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IMPROVED POLYMERS FOR ENHANCED OIL RECOVERY—SYNTHESIS AND RHEOLOGY

Final Report

By
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By
University of Southern Mississippi
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FINAL REPORT

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ABSTRACT

Research during FY-84 was centered on synthesis, characterization, and rheological behavior of copolymers of acrylamide (AM) with sodium-3-acrylamido-3-methyl-butanoate (NaAMB). Reactivity ratios were determined and copolymers with designated microstructures were synthesized in order to assess solution properties. Polymers were characterized by C-13 NMR and Infrared Spectroscopy, low angle laser light scattering, quasi-elastic light scattering, viscometry, turbidimetry, and potentiometric titration. New light scattering and size exclusion chromatographic (SEC) techniques have been developed for more accurately measuring molecular size of high molecular weight, water-soluble copolymers. The improved sensitivity of SEC methods is attributable to the development of a new syringe pump, a sensitive presssure detector, and deconvolution techniques in conjuction with the utilization of efficient column packing materials. The AM/NaAMB copolymers show immense potential for use as mobility control agents in enhanced oil recovery due to their remarkable calcium tolerance and unusually high molecular weights as compared to conventional acrylamide-sodium acrylate copolymers of similar microstructure.

PREFACE

During the seven years of our research endeavors on water-soluble polymers for enhanced oil recovery, valuable discoveries have been made by the team of research workers involved in this effort. It is hoped that these efforts will lead toward development of commercial polymer systems which will lessen our dependence on unstable foreign oil sources and enhance our ability to tap domestic petroleum sources.

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CHAPTER I

SUMMARY OF FY 1984 STUDIES

Charles L. McCormick and Roger D. Hester

INTRODUCTION

Research over the past seven years in our laboratories has conclusively demonstrated that water-soluble polymers can be tailored with significantly improved properties for utilization in enhanced oil recovery. An understanding of structure/solution property/performance interrelationships is rapidly emerging based on carefully prepared model compounds.

The most important single property of macromolecules for mobility control in EOR is that of hydrodynamic volume (HDV). HDV dictates polymer concentration for viscosity, rheological behavior, and the extent of pore and channel space penetration into the reservoir rock. HDV is a clear function of chemical structure, chain length, and polymer-solvent interaction.

RESEARCH ACCOMPLISHMENTS

In our continuing research we have probed the effects of mono- and multivalent electrolytes (NaCl and $CaCl_2$), temperature, pH, shear stress, and polymer-solvent interaction on rheological properties of macromolecules with tailored structures and molecular weight. Fundamental relationships have been developed based on measured behavior of well characterized models. In that regard, new analytical techniques, data acquisition and reduction routines, calibration procedures, and instrumentation have been developed specifically for water-soluble polymers with large HDV's.

All major objectives of our research proposal "Improved Polymers for Enhanced Oil Recovery - Synthesis and Rheology" have been met; and as expected from fundamental research efforts, some new exciting approaches have been uncovered. Significant research accomplishments to date are given below:

- Three families of copolymers of acrylamide have been synthesized which show greatly enhanced behavior in comparison to conventional hydrolyzed polyacrylamides.

  ▲Poly(acrylamide-co-sodium-2-acrylamido-2-methylpropane-sulfonate) AM/NaAMPS

  These copolymers maintain large dimensions in the presence of sodium chloride and calcium chloride and do not phase separate from aqueous solution at temperatures up to 100°C. Solution behavior is a function of microstructure.

  ▲Poly[acrylamide-co-N-(1,1-dimethyl-3-oxobutyl)acrylamide]

  AM/DAAM copolymers at 10 to 20 mole % DAAM exhibit significant viscosity increases in the presence of added NaCl or $CaCl_2$. No phase separation occurs in the presence of salts at temperatures up to 100°C although viscosity reduction is significant.

  ▲Poly[acrylamide-co-sodium-3-acrylamido-3-methylbutanoate]

  AM/NaAMB copolymers maintain unexpectedly high solution viscosities in the presence of NaCl and $CaCl_2$ with no phase separation up to 100°C. The tolerance of these copolymers to calcium ions is especially surprising since hydrolyzed polyacrylamides phase-separate readily due to ion binding. Apparently the bulk of the NaAMB monomer units and neighboring group hydrogen bonding are responsible for this remarkable behavior. The calcium tolerance and the attainment of high degrees of polymerization make these perhaps the synthetic polymers with greatest potential in EOR reported to date.

- A new model has been developed and tested which accurately predicts partitioning of macromolecules in porous media during fluid flow. A relationship has been defined between "pore entry diameter" distribution and molecular size distribution which allows prediction of chromatographic effects and accessible pore volume. This model is the basis for a new calibration technique for size exclusion chromatography and may well be a future predictor for optimizing polymer HDV relative to reservoir pore and channel geometry.

- A syringe pump/differential pressure detector system for size exclusion chromatography has been built and tested which allows greater reliability and sensitivity when compared to conventional systems. Computer-assisted data acquisition techniques, deconvolution routines, and plotting procedures have been developed for macromolecules with extremely large hydrodynamic volumes. Polymers of up to ten million molecular weight can be analyzed with these techniques.

- Quasielastic light scattering techniques have been developed to rapidly determine hydrodynamic dimensions of water-soluble polymers. Inter-chain associations or aggregations can also be detected.

- Turbidimetry and potentiometry procedures have been developed to follow phase behavior and conformational changes of polymer molecules in aqueous solutions. Ion binding and intra-chain associations have been assessed for AM/NaAMPS, AM/DAAM, and AM/NaAMB copolymers.

- The educational aspects of our research project cannot be overemphasized. Fifteen graduate students, ten undergraduates, and three faculty members have contributed to this interdisciplinary effort of chemistry and engineering. To date five Ph.D, four M.S. and eight B.S. degrees have been awarded to these students. The others will complete their research in the near future.

SUMMARY OF FY-1984 RESEARCH

In this section the highlights of our research efforts during FY-1984 are discussed. The detailed studies are reported in Chapters II through VII.

