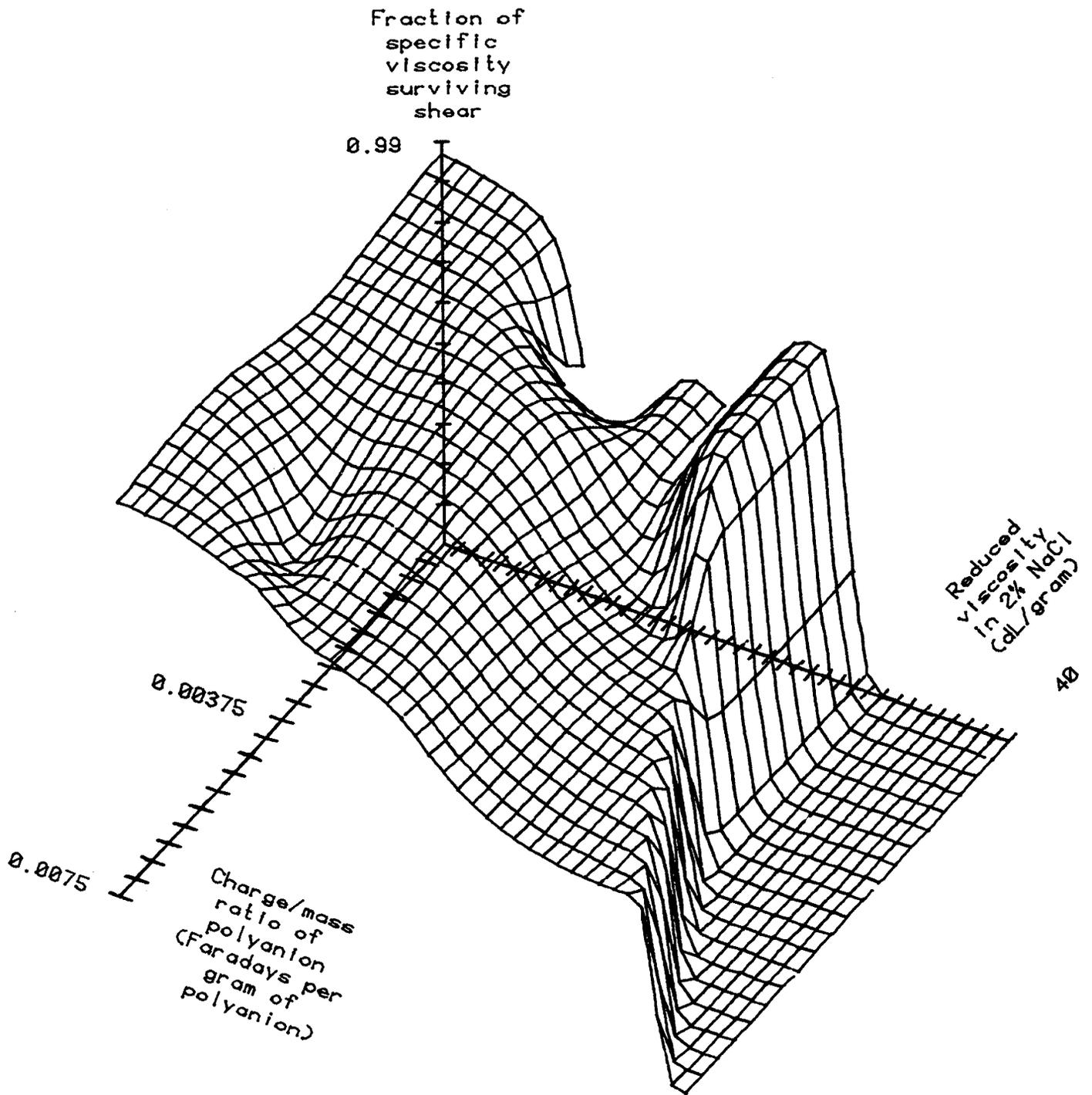


Figure 30. The effect of shear on specific kinematic viscosity of polymer solutions in 0.01% NaCl (aqueous)

Axes intersect at (0, 0, 0.45).

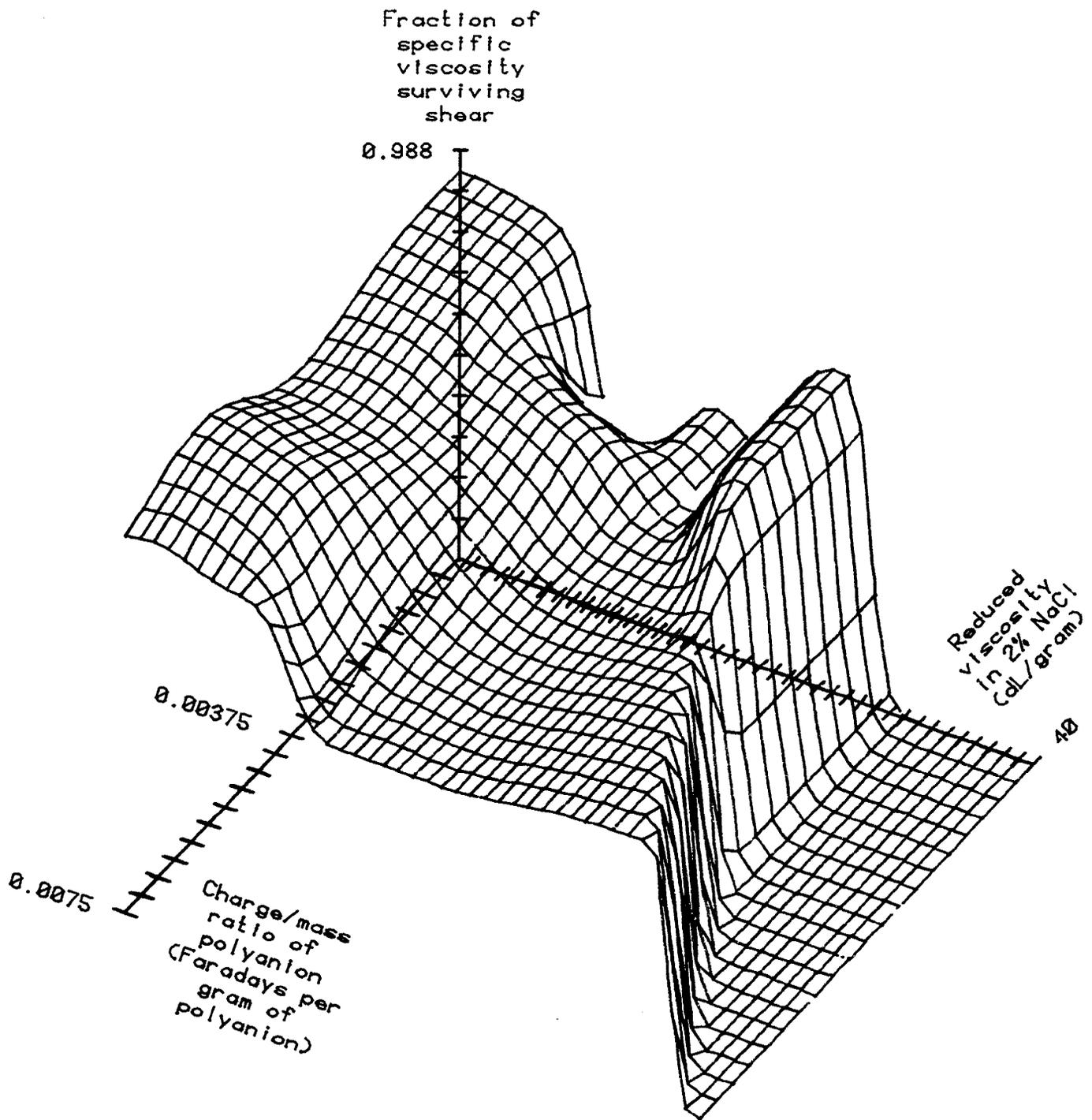


Figure 31. Effect of shear on specific kinematic viscosity of polymer solutions in 2% NaCl (aqueous)

Axes intersect at (0, 0, 0.496).

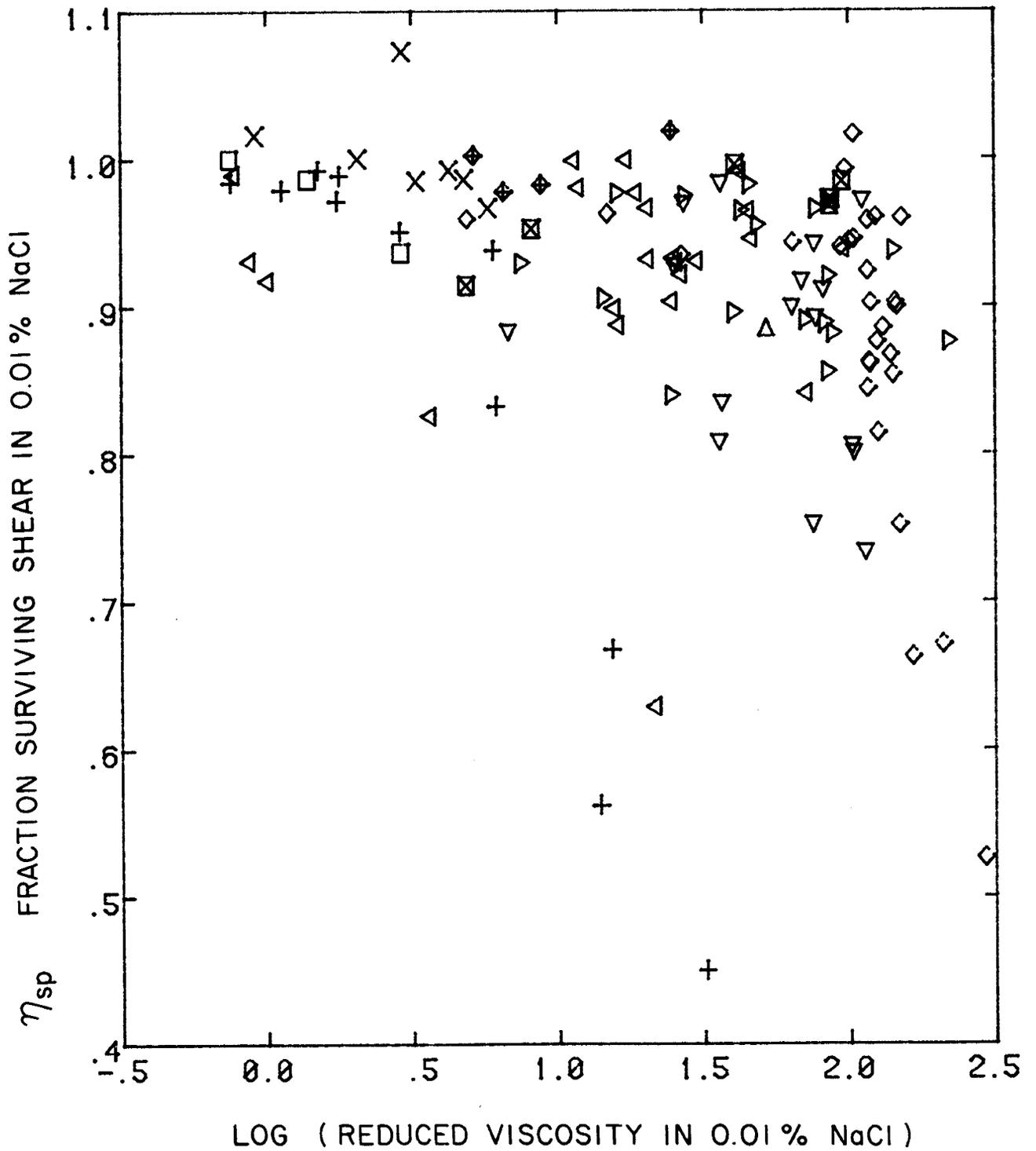


Figure 32. The effect of shear on specific kinematic viscosity of polymer solutions in 0.01% NaCl (aqueous)