Synthesis of Copolymers of acrylamide (AM) with sodium-3-acrylamido-3-methylbutanoate (NaAMB)

AM/NaAMB copolymers have been prepared (Chapter II) and their reactivity ratios studied. A value of $r_1 r_2$ of 0.56 has been determined for the AM/NaAMB monomer pair. Copolymers were prepared with designated microstructures and similar molecular weights in order to assess solution properties.

Characterization and Solution Properties of AM/NaAMB Copolymers

AM/NaAMB copolymers were characterized by elemental analysis and C-13 NMR (Chapter II). Mean sequence lengths were calculated for each synthetic copolymer and solution properties studied relative to predicted microstructure. Molecular weights by light scattering were in the range of 13 to 16 X 10^6 g/mole and were relatively unaffected by increasing NaAMB in the copolymer.

Solution studies (Chapter III) on the AM/NaAMB copolymers indicate unusually high viscosities in the presence of salts especially at certain copolymer compositions. These copolymers showed an unexpected resistance to calcium ion binding as indicated by turbidimetric and potentiometric studies despite the fact that these polymers exhibit pKa values similar to those of partially hydrolyzed polyacrylamides. The viscosity, salt tolerance, lack of divalent ion binding, and apparent pKa values suggest the importance of hydrogen bonding of nearest neighbors and steric effects along the macromolecular backbone.

Potentiometry and Turbidimetric Studies

Potentiometric and turbidimetric studies were also conducted on sodium acrylate/AM and sodium-2-acrylamido-2-methylpropane-sulfonate copolymers for comparison. These are reported in Chapter IV and compared to studies on the AM/NaAMB system. Hydrogen bonding by neighboring amide hydrogens and spacer groups greatly stabilizes the carboxy anions.

Characterization of Random Copolymers by C-13 NMR

AM/DAAM and AM/NaAMPS copolymers have been characterized by C-13 NMR spectrometry (Chapter V). The structural composition as determined by NMR is in excellent agreement with that from elemental analysis. NMR analyses are unaffected by bound water, are relatively fast, require little sample preparation, and are non-destructive.

Aqueous Size Exclusion Chromatography

Characterization of EOR polymers for size distribution is extremely important. During polymer flooding, macromolecules that are too large in size relative to the reservoir pore channels can shear degrade at the wellhead into smaller molecules. Smaller polymer molecules are not effective as mobility control agents. Thus a reservoir specific polymer size or size distribution is optimum for efficient flooding.

The hydrodynamic size distribution of a polymer can be determined by size exclusion chromatography (SEC). Previous

aqueous SEC analyses were limited to polymer hydrodynamic diameters that were less than 120 nm. Analytical techniques have now been developed which allow measurement of polymer diameters up to 280 nm, corresponding to molecular weights of about 10 million (Chapter V). This has been accomplished by constructing a new precision pump, new detector, and a sophisticated data collection and analysis system. The combination of this equipment has had a synergistic effect that has greatly enhanced SEC analysis separation range and sensitivity.

Rheological Measurements

We have also enhanced our capabilities of measuring the low shear, dilute solution rheological behavior of EOR polymers. This has been accomplished by placing a Contraves concentric cylinder rheometer into operation (Chapter VII). Several sources of operator and instrumental error have been reduced; also, the precision of data collection has been improved with the addition of an inexpensive data acquisition unit to the Contraves rheometer system. For EOR polymer solutions having large pseudoplastic behavior and for polymers that associate, the Contraves has been shown to be superior to a standard four bulb viscometer in determining rheological behavior.

DISSERTATIONS AND THESES

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2. "Synthesis, Characterization, and Dilute Solution Studies of Random Copolymers of Acrylamide," Ph.D. Dissertation, G. S. Chen, 1982.

3. "Synthesis, Characterization, and Rheological Studies of Model Dextran-Grafted Copolymers," Ph.D. Dissertation, L. S. Park, 1982.

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CHAPTER II

COPOLYMERS OF ACRYLAMIDE WITH SODIUM-3-ACRYLAMIDO-3-METHYLBUTANOATE: SYNTHESIS AND CHARACTERIZATION

C.L. McCormick and K.P. Blackmon

SYNOPSIS

The copolymerization of acrylamide (AM) with sodium-3-acrylamido-3-methylbutanoate (NaAMB) has been studied. The value of r_1r_2 has been determined to be 0.56 for the AM-NaAMB pair. The molecular weights of the copolymers were relatively unaffected by monomer feed ratios. The copolymer microstructures, including run numbers and sequence distributions, were calculated from the reactivity ratios. The solution properties of the AM-NaAMB copolymers, as well as the NaAMB homopolymer, will be reported in the next chapter.

INTRODUCTION

Water-soluble polymers have shown many properties lending themselves to a wide variety of industrial applications [1-3]. Copolymers of acrylamide have especially increased in importance due to their utility as water-soluble viscosifiers and displacement fluids in enhanced oil recovery [4-12].

The aim of our continuing research [13-21] is to prepare model water-soluble copolymers with large hydrodynamic volumes in solution. The NaAMB comonomer was chosen due to its structural similarity to sodium-2-acrylamido-2-methylpropanesulfonate (NaAMPS) in order to assess the effects of a carboxylic versus sulfonic acid moiety. In this paper we report the synthesis and molecular characterization of charged copolymers of acrylamide (AM) with sodium-3-acrylamido-3-methylbutanoate (NaAMB). The reactivity ratios were determined and the microstructures calculated. Additionally, molecular weights for selected polymers were determined by low angle laser light scattering. The solution properties of these copolymers will be reported in Chapter III.

EXPERIMENTAL

Materials

Sodium-3-acrylamido-3-methylbutanoate (NaAMB) was prepared by neutralization of 3-acrylamido-3-methylbutanoic acid (AMBA). AMBA was synthesized via a Ritter reaction involving equimolar amounts of acrylonitrile and 3,3-dimethylacrylic acid in the presence of water and a large excess of sulfuric acid. The synthesis of AMBA followed the procedure set forth by Hoke and Robins [22]. The crude AMBA was recrystallized twice from a mixture of methyl ethyl ketone and petroleum ether prior to use (m.p. 89-91°C). ANAL. Calculated for $C_8H_{13}NO_3$: C, 56.14% ; H, 7.60% ; N, 8.19%. Found: C, 55.98% ; H, 7.56% ; N, 8.20%. IR: N-H stretch, 3250 cm^{-1}; C=C-H, 3075 cm^{-1}; aliphatic C-H, 2950 cm^{-1}; amide C=O, 1660 cm^{-1} (s), 1530 cm^{-1} (m); acid C=O, 1720 cm^{-1}. Acrylamide (AM) from Aldrich Chemical Co. was recrystallized twice from acetone and vacuum dried at room temperature prior to use (m.p. 83-84°C). Potassium persulfate from J.T. Baker Co. was recrystallized twice from distilled water prior to use.

Poly(sodium-3-acrylamido-3-methylbutanoate) and Poly(acrylamide-co-sodium-3-acrylamido-3-methylbutanoate)

The copolymers of AM with NaAMB, as well as the homopolymer of NaAMB, were prepared in aqueous solution at 30°C using 0.1 mole percent potassium persulfate as the initiator. Each reaction was conducted in a 1000 ml 3-necked flask equipped with a mechanical stirrer and nitrogen inlet tube. A specified amount of 3-acrylamido-3-methylbutanoic acid was partially dissolved in deionized water followed by the addition of an equimolar amount of NaOH. A specified amount of acrylamide dissolved in deionized water was then added to the neutralized AMBA solution, and the pH of the entire mixture was adjusted to 9.0±0.1 by dropwise addition of 0.5M NaOH. The pH adjustment was performed to ensure that all of the carboxylated monomer was in the sodium salt form. Each reaction mixture was then deaerated with oxygen-free nitrogen for 20 minutes. The designated quantity of potassium persulfate initiator, dissolved in deionized water, was injected into the reaction vessel. The total monomer concentration in each reaction was held constant at 0.456M. An aliquot was taken at low conversion to allow reactivity ratio studies to be performed, and the reaction terminated at 30-50% conversion due to increasing viscosity in the reaction vessel. The reaction mixture was diluted with 2-4 volumes of deionized water and the polymer precipitated by pouring the solution slowly into 3 volumes of reagent grade acetone with gentle stirring. The polymers were further purified by reprecipitation into acetone followed by

freeze-drying and then vacuum drying for 2 days. Conversions were determined gravimetrically. Table I lists reaction parameters for the copolymerization series as well as for the homopolymerization of NaAMB.

IR: AMB homopolymer, N-H stretch (broad), 3320 cm^{-1}; C-H, 2955 cm^{-1}; amide C=O, 1655 cm^{-1}; sodium salt C=O, 1680 cm^{-1}. Typical copolymer: AMB-40-2, N-H stretch (broad), 3450-3300 cm^{-1}; AM amide C=O, 1565 cm^{-1}; NaAMB amide C=O, 1520 cm^{-1}; sodium salt C=O, 1680 cm^{-1}.

Elemental Analysis

Elemental analyses for carbon, hydrogen, and nitrogen of the AM-NaAMB copolymers were conducted by M-H-W Laboratories of Phoenix, AZ. The copolymer compositions were calculated based on C/N ratios because of the variability of absolute values due to the hygroscopic nature of the polymers. Elemental analyses were conducted at two polymer conversion levels, i.e., low and high, to assess drift in the copolymer composition. However, compositions at low and high conversions are in excellent agreement; thus, the effects of compositional drift are minimal.

C-13 Nuclear Magnetic Resonance Spectroscopy

Carbon-13 NMR spectra for the AM-NaAMB copolymers and NaAMB homopolymer were obtained at 22.5 MHz on a JEOL FX-90Q Spectrometer using 5-10 wt% aqueous (D_2O) polymer solutions in 10 mm tubes. A pulse repetition of 7-8 sec with gated decoupling to remove all NOE was used to obtain the quantitations.

Low Angle Laser Light Scattering

Low angle laser light scattering measurements to determine molecular weights were performed with a Chromatix KMX-6 photometer [23]. Refractive index increments were determined with a Chromatix KMX-16 laser differential refractometer. All measurements were performed at 25°C in 1.0M NaCl aqueous solutions at a pH of 6.0. Weight-average molecular weights and second virial coefficients derived from these data are given in Table II for selected polymers.

RESULTS AND DISCUSSION

Reactivity Ratio Studies

The feed ratios of monomers and the resultant copolymer compositions (Table I) as determined from elemental analyses were used to calculate reactivity ratios for the AM-NaAMB copolymer system. The Fineman-Ross method [24] and the Kelen-Tüdos method [25] were employed to determine the monomer reactivity ratios at low conversion. Figure 1 is the Fineman-Ross plot for acrylamide (M_1) and sodium-3-acrylamido-3-methylbutanoate (M_2). The reactivity ratio r_1 was determined to be 1.23±0.02 from the slope and r_2 = 0.50±0.04 from the intercept. A plot of the data according to the Kelen-Tüdos method is shown in Figure 2. Graphical evaluation of Figure 2 yields reactivity ratios for the AM-NaAMB monomer pair of r_1 = 1.20±0.02 and r_2 = 0.47±0.05 respectively, Table III. The observed data in the Kelen-Tüdos plot (Figure 2) are linear, an indication that these copolymerizations follow the conventional copolymerization kinetics under a prerequisite that the reactivity of a polymer radical is only determined by the terminal monomer unit [26]. Figure 3 shows the copolymer composition as determined from elemental analysis as a function of feed composition for the copolymerization of AM with NaAMB. The copolymerization curve is based on the experimentally determined reactivity ratios. The AM-NaAMB copolymers with $r_1 r_2$ = 0.56 are generally random in nature, possessing a slight tendency toward alternation with respect to the NaAMB (M_2) monomer.

Macromolecular Structure

The structures of the AM-NaAMB copolymers and NaAMB homopolymer were verified by IR, C-13 NMR, and elemental analysis. The copolymer compositions obtained from C-13 NMR were determined using the procedure described for random copolymers of acrylamide with sulfonated comonomers [16]. Briefly, the amide carbonyl at 181.9 ppm is used as a standard, and other NaAMB peaks (nos. 4,5,6 in Figure 4) are integrated to give the percent of NaAMB in the copolymer. The copolymer compositions as determined by C-13 NMR are shown in Table I, and agree favorably with the compositions as determined from elemental analysis. Typical copolymer peak assignments and spin-lattice relaxation times, T_1, are shown in Table IV. Figure 4 shows a typical C-13 NMR spectrum of a copolymer of AM with NaAMB (AMB-40-1). Furthermore, the weight-average molecular weights of the AM-NaAMB copolymers were similar; thus, the properties exhibited by the polymers may be attributed to composition.