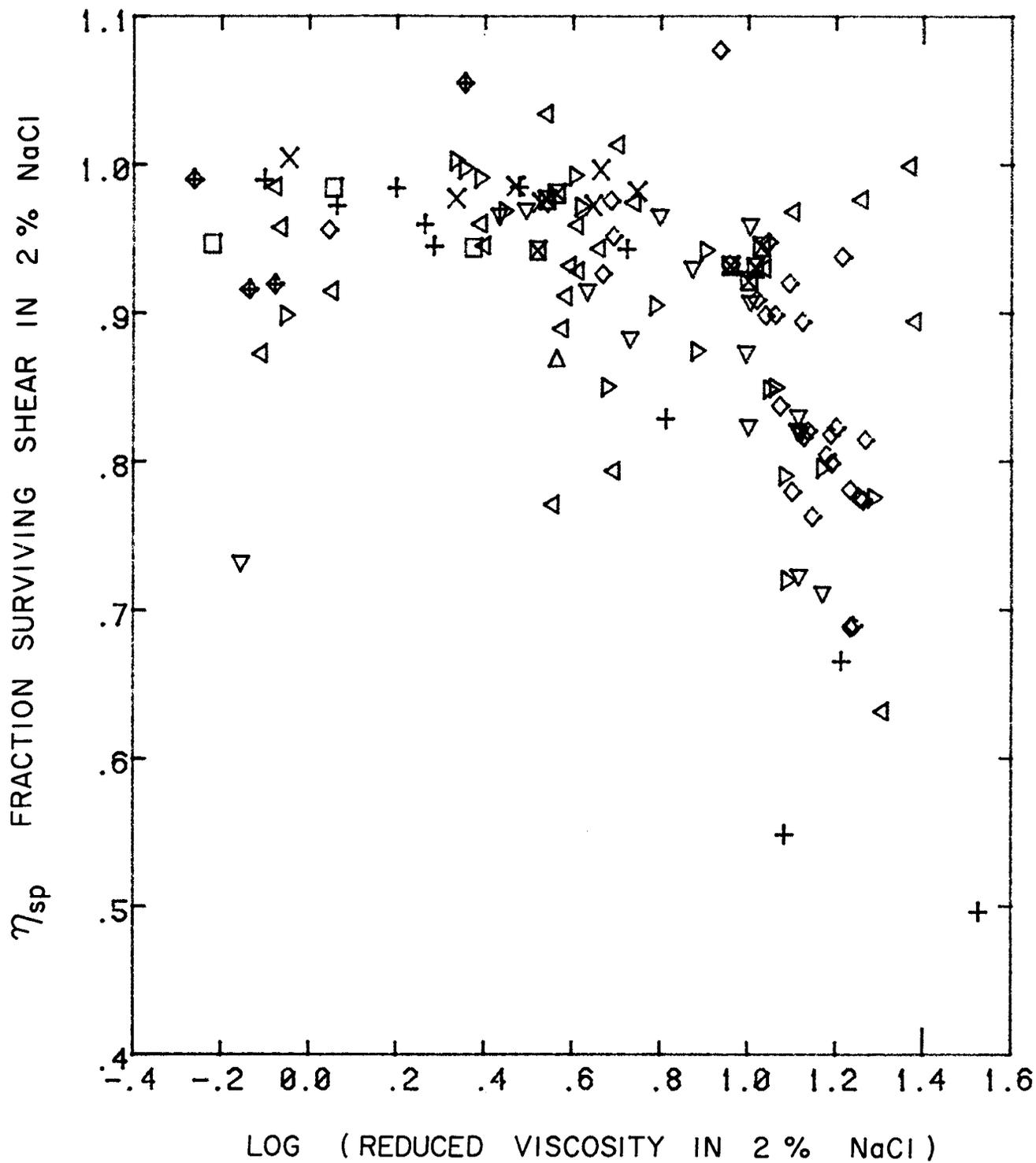


Figure 33. Effect of shear on specific kinematic viscosity of polymer solutions in 2% NaCl (aqueous)

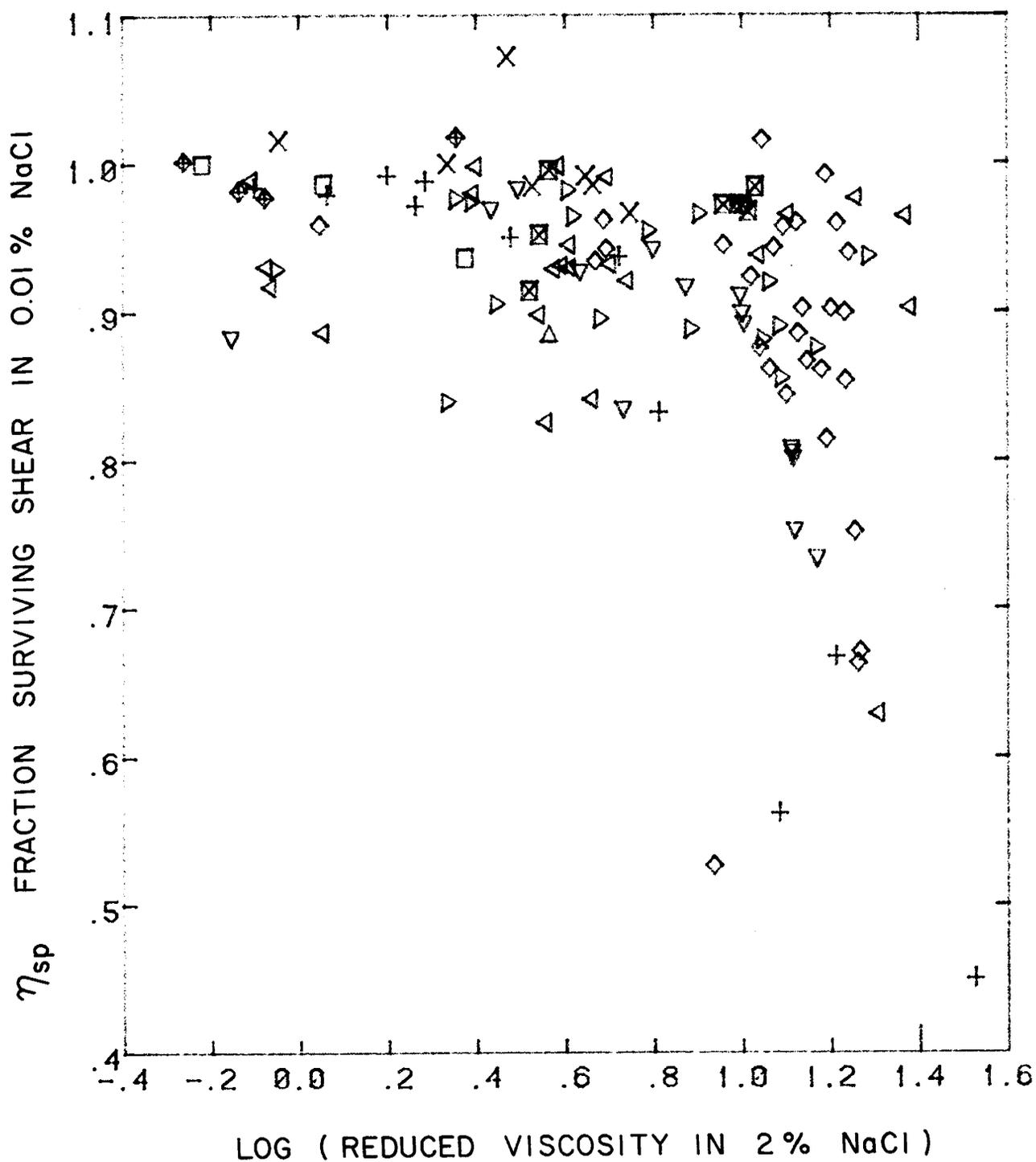


Figure 34. The effect of shear on specific kinematic viscosity of polymer solutions in 0.01% NaCl (aqueous)

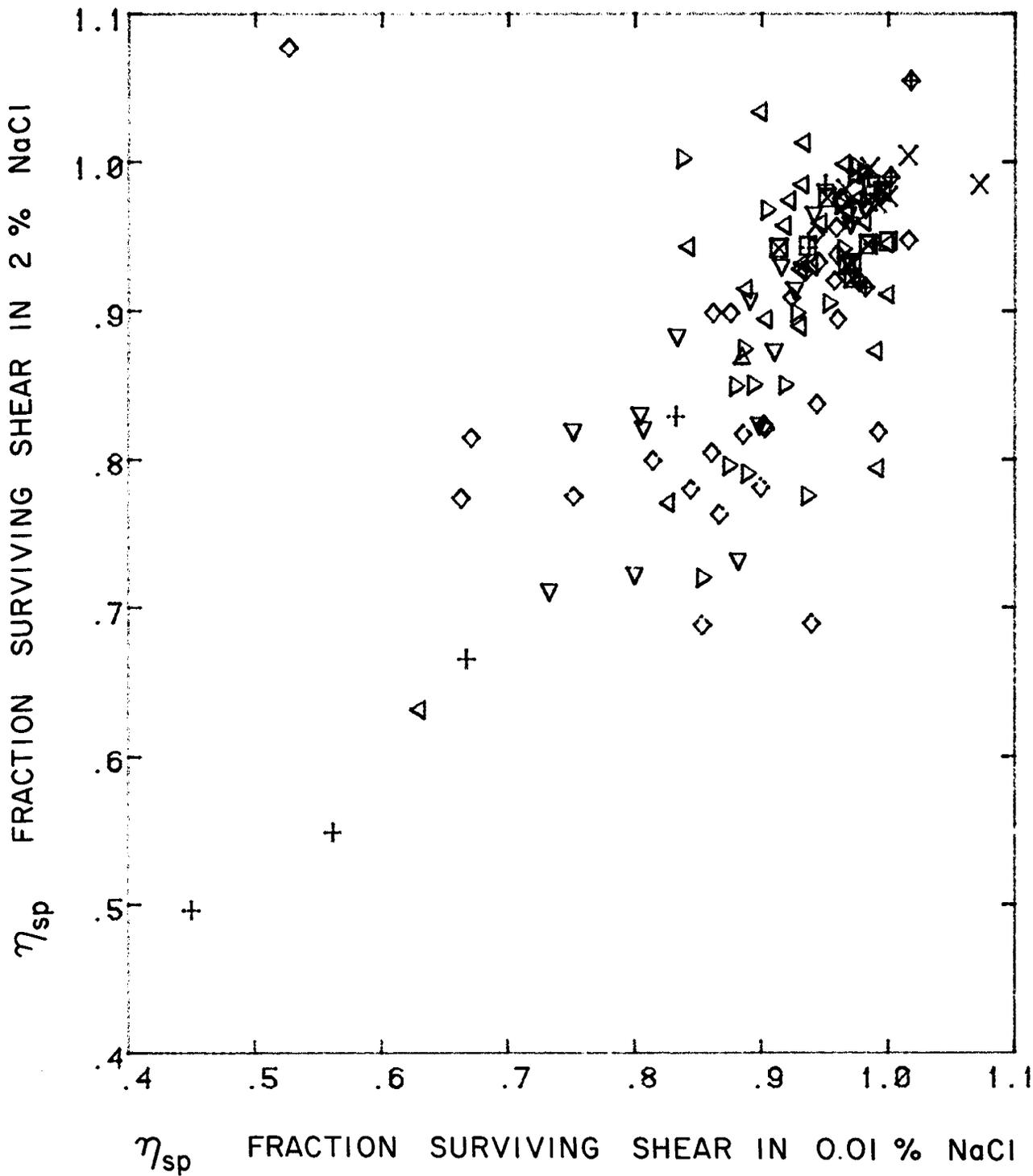


Figure 35. The effect of shear on specific kinematic viscosity of polymer solutions in 0.01% and 2% NaCl (aq)

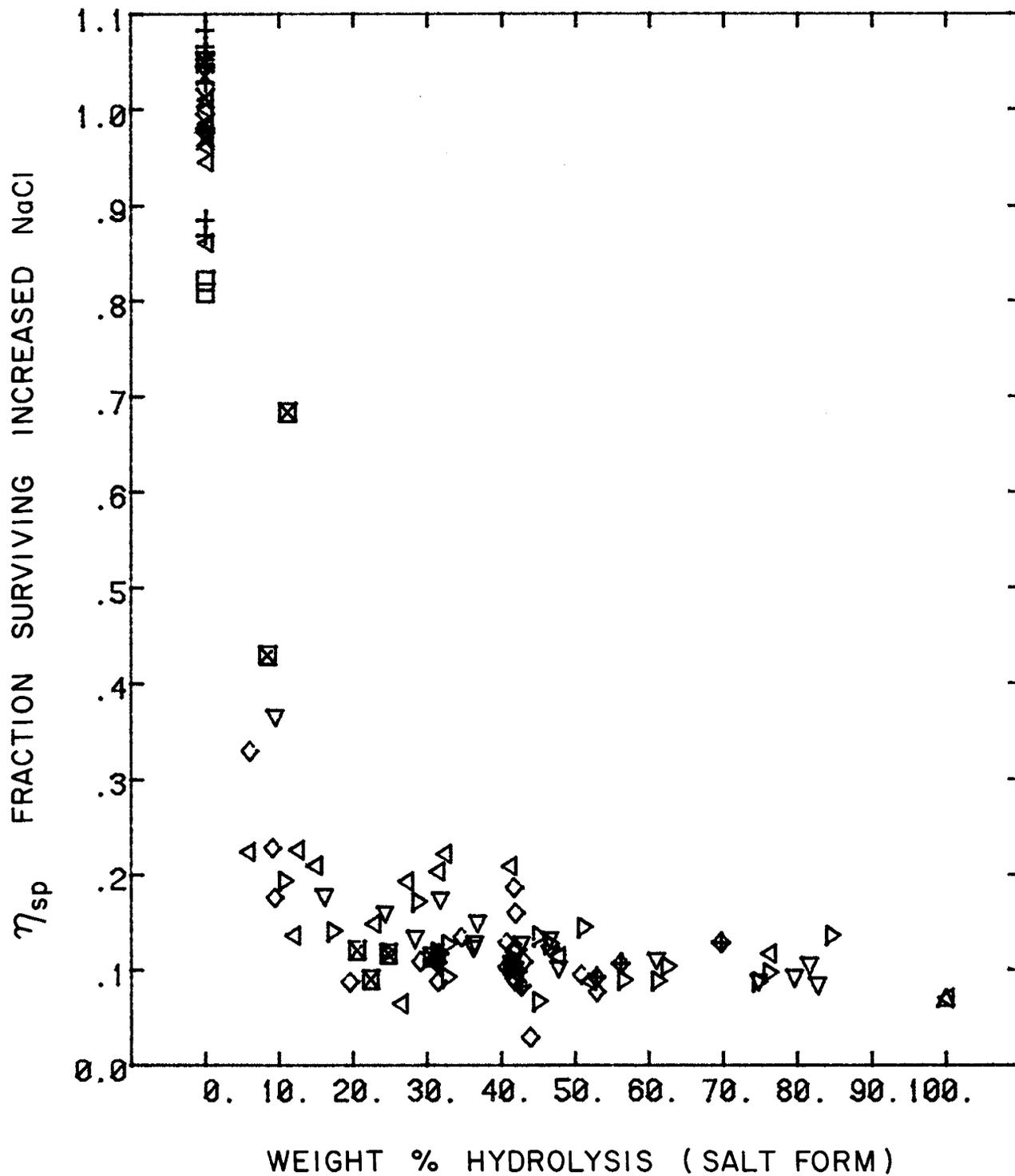


Figure 36. The effect of NaCl on specific kinematic viscosity of unsheared polymer solutions in aqueous NaCl