Copolymer Microstructure

The microstructure of the AM-NaAMB copolymers is expected to be important in determining the solution properties which the copolymers exhibit. As mentioned previously, the observed data follow the conventional copolymerization equation, and the adherence of the data to this equation is an important point in establishing the validity of the statistical microstructure analysis. Thus, the calculation of the statistical distribution of monomer sequences, M_1-M_1, M_2-M_2, and M_1-M_2 may be performed utilizing equations (1)-(3) [27]:

$$X = \phi_1 - 2\phi_1(1-\phi_1)/\{1+[(2\phi_1-1)^2 + 4r_1r_2\phi_1(1-\phi_1)]^{1/2}\} \quad (1)$$

$$Y = (1-\phi_1) - 2\phi_1(1-\phi_1)/\{1+[(2\phi_1-1)^2 + 4r_1r_2\phi_1(1-\phi_1)]^{1/2}\} \quad (2)$$

$$Z = 4\phi_1(1-\phi_1)/\{1+[(2\phi_1-1)^2 + 4r_1r_2\phi_1(1-\phi_1)]^{1/2}\} \quad (3)$$

The mole fractions of M_1-M_1, M_2-M_2, and M_1-M_2 sequences in the copolymer are designated by X, Y, and Z, respectively. ϕ_1 represents the mole fraction of M_1 in the copolymer, and r_1 and r_2 are the reactivity ratios for the monomer pair. Mean sequence lengths, μ_1 and μ_2, can be calculated utilizing equations (4) and (5) [28]:

$$\mu_1 = 1 + r_1[M_1]/[M_2] \quad (4)$$

$$\mu_2 = 1 + r_2[M_2]/[M_1] \quad (5)$$

Table V lists the structural data for the copolymers of AM with NaAMB. For the series of AM-NaAMB copolymers, the mean sequence length of acrylamide, μ_{AM}, varied from 23.8 at a 94.0/6.0 mole ratio of AM/NaAMB in the copolymer to 1.4 at a 36.9/63.1 mole ratio. For those copolymer compositions, values of μ_{NaAMB} were 1.0 and 2.4, respectively. Table VI lists additional structural data for a broad spectrum of AM-NaAMB copolymers involving higher-order sequence distributions, i.e., triads and pentads, calculated using the method of Harwood and Ritchey [29]. The feed ratios of AM and NaAMB are designated by M1F and M2F, respectively. The values of M1C and M2C are the mole percents of AM and NaAMB in the copolymer obtained from the copolymerization equation using the experimentally derived Kelen-Tüdos reactivity ratios of r_1 = 1.20 and r_2 = 0.47. R represents the run number while PABA and PAABAA are the probabilities of a NaAMB-centered triad and pentad, respectively. NABA and NAABAA are the expected numbers of NaAMB-centered triads and pentads per 100 monomer units, obtained by multiplying the respective probabilities by the number of NaAMB units, M2C. The maximum frequency of NaAMB-centered triads occurs at a copolymer composition containing about 36 mole% NaAMB, while the maximum frequency of

NaAMB-centered pentads occurs at a copolymer composition containing approximately 20 mole% NaAMB. Solution properties of AM-NaAMB copolymers as related to the microstructure will be discussed in a subsequent chapter.

Effect of Feed Composition

The effect of feed composition on molecular weight was studied for the polymers listed in Table II. Second virial coefficients were also obtained from the light scattering measurements. Since the weight-average molecular weights of the copolymers were similar and ranged from 13-16 X 10^6 g/mol, the molecular weight appears to be relatively independent of copolymer composition up to at least 50 mole% NaAMB. It is interesting to note that in a copolymerization involving acrylamide, the molecular weight generally decreases with increasing comonomer content [15,20] which may be explained by increased cross-termination rates in copolymerization as compared to the very slow rate of termination observed for homopolyacrylamide [30,31]. The high molecular weights attainable in the AM-NaAMB system would indicate that NaAMB also shows low termination rates in copolymerization. The somewhat lower molecular weight for the homopolymer of NaAMB indicates a lower rate of propagation as compared to AM. This phenomenon is important since it is unusual to obtain such high molecular weights in free-radical copolymerizations.

CONCLUSIONS

Random copolymers of acrylamide with sodium-3-acrylamido-3-methylbutanoate have been prepared in aqueous solution. Elemental analyses and C-13 NMR were used to determine the copolymer compositions. The reactivity ratios, $r_1 r_2 = 0.56$, have been determined by two low conversion techniques using the copolymer compositions obtained from elemental analysis, and indicate the randomness of addition of these two monomers. C-13 NMR peak assignments, including spin-lattice relaxation times, T_1, have been determined. The copolymer microstructure has been calculated utilizing the methods of Igarashi [27] and Harwood and Ritchey [29]. The maximum frequency of NaAMB-centered triads was found to occur at a copolymer composition containing about 36 mole% NaAMB, while the maximum frequency of NaAMB-centered pentads occurred at approximately 20 mole% NaAMB. Weight-average molecular weights in the range of 13-16 X 10^6 g/mole have been determined for selected AM-NaAMB copolymers, and found to be relatively independent of the copolymer composition. The knowledge of molecular weight and microstructure of these copolymers will be used for the development of structure/property relationships in a subsequent chapter.

TABLE I

Reaction Parameters for the Copolymerization of Acrylamide (M_1) with Sodium-3-Acrylamido-3-Methylbutanoate (M_2) and Homopolymerization of NaAMB

Sample Number	Feed Ratio $M_1:M_2$	Reaction Time (min)	Conversion (%)	Weight (% C)	Weight (% N)	M_2 in Copolymer (mol%)[a]	M_2 in Copolymer (mol%)[b]
AMB-5-1	95:5	60	2.6	44.89	15.87	5.99±0.10	3.38±0.17
AMB-5-2	95:5	300	40.4	44.23	15.63	6.04±0.15	------
AMB-10-1	90:10	80	7.6	47.86	16.41	8.04±0.13	7.54±0.38
AMB-10-2	90:10	300	35.4	46.77	15.96	8.37±0.14	-------
AMB-25-1	75:25	80	6.3	46.31	13.46	20.27±0.39	18.88±0.94
AMB-25-2	75:25	300	49.2	46.49	13.55	20.05±0.38	-------
AMB-33-1	67:33	60	6.1	44.63	11.97	26.99±0.57	25.30±1.27
AMB-33-2	67:33	300	48.6	44.54	11.65	29.19±0.63	-------
AMB-40-1	60:40	80	3.1	47.08	12.04	31.23±0.65	31.32±1.57
AMB-40-2	60:40	300	42.3	46.47	11.86	31.41±0.66	-------
AMB-60-1	40:60	80	3.5	46.83	10.08	48.39±1.17	48.83±2.44
AMB-60-2	40:60	300	37.0	45.78	9.73	49.77±1.24	-------
AMB-75-1	25:75	80	4.2	46.49	8.81	63.11±1.70	63.15±3.16
AMB-75-2	25:75	300	34.1	45.29	8.55	63.58±1.77	-------
AMB	0:100	270	7.2	49.74[c]	7.25[c]	100	100

[a]From Elemental Analysis, [b]From C-13 NMR, [c]Theoretical value

TABLE II

Molecular Weight and Second Virial Coefficient Data for the Copolymers of Acrylamide (AM) with Sodium-3-Acrylamido-3-Methylbutanoate (NaAMB) and Homopolymer of NaAMB

Sample Number	Composition (mol%)[a]		$\overline{M}_W$ ($\times 10^{-6}$ g/mol)	A_2 ($\times 10^4 \frac{ml./mole}{g^2}$)
	AM	NaAMB		
AMB-10-2	91.63	8.37	15.6	4.28
AMB-25-2	79.95	20.05	12.9	1.52
AMB-60-2	50.23	49.77	14.0	3.49
AMB	0	100	3.23	4.34

[a]from elemental analysis

TABLE III

Reactivity Ratios for the Copolymerization of Acrylamide (M_1) with Sodium-3-Acrylamido-3-Methylbutanoate (M_2)

Method	r_1	r_2	r_1r_2
Fineman-Ross	1.23±0.02	0.50±0.04	0.62
Kelen-Tüdos	1.20±0.02	0.47±0.05	0.56

TABLE IV

C-13 NMR Peak Assignments for Copolymers of Acrylamide with Sodium-3-Acrylamido-3-Methylbutanoate

Peak Number	Chemical Shift (ppm)	Spin-Lattice Relaxation Times T_1 (sec)
1	37.2	0.04
2	44.3	0.08
3	181.9	1.30
4	55.8	0.90
5	28.9	0.15
6	49.6	0.04
7	175.1	1.05

TABLE V

Structural Data for the Copolymers of Acrylamide (AM) with Sodium-3-Acrylamido-3-Methylbutanoate (NaAMB)

Sample Number	Composition (mol %)[a]		Blockiness (mol %)[b]		Alternation (mol %)[b]	Mean Sequence Length	
	AM	NaAMB	AM-AM	NaAMB-NaAMB	AM-NaAMB	μ_{AM}	μ_{NaAMB}
AMB-5-1	94.01	5.99	88.2	0.2	11.6	23.8	1.0
AMB-10-1	91.96	8.04	84.3	0.4	15.3	11.8	1.1
AMB-25-1	79.73	20.27	62.2	2.8	35.0	4.6	1.2
AMB-33-1	73.01	26.99	51.2	5.2	43.6	3.4	1.2
AMB-40-1	68.77	31.23	44.8	7.2	48.0	2.8	1.3
AMB-60-1	51.61	48.39	23.1	19.9	57.0	1.8	1.7
AMB-75-1	36.89	63.11	10.6	36.8	52.6	1.4	2.4

[a]from elemental analysis; [b]statistically calculated using reactivity ratios

TABLE VI

Calculated Structural Data for the AM-NaAMB Copolymer System

M1F	M2F	M1C	M2C	R	PABA	PAABAA	NABA	NAABAA
5.00	95.00	9.67	90.33	18.19	0.01	0.00	0.92	0.00
10.00	90.00	17.81	82.19	31.43	0.04	0.00	3.00	0.04
15.00	85.00	24.86	75.14	41.02	0.07	0.00	5.60	0.17
20.00	80.00	31.10	68.90	47.85	0.12	0.01	8.31	0.44
25.00	75.00	36.75	63.25	52.49	0.17	0.01	10.89	0.89
30.00	70.00	41.94	58.06	55.39	0.23	0.03	13.21	1.52
35.00	65.00	46.78	53.22	56.83	0.29	0.04	15.17	2.34
40.00	60.00	51.36	48.64	57.06	0.34	0.07	16.73	3.31
45.00	55.00	55.73	44.27	56.24	0.40	0.10	17.86	4.38
50.00	50.00	59.95	40.05	54.50	0.46	0.14	18.54	5.51
55.00	45.00	64.05	35.95	51.93	0.52	0.18	18.75	6.63
60.00	40.00	68.07	31.93	48.62	0.58	0.24	18.51	7.65
65.00	35.00	72.04	27.96	44.63	0.64	0.30	17.81	8.48
70.00	30.00	75.98	24.02	39.99	0.69	0.38	16.64	9.04
75.00	25.00	79.91	20.09	34.74	0.75	0.46	15.02	9.20
80.00	20.00	83.85	16.15	28.91	0.80	0.55	12.94	8.86
85.00	15.00	87.81	12.19	22.52	0.85	0.65	10.40	7.90
90.00	10.00	91.81	8.19	15.56	0.90	0.76	7.39	6.19
95.00	5.00	95.87	4.13	8.06	0.95	0.87	3.93	3.61