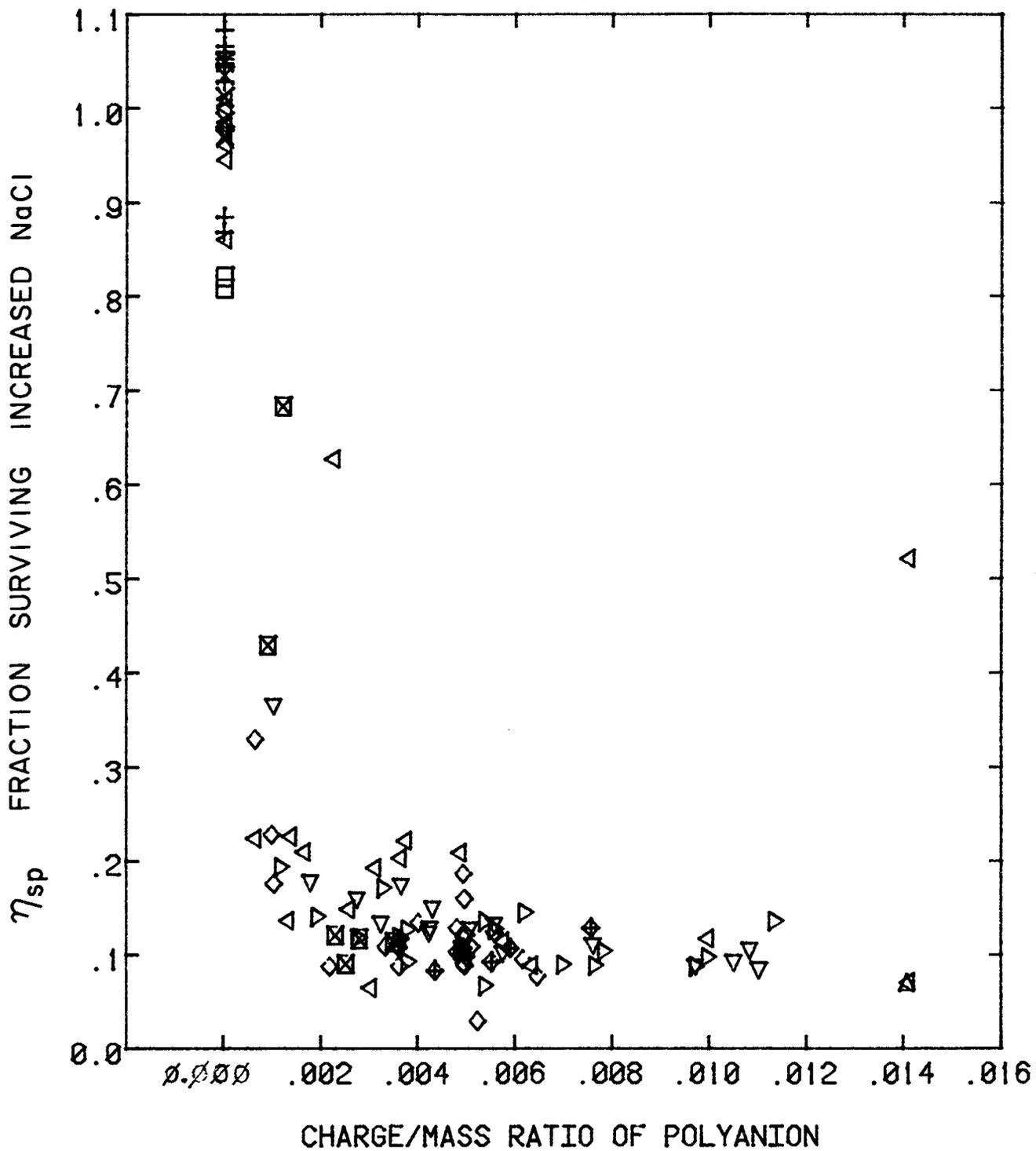


Figure 37. The effect of NaCl on specific kinematic viscosity of unsheared polymer solutions in aqueous NaCl

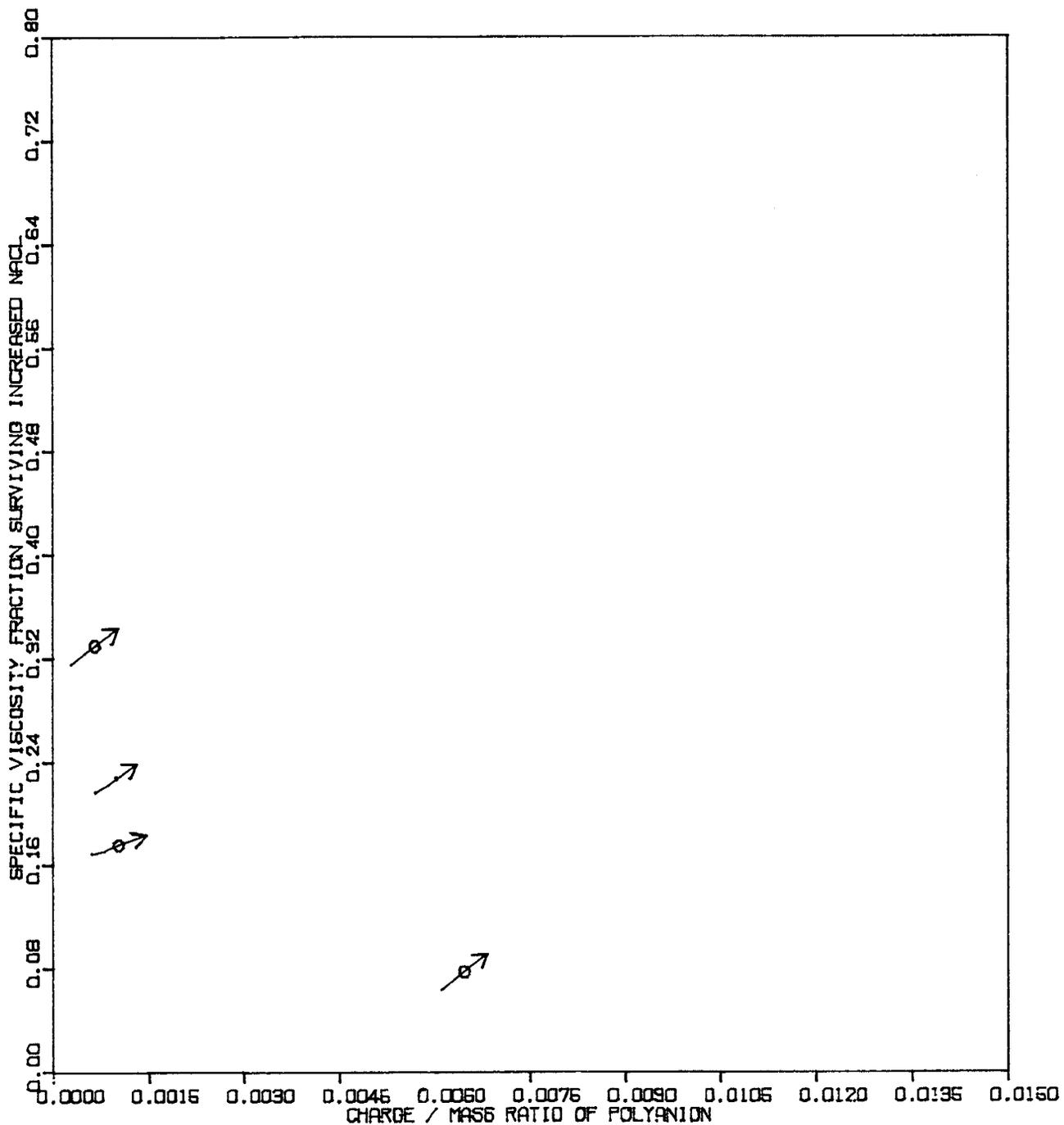


Figure 38. NaCl resistance of samples exhibiting reduced kinematic viscosity in 2% NaCl  $\leq$  8 dL/g

1 Poly(acrylamide-co-sodium acrylate)

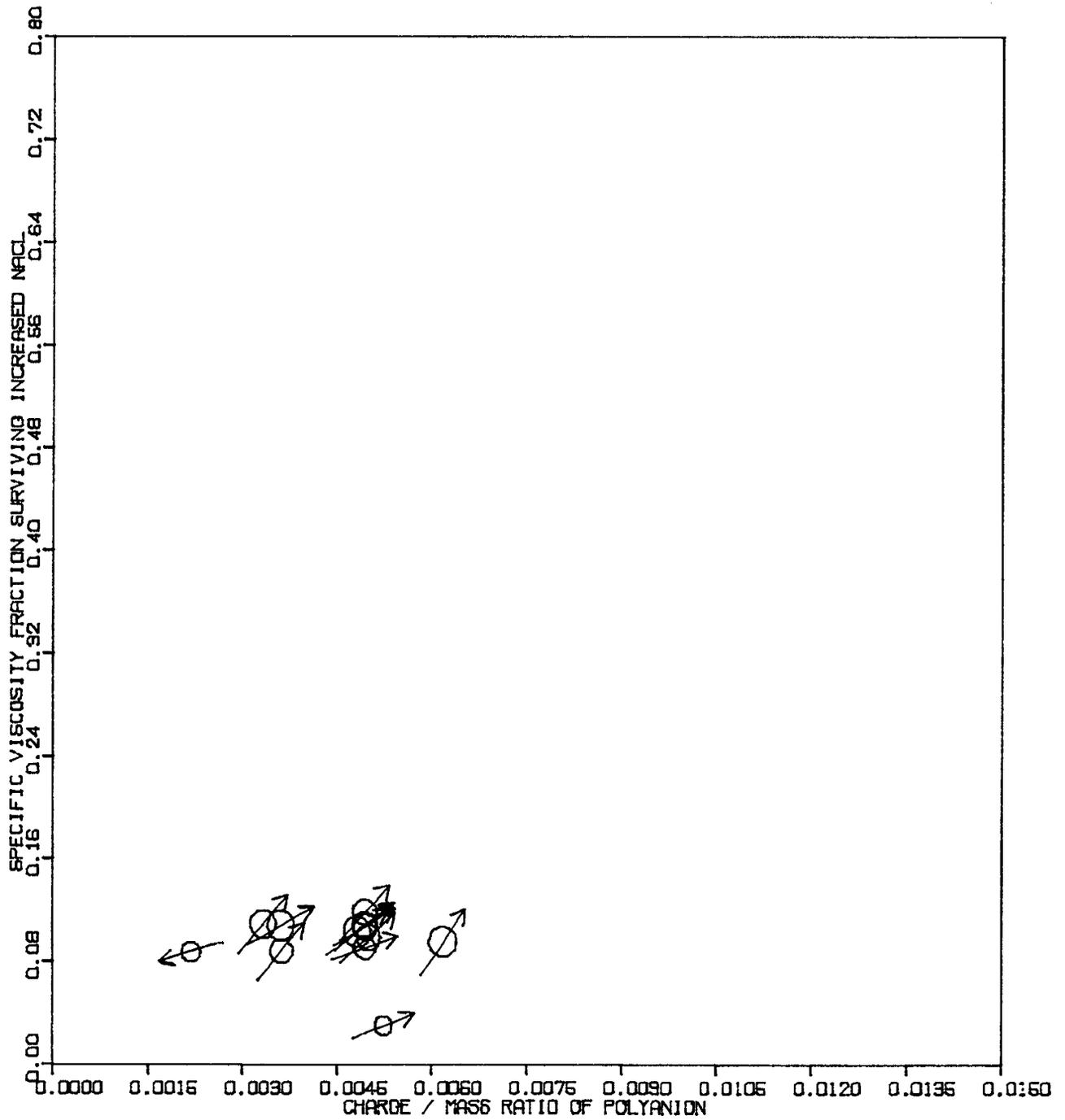


Figure 39. NaCl resistance of samples exhibiting  $8 < \text{reduced kinematic viscosity in } 2\% \text{ NaCl} \leq 14 \text{ dL/g}$

1 Poly(acrylamide-co-sodium acrylate)

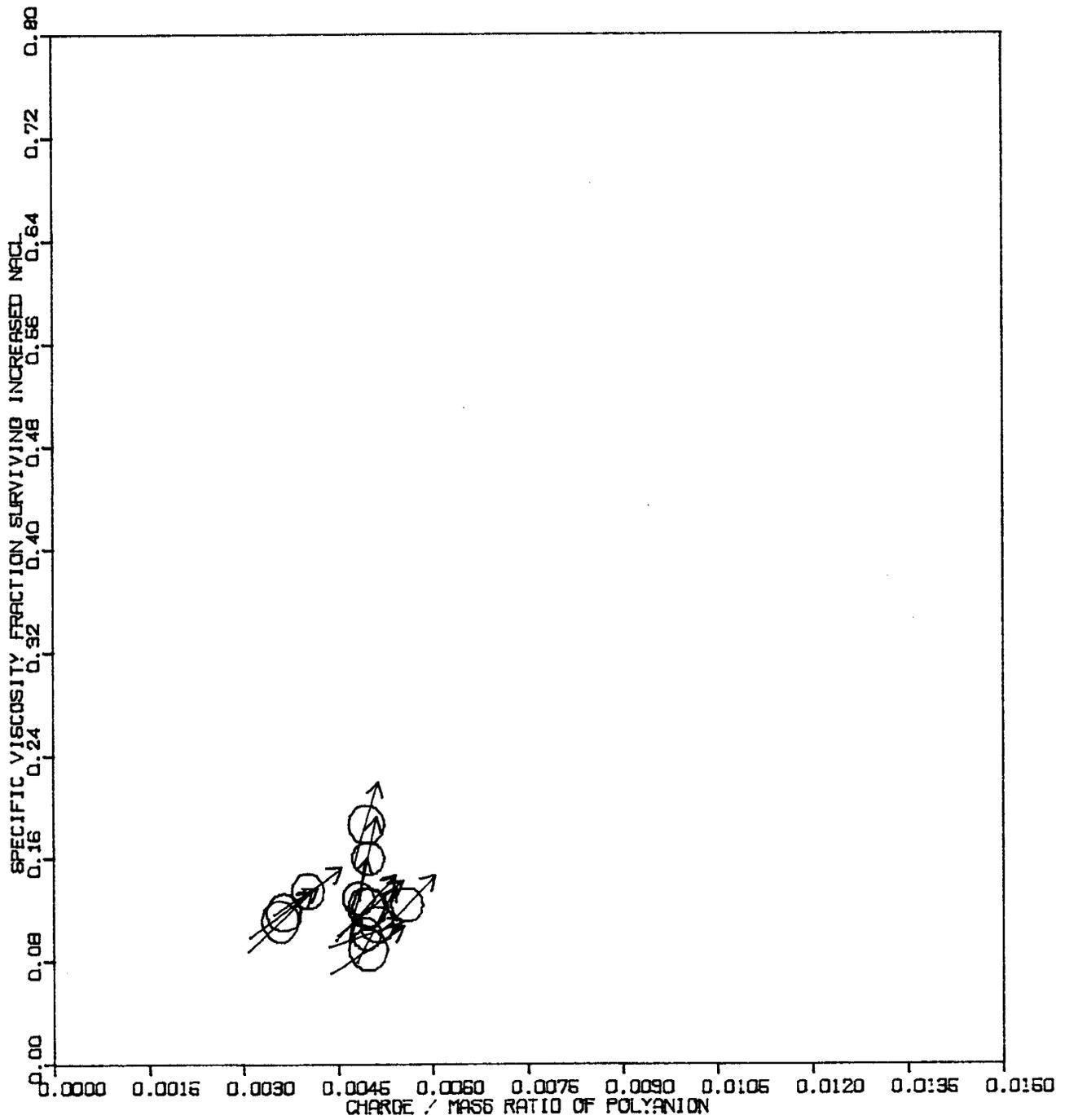


Figure 40. NaCl resistance of samples exhibiting reduced kinematic viscosity in 2% NaCl > 14 dL/g

1 Poly(acrylamide-co-sodium acrylate)

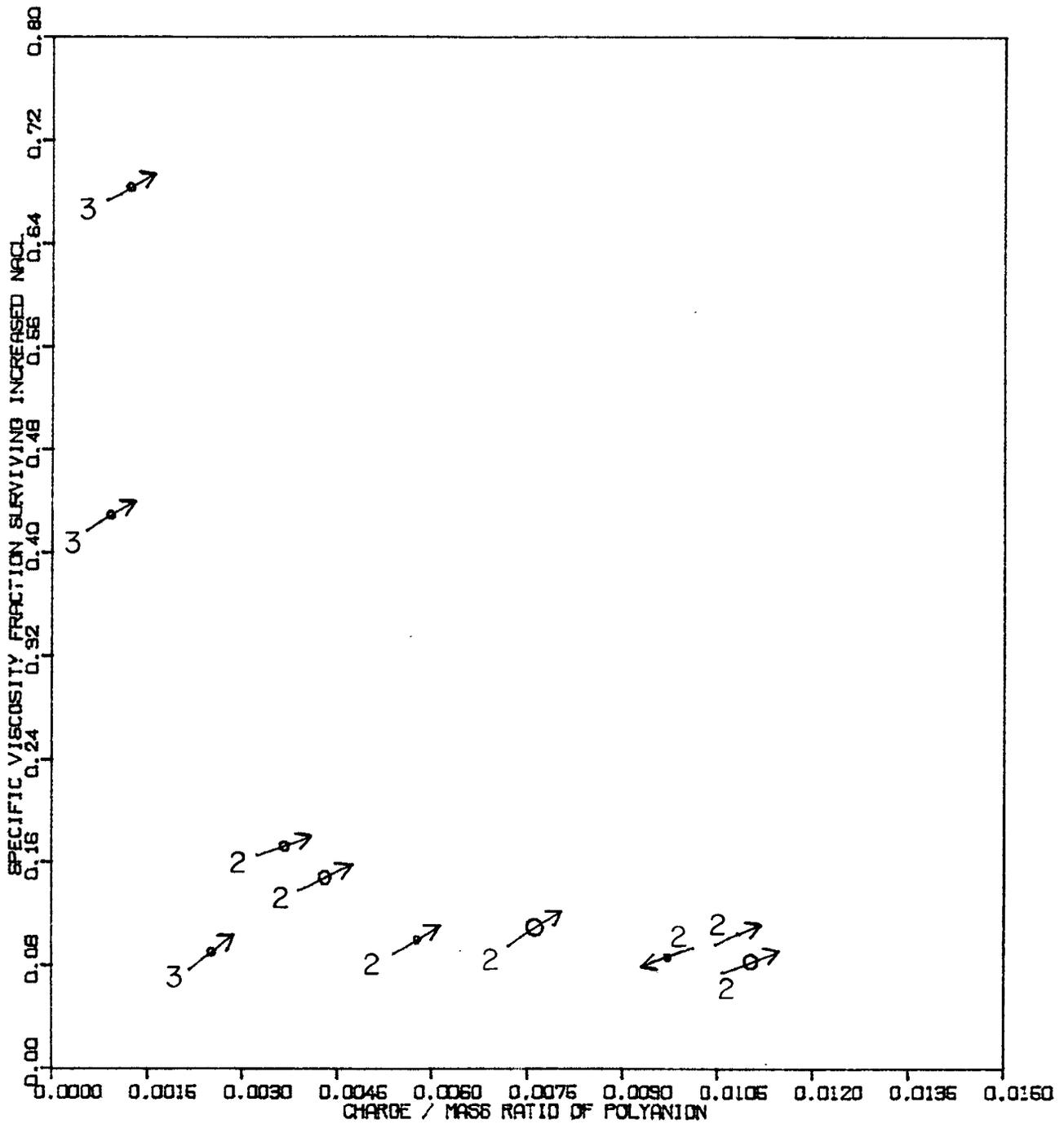


Figure 41. NaCl resistance of samples exhibiting reduced kinematic viscosity in 2% NaCl  $\leq 8$  dL/g

- 2 Poly(N-methylacrylamide-co-sodium acrylate), synthesized by copolymerization
- 3 Poly(N-methylacrylamide-co-sodium acrylate), synthesized by partial hydrolysis of homopolymer

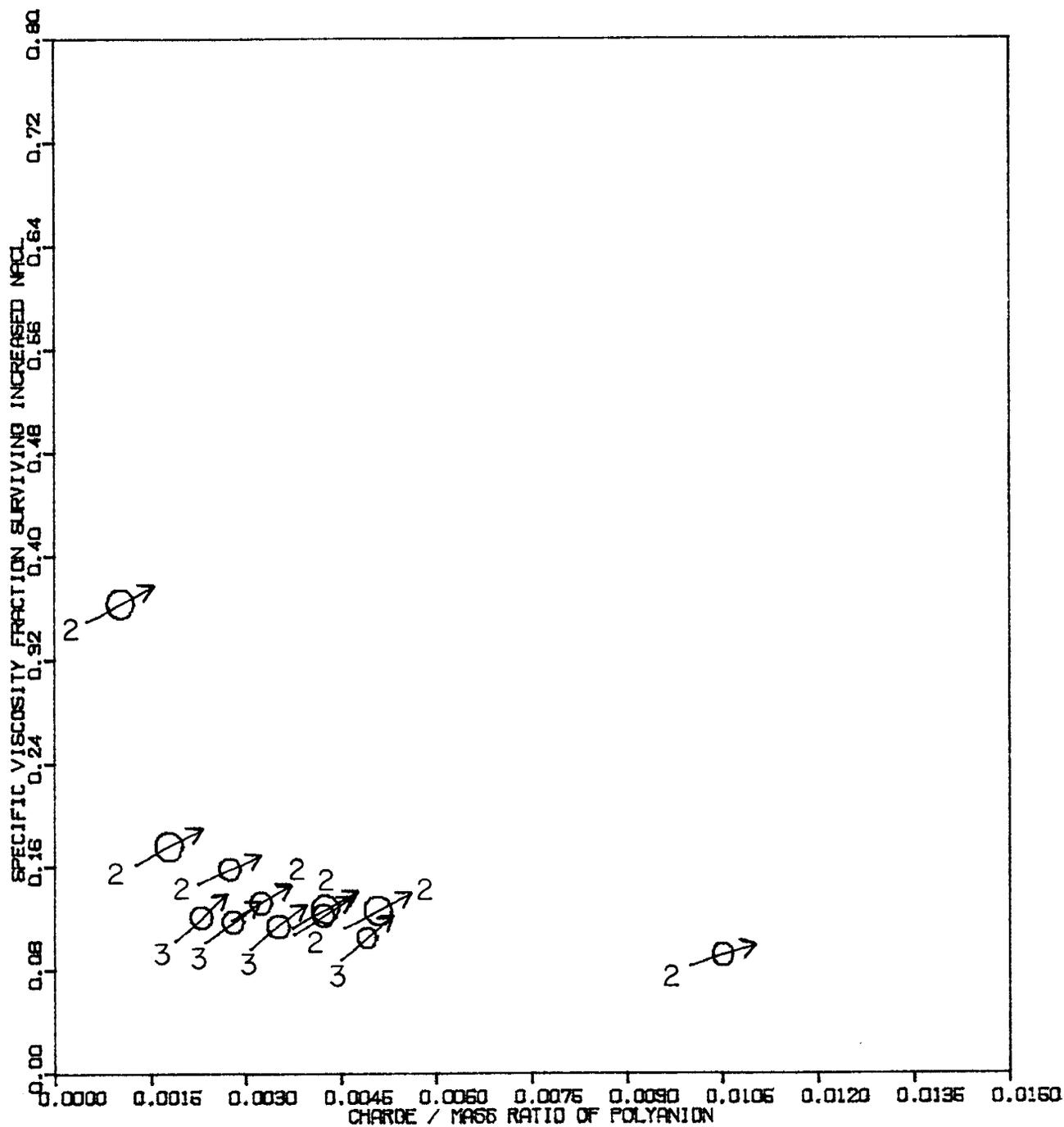


Figure 42. NaCl resistance of samples exhibiting  $8 < \text{reduced kinematic viscosity in } 2\% \text{ NaCl} \leq 14 \text{ dL/g}$

- 2 Poly(N-methylacrylamide-co-sodium acrylate), synthesized by copolymerization
- 3 Poly(N-methylacrylamide-co-sodium acrylate), synthesized by partial hydrolysis of homopolymer