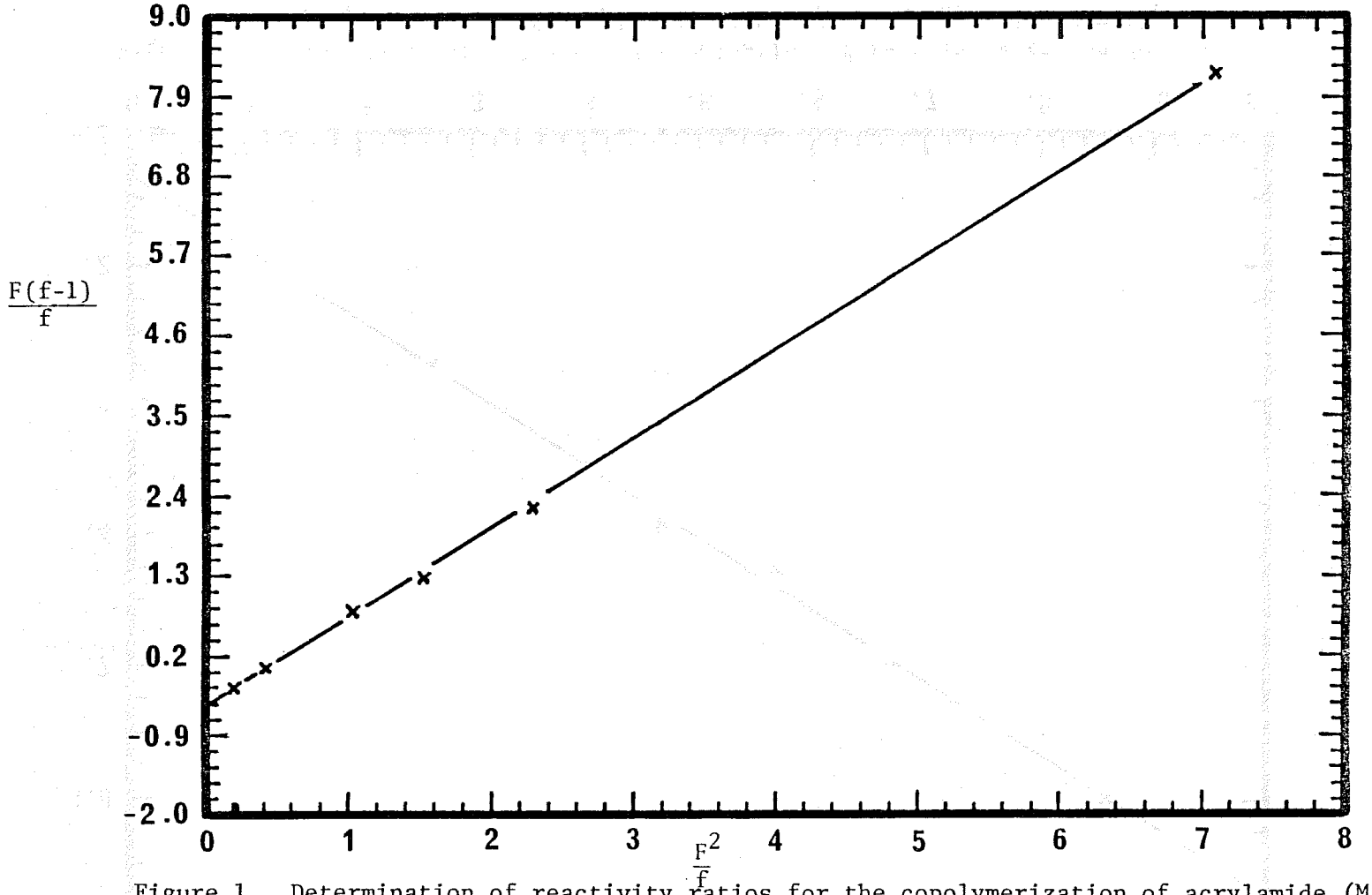

Figure 1. Determination of reactivity ratios for the copolymerization of acrylamide (M_1) with sodium-3-acrylamido-3-methylbutanoate (M_2) by the Fineman-Ross method.