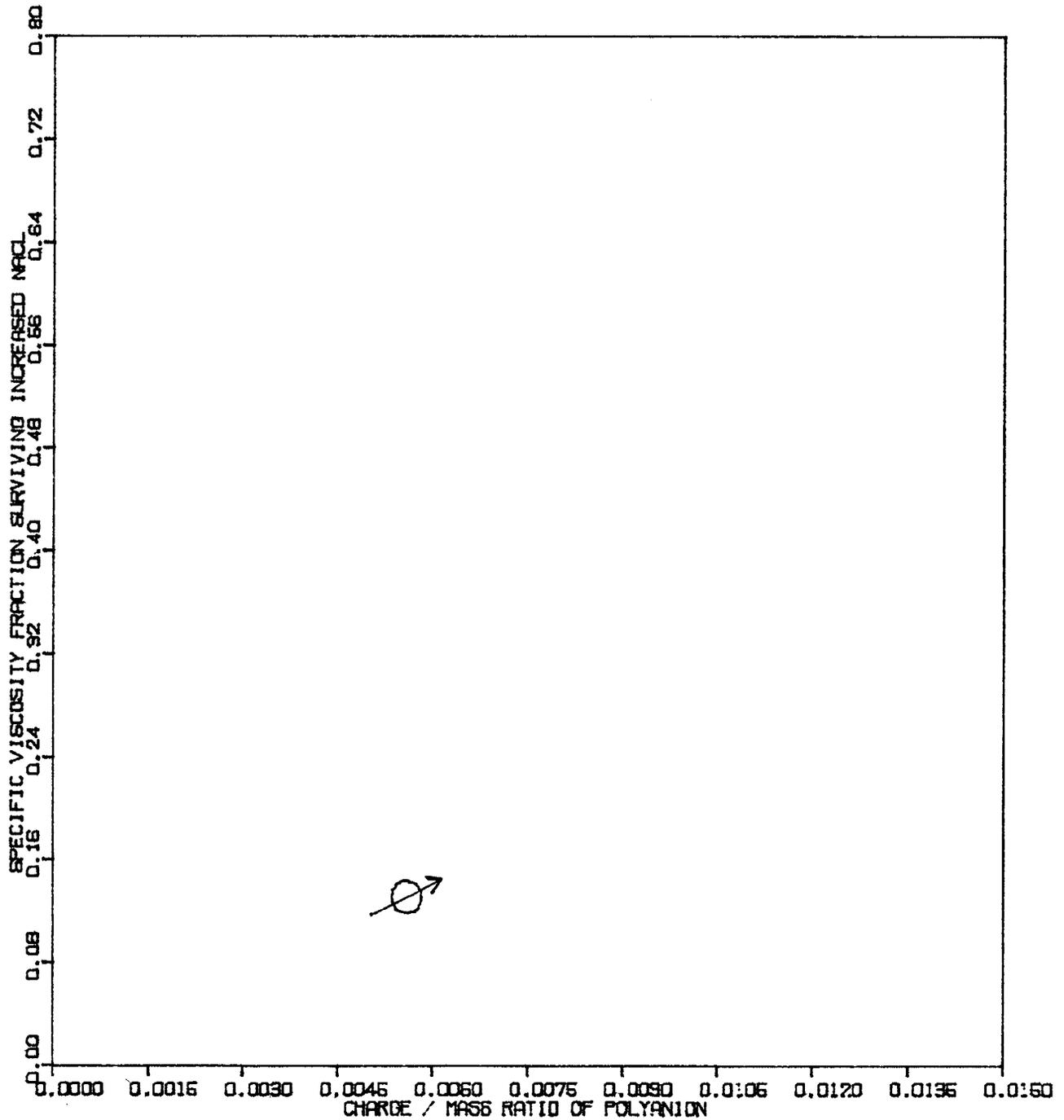


Figure 43. NaCl resistance of sample exhibiting reduced kinematic viscosity in 2% NaCl > 14 dL/g

- 2 Poly(N-methylacrylamide-co-sodium acrylate), synthesized by copolymerization

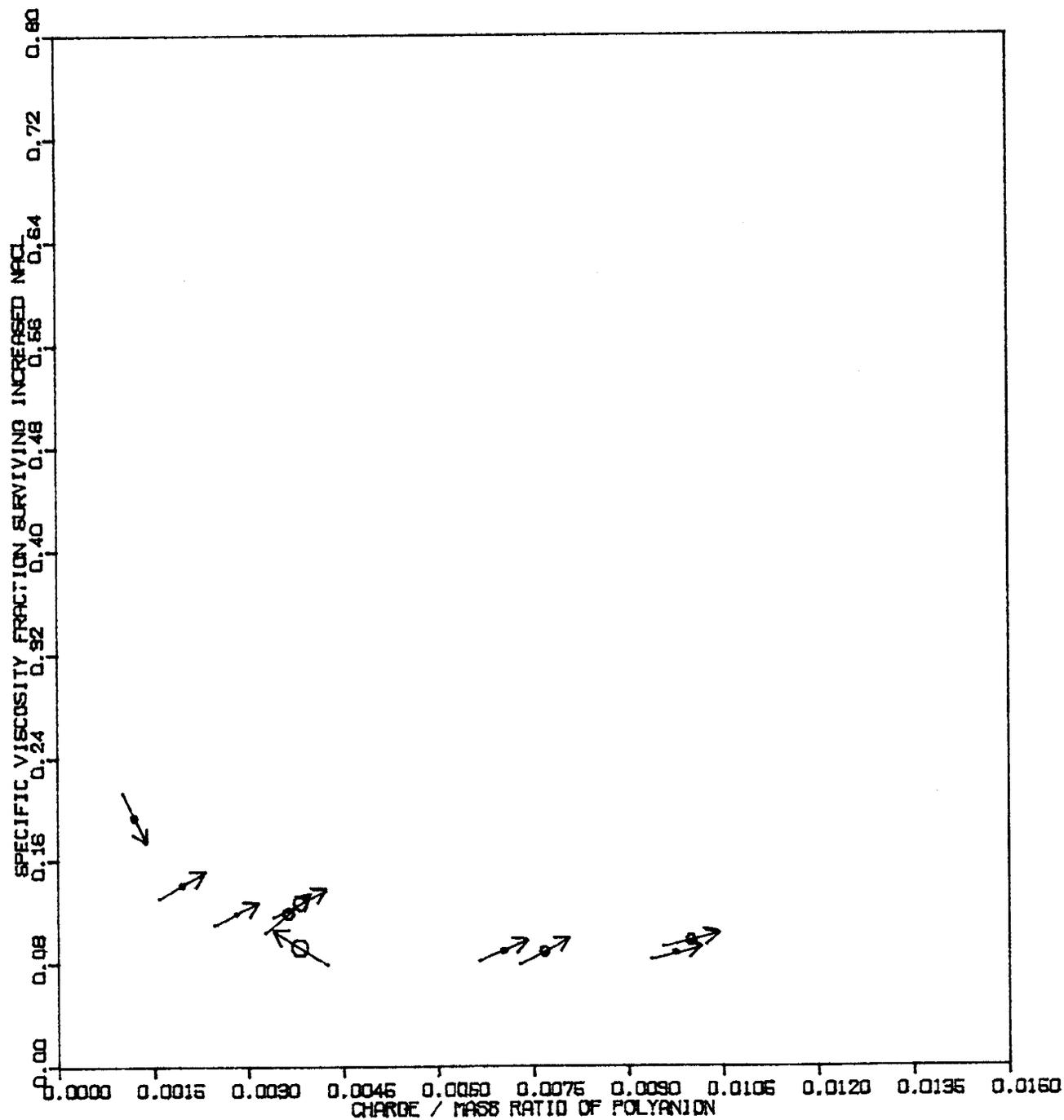


Figure 44. NaCl resistance of samples exhibiting reduced kinematic viscosity in 2% NaCl  $\leq 8$  dL/g

4 Poly(N-isopropylacrylamide-co-sodium acrylate)

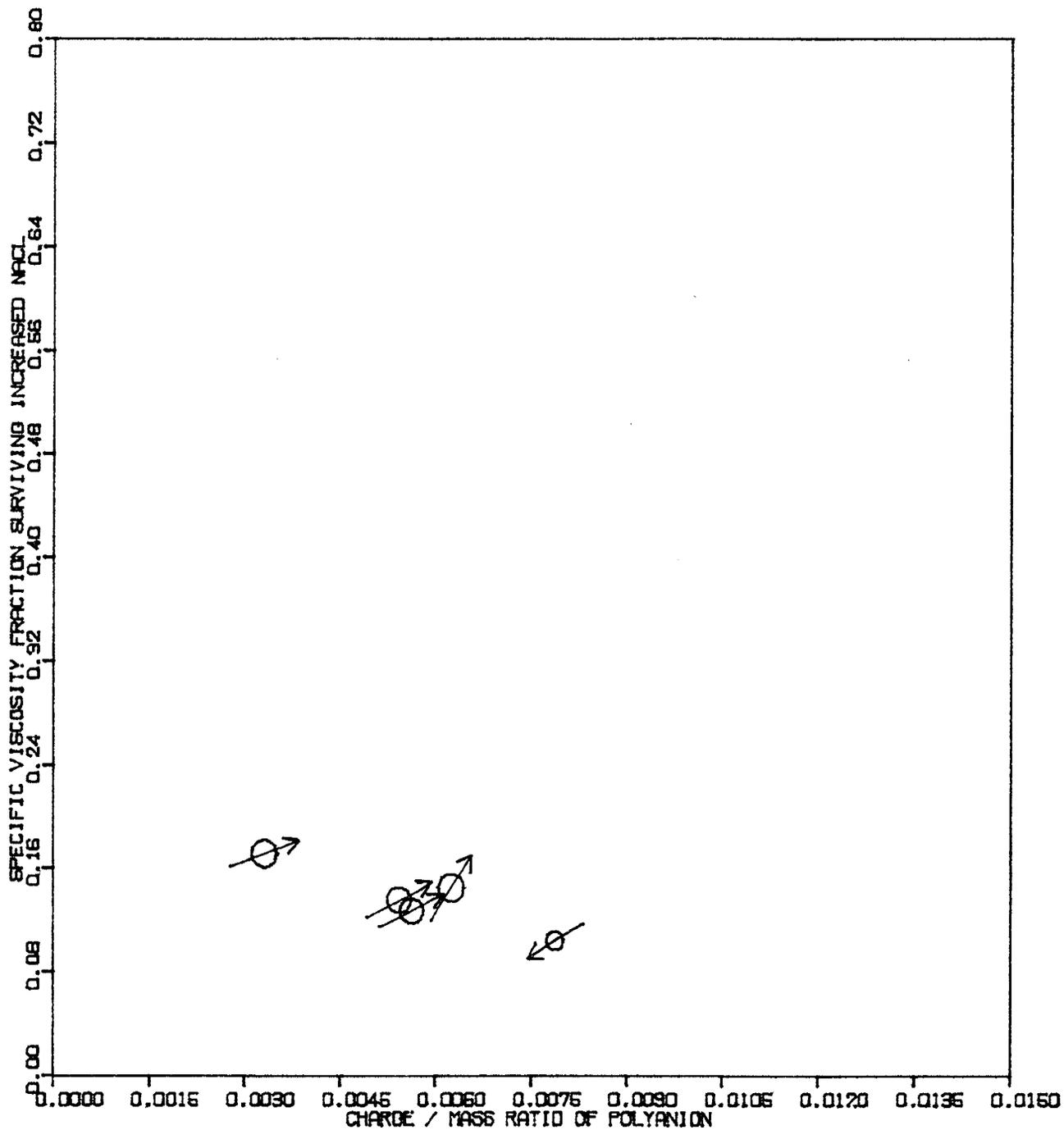


Figure 45. NaCl resistance of samples exhibiting  $8 < \text{reduced kinematic viscosity in } 2\% \text{ NaCl} \leq 14 \text{ dL/g}$

4 Poly(N-isopropylacrylamide-co-sodium acrylate)

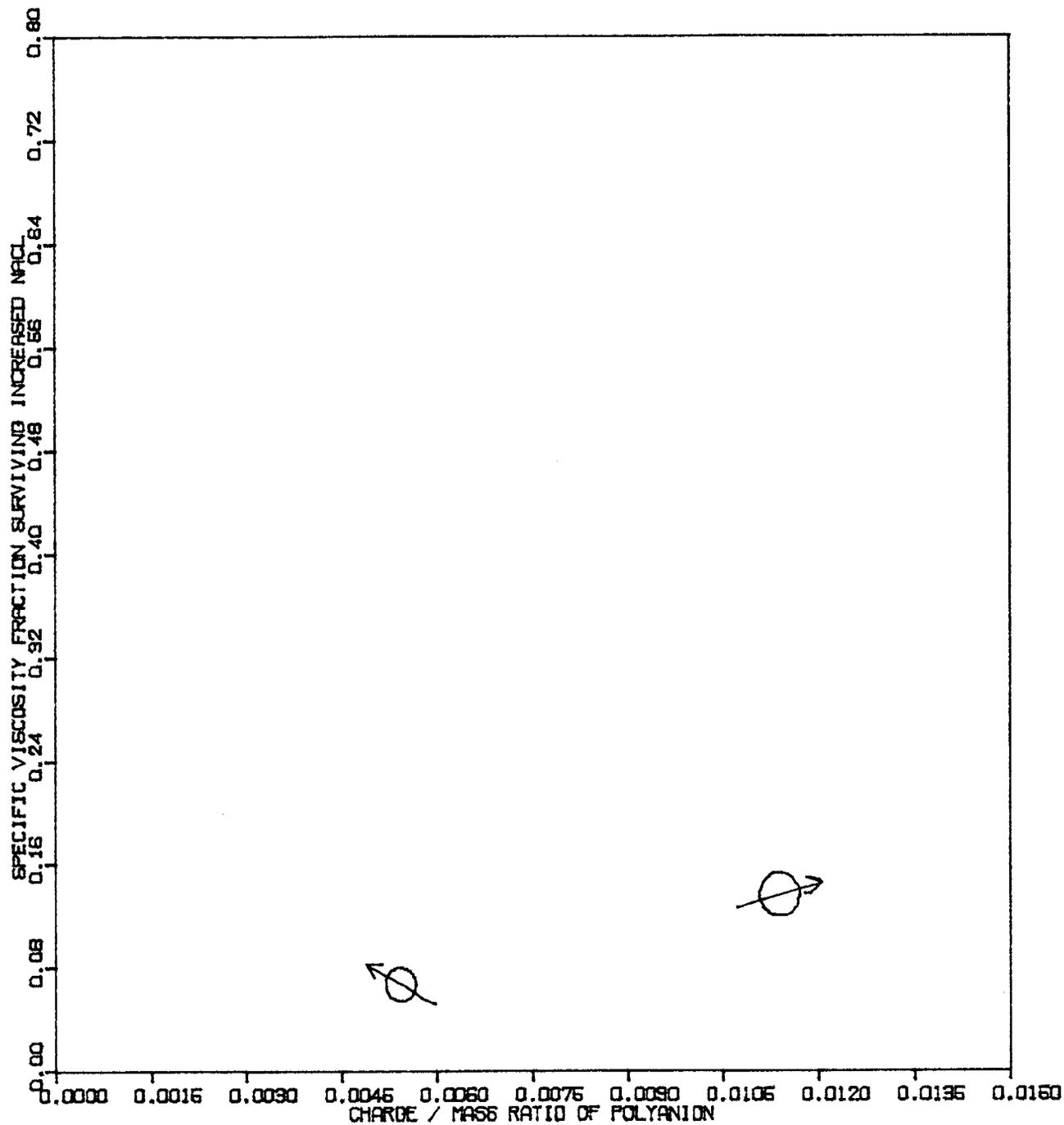


Figure 46. NaCl resistance of samples exhibiting reduced kinematic viscosity in 2% NaCl > 14 dL/g

4 Poly(N-isopropylacrylamide-co-sodium acrylate)

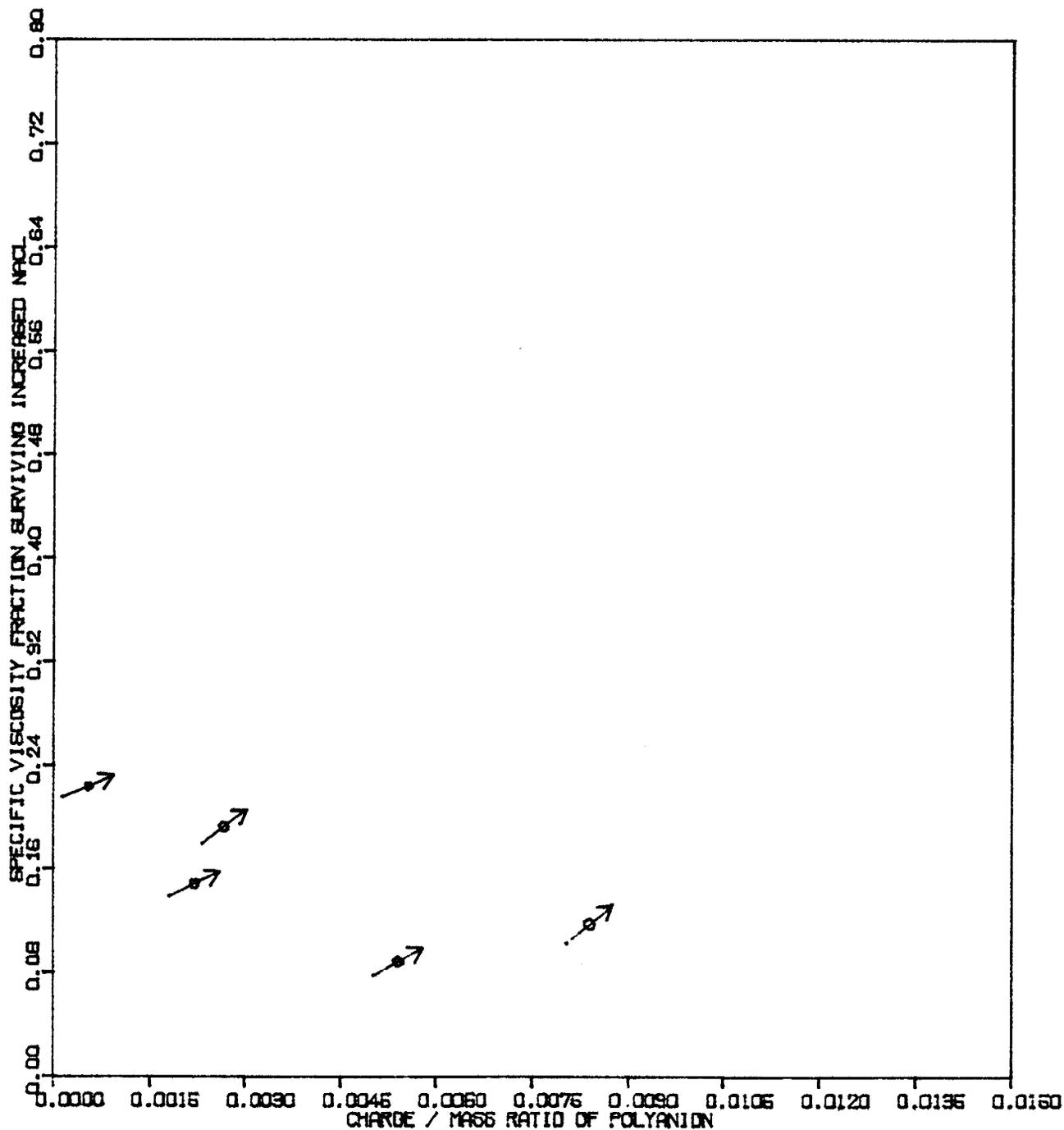


Figure 47. NaCl resistance of samples exhibiting reduced kinematic viscosity in 2% NaCl  $\leq$  8 dL/g

5 Poly(methacrylamide-co-sodium methacrylate)

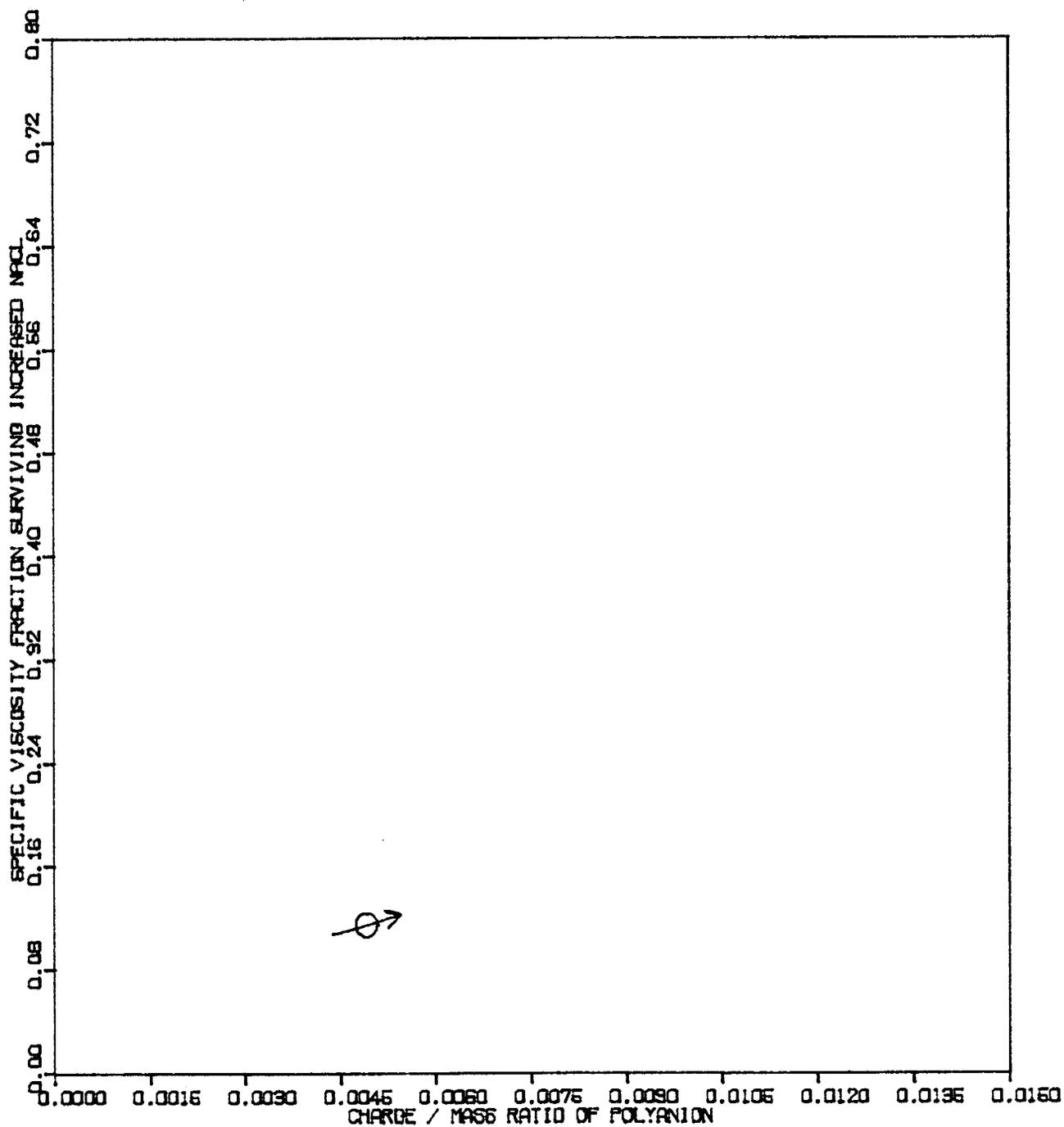


Figure 48. NaCl resistance of sample exhibiting  $8 < \text{reduced kinematic viscosity in } 2\% \text{ NaCl} \leq 14 \text{ dL/g}$

5 Poly(methacrylamide-co-sodium methacrylate)

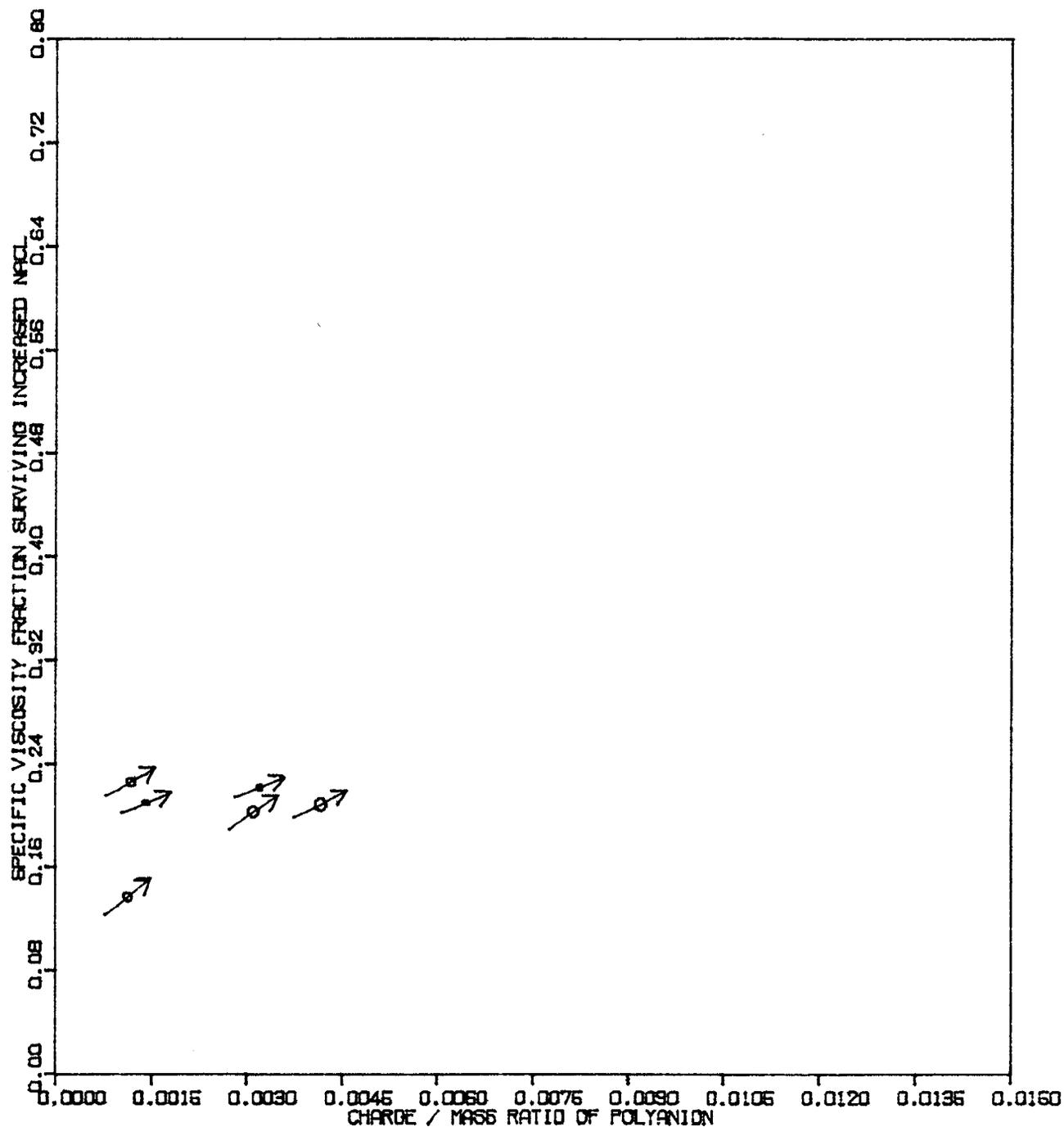


Figure 49. NaCl resistance of samples exhibiting reduced kinematic viscosity in 2% NaCl  $\leq 8$  dL/g