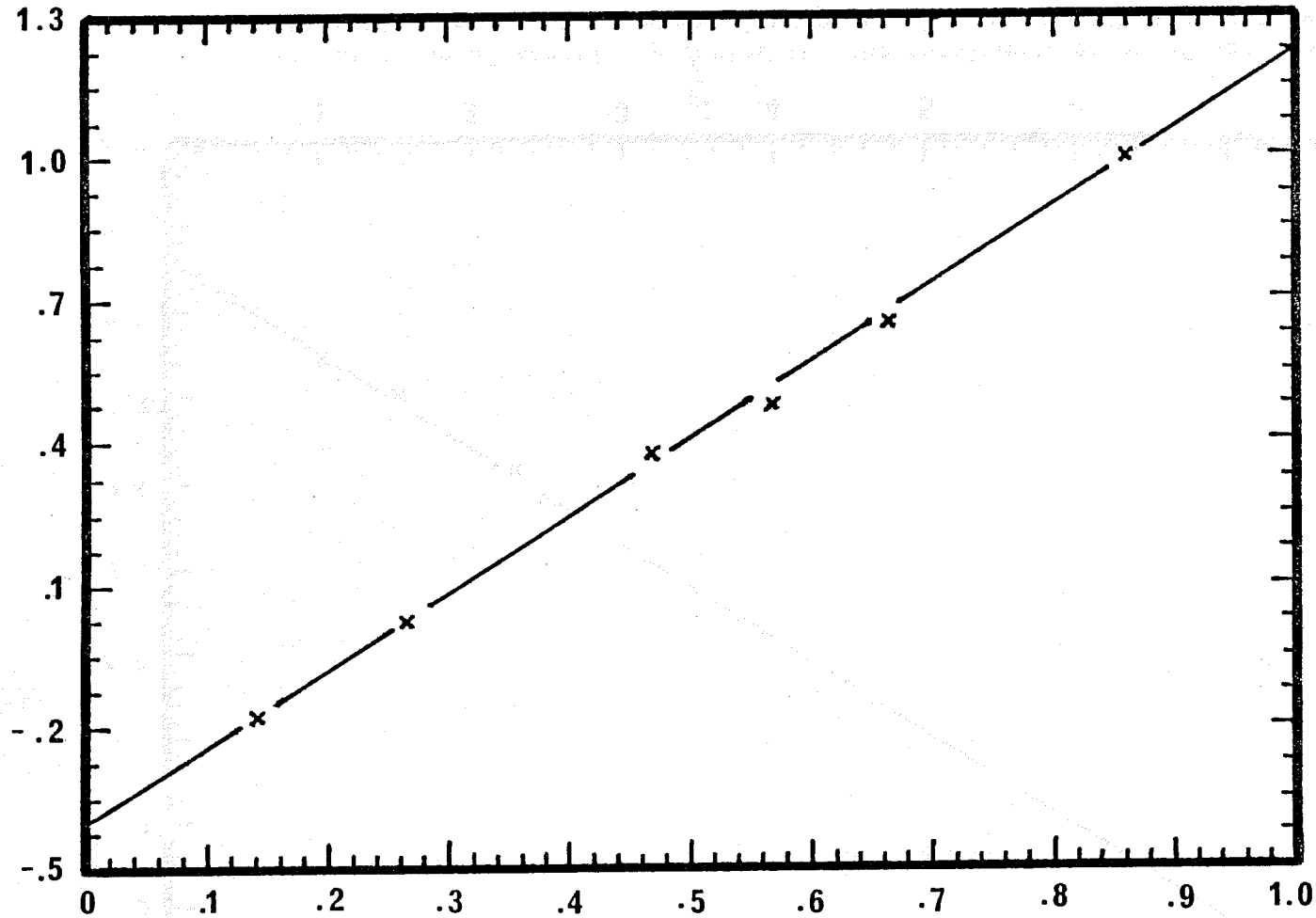

Figure 2. Kelen-Tüdos plot for the determination of reactivity ratios for the copolymerization of acrylamide with sodium-3-acrylamido-3-methylbutanoate.

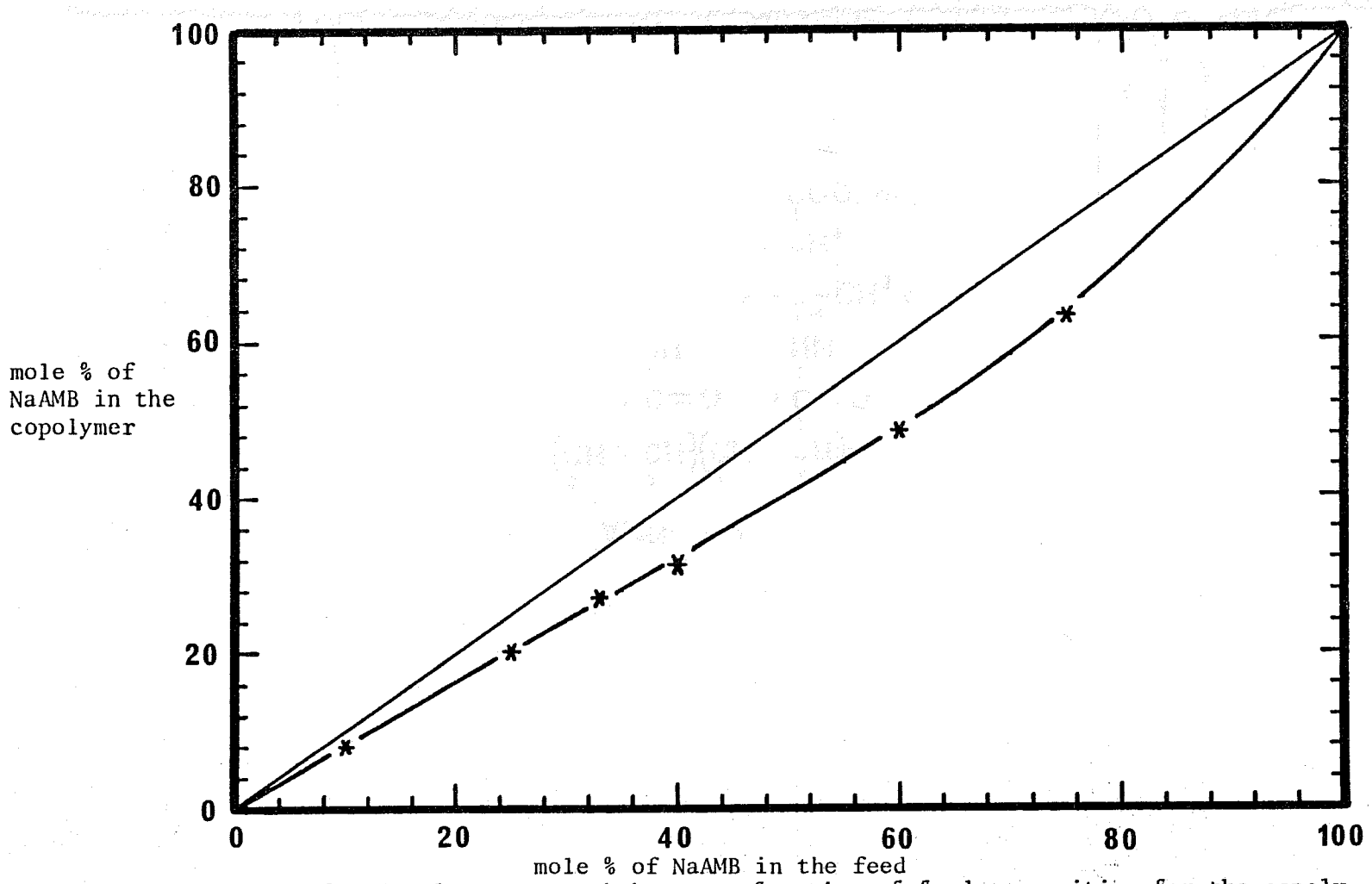

Figure 3. Copolymer composition as a function of feed composition for the copolymerization of acrylamide with sodium-3-acrylamido-3-methylbutanoate.