31 Poly(N-methylmethacrylamide-co-Na methacrylate)

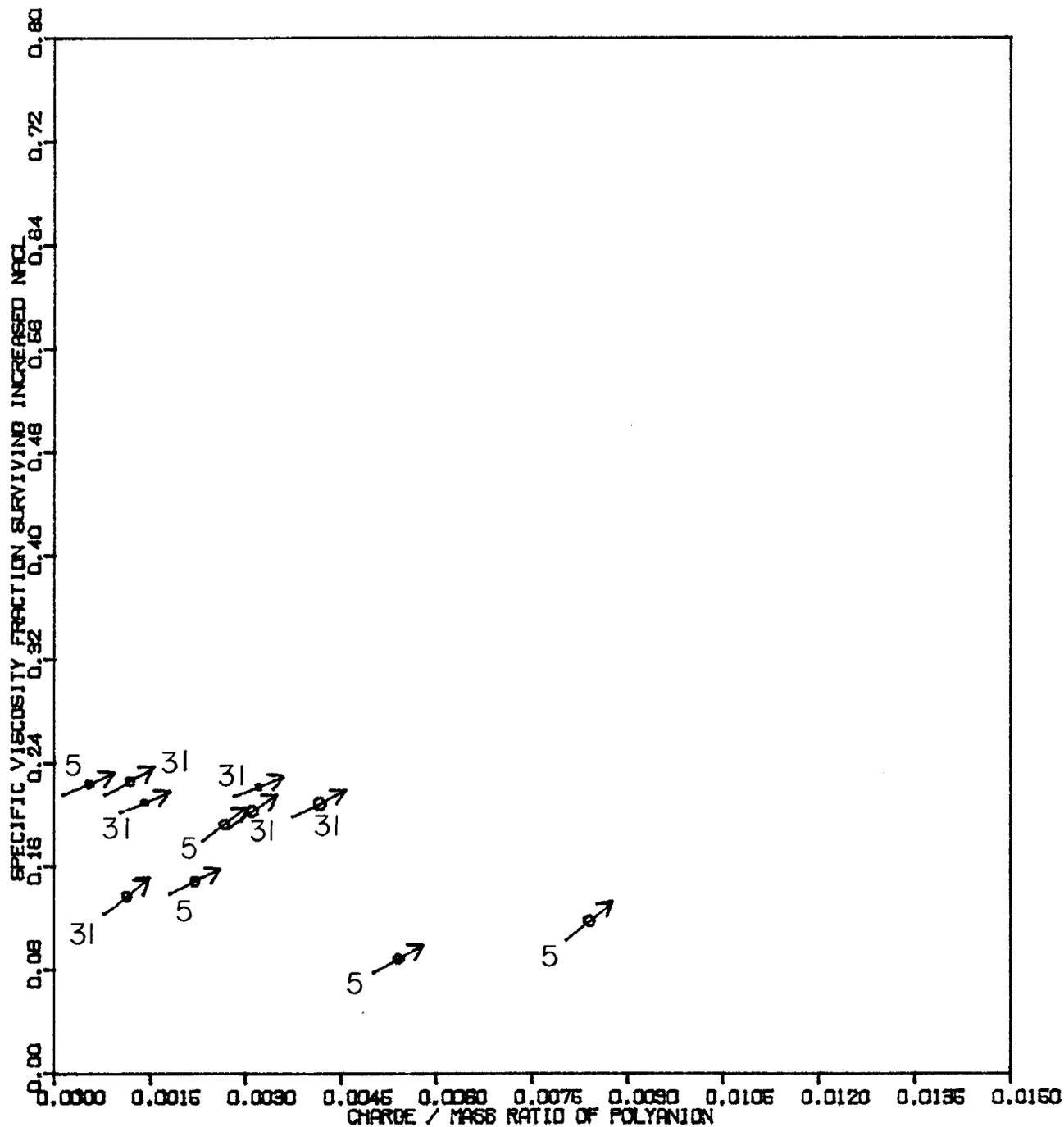


Figure 50. NaCl resistance of samples exhibiting reduced kinematic viscosity in 2% NaCl  $\leq$  8 dL/g

- 5 Poly(methacrylamide-co-sodium methacrylate)
- 31 Poly(N-methylmethacrylamide-co-sodium methacrylate)

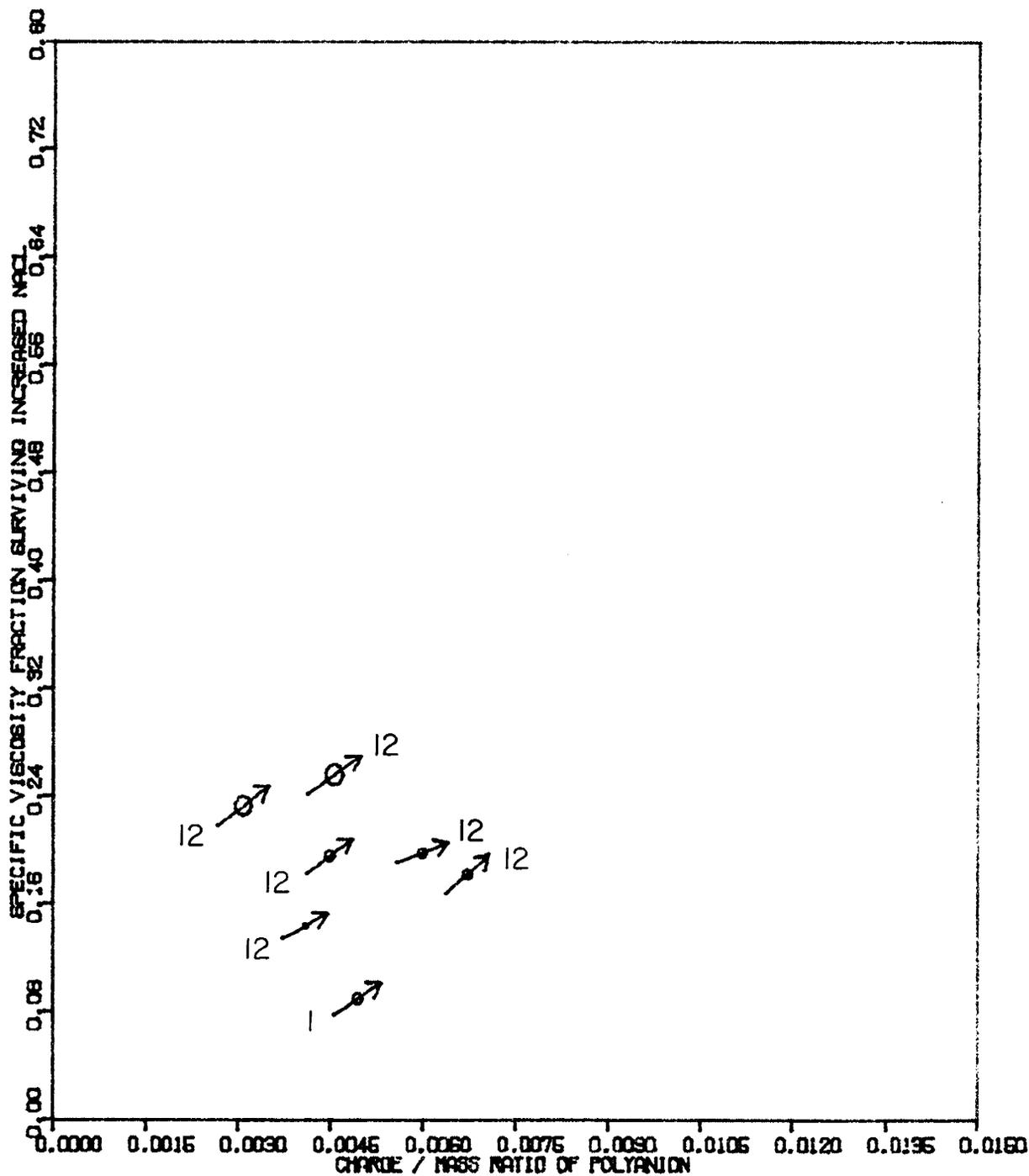


Figure 51. Effect of NaCl on specific kinematic viscosity of unsheared polymer solutions in 1.6% ethylene glycol (aqueous)

- 1 Poly(acrylamide-co-sodium acrylate)
- 12 Poly(methacrylamide-co-sodium methacrylate), imide

## X. APPENDICES

### A. APPENDIX A

#### DETERMINATION OF WEAK ACID RESIDUES IN WATER-SOLUBLE ACRYLAMIDE- ACRYLIC ACID TYPE COPOLYMERS<sup>20</sup>

Potentiometric titrations of weak polyacids pose a problem not encountered in titrations of monoprotic acids: The  $pK_a$  values of the weak acid residues being neutralized change during the course of the titration. It is not even reliable to use the maximum slope of the pH vs volume of titrant plot to indicate the equivalence point.

In some cases, it is convenient to begin with a partially-neutralized polymer. The addition of excess strong acid assures that all of the polymer is in the free acid form. However, another problem is created-- the beginning equivalence point must now be found in addition to the end equivalence point. Although methacrylic acid residues exhibit a sufficiently pronounced relative maximum slope in a pH vs volume of titrant plot to locate this beginning point, acrylic acid residues do not.

An iterative method has been derived for accurate determination of the amount of weak acid present in a polymeric sample. First, the data are smoothed by calculating a cubic spline.<sup>22</sup> Then, the two equivalence points are estimated. The beginning point is estimated by the following approximation. This approximation would be theoretically valid in a limiting case for a weak monoprotic acid that exhibits only a small degree of ionization  $\alpha$  when  $[H^+] = [A^-]$ .

$$\lim_{\alpha \rightarrow 0} \left[ \frac{\partial (\text{strong base consumed by } HA + OH^- \rightarrow H_2O + A^-)}{\partial (\text{total amount of strong base added})} \right] =$$

$$\lim_{\alpha \rightarrow 0} \left[ \frac{\alpha - \alpha^2}{2\alpha - \alpha^2} \right] = \frac{1}{2}$$

The relation  $[H^+] = [A^-]$  defines the beginning equivalence point for a monoprotic weak acid that is still a much stronger acid than water. For an acid of such strength, the ions produced by the ionization  $H_2O \rightleftharpoons H^+ + OH^-$  can be neglected compared to those produced by  $HA \rightleftharpoons H^+ + A^-$ . The partial derivative is estimated by

$$1 + \frac{\Delta ((\text{total volume of solution being titrated, ml}) \times 10^{-pH})}{\Delta (\text{milliequivalents of strong base added})}$$

Initially, the end point is estimated by the common method of using relative maximum slope of the pH vs volume of titrant data. Points near mid-titration are used to estimate  $pK_a$  values. Linear extrapolation of the  $pK_a$  vs percent neutralization data is used to estimate  $pK_a$  values at the starting and end points. These  $pK_a$  values are used to estimate what the pH would be at the beginning and end points. Revised beginning and end points then are located to correspond with these pH values. Successive iterations use increasingly larger portions of the data for linear extrapolation, until the final

iteration uses all of the smoothed data from 0% to 90% neutralization. This method was tested by titration of poly(acrylic acid), "MW 250,000," Catalog #3312, Lot #683-066, from Polysciences, Inc. It is assumed that this compound contains 100.0% acrylic acid residues if the weight used is corrected for sorbed water. The results were correct within experimental uncertainty. This iterative method gave percent acrylic acid values closer to the expected 100.0% than did any of the other three methods tested by treating the same data (see Table A-1).

A plot of pH vs volume of NaOH (aq) added (from Trial 1 titration data) is shown in Figure A-1. The difficulty of obtaining the beginning equivalence point from a relative maximum slope can be understood readily by looking at this plot. It also can be seen that the end point determined by the iterative method lies beyond the end point determined by maximum slope.

A  $pK_a$  vs percent neutralization plot gives some indication of the reliability of the titration results. Figure A-2 shows such a plot resulting when the equivalence points determined by Method C are used with data from Trial 1. In addition to individual data points, a solid curve calculated from the smoothed data and a dashed line determined by linear regression on the 30% to 60% neutralization portion of the smoothed data are shown. The  $pK_a$  seems to be generally increasing, as is expected. However, the  $pK_a$  during 0% to 10% neutralization seems to be virtually constant. This may be a symptom of an incorrect equivalence point. The 90% to 100% neutralization portion of such a plot is unreliable and may be disregarded. Figure A-3 shows a similar plot, which results when the equivalence points determined by Method D are used with data from Trial 1. In this figure, the dashed line is the linear regression line determined by the smoothed data from 0% to 90% neutralization. The virtually constant, positive slope (except for minor, localized fluctuations) of the data from 0% to 90% neutralization seems to indicate that the equivalence points have been well chosen. The abundance of data points throughout the plot also is encouraging. Method D, being an iterative procedure, occasionally diverges and gives an obviously high percent acrylic acid value and a plot displaying all of its data points bunched up in only a part of the plot and exhibiting an abnormally large slope. This is obviously not the case in this figure.

For Method D to be applicable, the  $pK_a$  of the compound being titrated must vary linearly with percent neutralization. If the system actually does not exhibit this behavior, then a  $pK_a$  vs percent neutralization plot would be nonlinear, thus providing an indication that this method would not apply to that system. One instance of such a nonlinear plot occurred when treating data from titration of a polysaccharide that contained both pyruvate and glucuronic acid moieties. Apparently, the intrinsic  $pK_a$  values of the two weak acids are sufficiently different that the  $pK_a$  of the biopolymer does not vary linearly with percent neutralization.

Although Methods A, B, and C may be applicable for a number of systems, Method D has been shown to be more generally applicable. In addition, the resulting  $pK_a$  vs percent neutralization plot provides an indication of the validity of this method for a given system.

TABLE A-1

Comparison of Results Obtained by Various Methods of Treating Titration Data for Poly(acrylic acid)

Method	Starting point defined by	End point defined by	Calculated percent acrylic acid residues in poly(acrylic acid)	
			Trial 1	Trial 2
A	pH = 3.5	pH = 8.2	93.20	92.15
B			98.89	95.82
C	$1 + \frac{\Delta (10^{-\text{pH}})}{\Delta (C_{\text{Na}})} = \frac{1}{2}$	Relative maximum slope of pH vs volume of NaOH plot	94.60	92.44
D	Iterative method described in text. (Starting and end points defined by Method C are used as initial values.)		100.70	99.20

B. APPENDIX B

COMPARISONS OF SIMILAR GROUPS AND USE OF A MODIFIED  
MANN-WHITNEY STATISTIC

Polymer samples in the concentration range from 0.01 to 0.02 g/dL with reduced viscosities (unsheared) in 2% NaCl (aq) greater than 2 dL/g and charge/mass ratios from 0.0005 to 0.016 were considered in this analysis.

Each polymer satisfying these restrictions was classified in one of a possible fifteen categories. These categories were defined by three classes of reduced viscosity in 2% NaCl (unsheared) x five classes of charge/mass ratio of polyanion. If  $\eta_1$ ,  $\eta_2$ , and  $\eta_3$  represent the reduced viscosity classes 1, 2, and 3, respectively, then  $2 < \eta_1 \leq 8 < \eta_2 \leq 14 < \eta_3 \leq 25$  dL/g. Similarly, if  $CMR_i$  represents the charge/mass ratio of a polyanion in charge/mass ratio class  $i$ , then

$$\begin{aligned} 0.0005 < CMR_1 &\leq 0.001, \\ 0.001 < CMR_2 &\leq 0.002, \\ 0.002 < CMR_3 &\leq 0.004, \\ 0.004 < CMR_4 &\leq 0.008, \text{ and} \\ 0.008 < CMR_5 &\leq 0.016. \end{aligned}$$

Polymer samples were ranked according to values of  $(\eta_{sp})_2/(\eta_{sp})_{.01}$ . When these values were used directly, the data are designated "untransformed data." On the other hand, "transformed data" indicates that rankings were based on values of

$$[(\eta_{sp})_2/(\eta_{sp})_{.01} - 0.07] \times [\text{charge/mass ratio of polyanion}].$$

This transformation was made to reduce the effect of charge-to-mass ratio on the dependent variable.

In this set of comparisons, a sample of one polymer type was compared with a sample of another polymer type only if both samples were in the same category for both reduced viscosity in 2% NaCl (unsheared) and charge/mass ratio. If a valid comparison occurred between two given polymer types in a given category, then the rank sum minus the smallest possible value was computed for each. The result for each sample at this point is called the Mann-Whitney statistic. However, further calculations were performed. Each of these two values was divided by the smaller number of samples in that category. That is, if one polymer type has  $m$  samples in one category which contains  $n$  samples of the other polymer type being compared, and if  $m \leq n$ , both results would be divided by  $m$ . This division compensates for the fact that each of these samples are involved in  $m$  comparisons. If such compensations were omitted when different categories had different values of  $m$ , then

results from categories having higher values of  $m$  would be given disproportionately high weights, as the expected value of the rank sum minus the smallest possible value is  $mn/2$ . Finally, results are summed over all the categories in which valid comparisons occur. In this report, the resulting value for each sample is called the "modified Mann-Whitney statistic."

The Mann-Whitney statistic  $W_{xy}$  is the number of pairs  $(X_i, Y_j)$  with  $X_i < Y_j$ . The Mann-Whitney statistic also can be considered to be a modification of the Wilcoxon rank-sum statistic and is well known in statistics.<sup>21</sup> The modification of Kilmer to the Mann-Whitney statistic made by dividing by  $m$  in each category and summing over all categories containing valid comparisons has been introduced in this work.

A hypothetical example may help to illustrate calculation of the modified Mann-Whitney statistic. Assume that polymer types A and B have samples distributed as shown in Table B-1. The inequalities represent comparisons of the effect (e.g., fraction of viscosity retained). Samples A<sub>111</sub>, A<sub>231</sub>, B<sub>241</sub>, and A<sub>251</sub> are not involved in any comparisons because, in each case, there is no sample of the other polymer type in the same category. There are two comparisons of one sample vs one sample (A<sub>221</sub> vs B<sub>221</sub> and A<sub>341</sub> vs B<sub>341</sub>). In each of these cases, the Mann-Whitney statistic  $W_{AB}$  is

(rank sum for B) - (smallest possible value of rank sum for B) = 2 - 1 = 1,

and  $W_{BA}$  is

(rank sum for A) - (smallest possible value of rank sum for A) = 1 - 1 = 0.

For the comparison involving three samples, the rank sum for A is 1, and the rank sum for B is 2 + 3 = 5. Thus, the values of the Mann-Whitney statistic in that category are

$$W_{AB} = 5 - 3 = 2 \quad \text{and}$$

$$W_{BA} = 1 - 1 = 0.$$

For the comparison involving five samples, the rank sum for A is 1 + 2 + 4 = 7, and the rank sum for B is 3 + 5 = 8. Thus, the values of the Mann-Whitney statistic in that category are

$$W_{AB} = 8 - 3 = 5 \quad \text{and}$$

$$W_{BA} = 7 - 6 = 1.$$

The modified Mann-Whitney statistic for  $A < B$  is calculated using the preceding results:

$W_{AB}$	/	the smaller number of samples		
1	/	1	=	1
1	/	1	=	1
2	/	1	=	2
5	/	2	=	2.5
		Modified Mann-Whitney statistic	=	<u>6.5</u>

Similarly, the modified Mann-Whitney statistic for  $B < A$  is calculated:

$W_{BA}$	/	the smaller number of samples		
0	/	1	=	0
0	/	1	=	0
0	/	1	=	0
1	/	2	=	0.5
		Modified Mann-Whitney statistic	=	<u>0.5</u>

The difference between the two values of the modified Mann-Whitney statistic in the preceding example is impressive, but is it statistically significant? To determine this, one can calculate what the distribution of the modified Mann-Whitney statistic would be if each of the

$$2 \times 2 \times 3 \times \frac{(5!)}{(2!)(3!)} = 120 \text{ possible cases were equally likely.}$$

For the sum from the one sample vs one sample comparisons, the binomial distribution can be used. Thus,

<u>Sum</u>	<u>Probability</u>
0	1/4
1	1/2
2	1/4.

For the three-sample comparison, it is obvious that the probabilities are given by:

<u>Mann-Whitney statistic</u>	<u>Probability</u>
0	1/3
1	1/3
2	1/3.

Vector convolution of these two results gives:

<u>Modified Mann-Whitney statistic so far</u>	<u>Probability</u>
0	1/12
1	1/4
2	1/3
3	1/4
4	1/12.

For the five-sample comparison,<sup>21</sup> (page 7)

<u>Mann-Whitney statistic</u>	<u>Probability</u>
0	0.1
1	0.1
2	0.2
3	0.2
4	0.2
5	0.1
6	0.1

These values of the Mann-Whitney statistic are each divided by 2 (because the smaller sample size is 2). Vector convolution of the

probability vectors

$$\begin{bmatrix} 1/12 \\ 0 \\ 1/4 \\ 0 \\ 1/3 \\ 0 \\ 1/4 \\ 0 \\ 1/12 \end{bmatrix} \quad \text{and} \quad \begin{bmatrix} 0.1 \\ 0.1 \\ 0.2 \\ 0.2 \\ 0.2 \\ 0.1 \\ 0.1 \end{bmatrix} \quad \text{gives}$$

the distribution given in the second column of Table B-2.

It is the two-tailed cumulative probability that is appropriate in judging the significance of a value of the modified Mann-Whitney statistic. For the modified Mann-Whitney statistic value of 0.5 in this example, this probability is seen to be 0.033333.... Thus, in this example, the probability (two-tailed) that the modified Mann-Whitney statistic would be at least this far from the expected value for purely random ordering is 0.033333.... Actually, it is rather easy to see in this example that there is only one case each that would give modified Mann-Whitney statistic values of 0, 0.5, 6.5, and 7, an observation which leads immediately to the correct probability of 4/120 or 1/30. Since this probability is less than 0.05, the difference between polymer types A and B is judged to be statistically significant.

A computer program has been written and used to treat actual experimental data. Probabilities of obtaining specified values of the Mann-Whitney statistic are calculated with help from an exact recursion relation and exact equations given in the literature.<sup>23</sup> Since exact equations<sup>23</sup> are used instead of an approximation that is also given in the literature,<sup>23</sup> valid probabilities can be calculated for any sample size. These probabilities are used as intermediate results in calculating the significance probability by a method similar to that given in the example.

TABLE B-1

Hypothetical Example to Help Illustrate Calculation  
of the Modified Mann-Whitney Statistic

		Charge/Mass Ratio					
		0.0005	0.001	0.002	0.004	0.008	0.016
η reduced in 2% NaCl (aq), unsheared (dL/g)	2	A <sub>111</sub>		A <sub>131</sub> < B <sub>131</sub> < B <sub>132</sub>			
	8		A <sub>221</sub> < B <sub>221</sub>	A <sub>231</sub>	B <sub>241</sub>	A <sub>251</sub>	
	14			A <sub>331</sub> < A <sub>332</sub> < B <sub>331</sub> < A <sub>333</sub> < B <sub>332</sub>	A <sub>341</sub> < B <sub>341</sub>		
	25						

TABLE B-2

Distribution of the Modified Mann-Whitney Statistic  
for Hypothetical Example

<u>Modified Mann-Whitney statistic</u>	<u>Probability (one-tailed) Difference</u>	<u>Cumulative</u>	<u>Probability (two-tailed) Cumulative</u>
0.00000	0.00833333	0.00833333	0.01666667
0.50000	0.00833333	0.01666667	0.03333333
1.00000	0.04166667	0.05833333	0.11666667
1.50000	0.04166667	0.10000000	0.20000000
2.00000	0.10000000	0.20000000	0.40000000
2.50000	0.09166667	0.29166667	0.58333333
3.00000	0.15000000	0.44166667	0.88333333
3.50000	0.11666667	0.55833333	1.00000000
4.00000	0.15000000	0.70833333	1.00000000
4.50000	0.09166667	0.80000000	1.00000000
5.00000	0.10000000	0.90000000	1.00000000
5.50000	0.04166667	0.94166667	1.00000000
6.00000	0.04166667	0.98333333	1.00000000
6.50000	0.00833333	0.99166667	1.00000000
7.00000	0.00833333	1.00000000	1.00000000