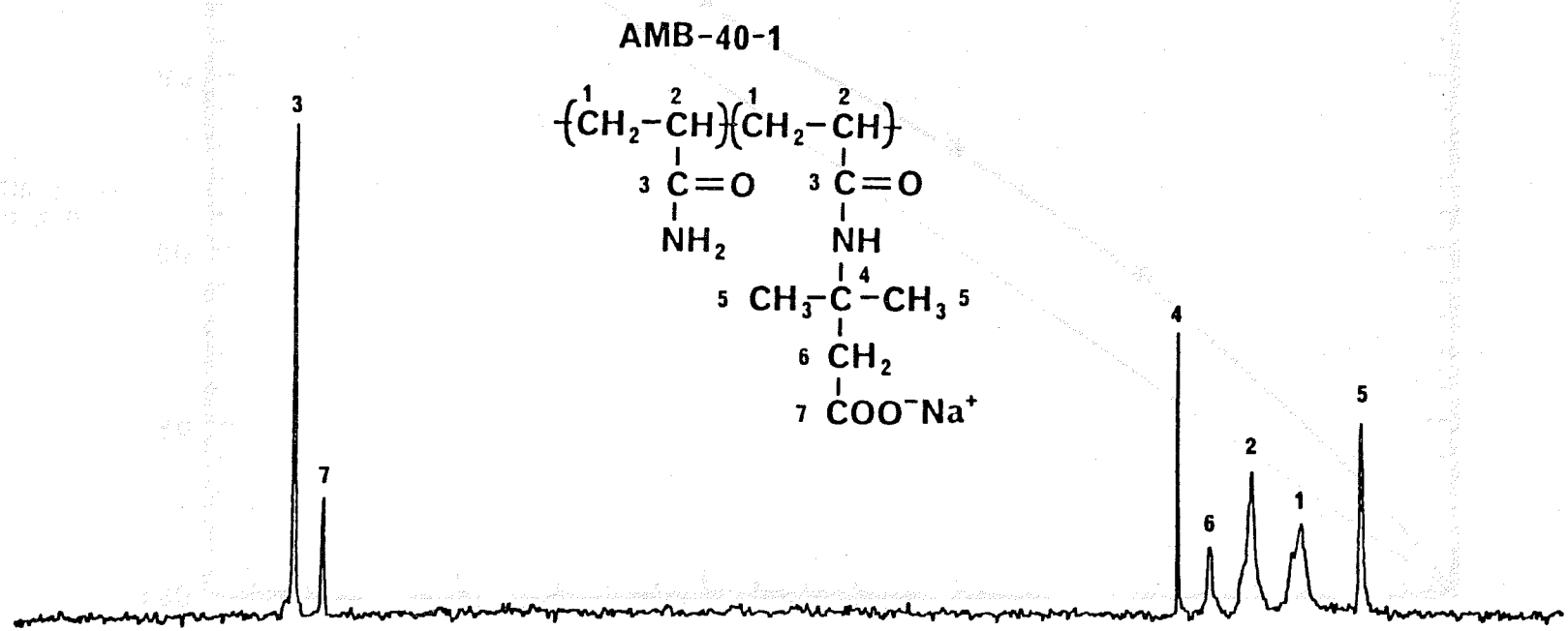

Figure 4. Typical C-13 NMR spectrum of a copolymer of acrylamide with sodium-3-acrylamido-3-methylbutanoate.

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CHAPTER III

COPOLYMERS OF ACRYLAMIDE WITH SODIUM-3-ACRYLAMIDO-3-METHYLBUTANOATE: SOLUTION PROPERTIES

C.L. McCormick, K.P. Blackmon, and D.L. Elliott

SYNOPSIS

Dilute solution properties of copolymers of acrylamide (AM) with sodium-3-acrylamido-3-methylbutanoate (NaAMB) of known molecular weight have been studied as a function of composition, temperature, time, pH, and added electrolytes. Phase separation and potentiometric studies have also been performed. The AM-NaAMB copolymers exhibit high solution viscosities, good salt tolerance, and moderate viscosity-temperature coefficients. In addition, these copolymers exhibit no phase separation in the presence of divalent cations as is common with many such carboxylated polyelectrolytes. These properties are due to favorable conformations in solution resulting from microstructure and hydrogen bonding effects.

INTRODUCTION

Anionic polyelectrolytes such as poly(acrylamide-co-sodium acrylates) are known to exhibit large reductions in solution viscosities as a function of added electrolytes, increased temperature, and changes in pH. Furthermore, these copolymers exhibit phase separation in the presence of divalent cations [1-4].

Recently we have initiated investigations of the solution behavior of copolymers of AM with NaAMB, a carboxylated analog of sodium-2-acrylamido-2-methylpropanesulfonate (NaAMPS). In this work we report the solution properties of the AM-NaAMB copolymers; in the previous chapter, details of synthesis and characterization are presented.

EXPERIMENTAL

Materials

Copolymers of acrylamide (AM) with sodium-3-acrylamido-3-methylbutanoate (NaAMB) were prepared at 30°C in aqueous solution at a pH of 9 using potassium persulfate as the initiator. Details of the synthesis, purification, and characterization

procedures have been reported in the previous chapter. The polymers were freeze-dried and stored in a vacuum dessicator.

Reagent grade sodium chloride and potassium chloride from J.T. Baker Co. were used without purification. Calcium chloride from J.T. Baker Co. was dissolved in water, filtered, and dried at 175°C prior to use. All aqueous salt solutions were prepared using deionized water.

Characterization

The copolymer compositions of all polymers were determined from elemental analysis and Carbon-13 NMR. Microstructures (Tables I and II) were calculated using the statistical methods reported in the previous chapter [23-24].

Viscosity Measurements

Stock solutions of sodium chloride (0.043, 0.086, 0.257, 0.514 M NaCl) were prepared by dissolving the appropriate amount of salt in deionized water in volumetric flasks. The required quantities of the dry copolymers were dissolved in the salt solutions. The dissolution process was generally complete within 1-2 days. Care was taken to avoid excessive shear during dissolution of the polymers.

Solution viscosities were measured in Cannon-Ubbelohde four-bulb shear dilution capillary viscometers (sizes 100 and 150). The shear rate constants and viscometer constants were provided by the manufacturer. Zero-shear intrinsic viscosities, $[\eta]_o$, were obtained by use of the Carreau model [5] to calculate zero-shear apparent viscosities which were then used in the Huggins equation to obtain zero-shear intrinsic viscosities by extrapolation of the reduced viscosity, $\eta sp/c$, to infinite dilution [6].

Solution viscosities were also measured using a Contraves Low Shear Viscometer at several copolymer concentrations and ionic strengths. The viscosities at 5 sec^{-1} were measured and compared to values projected from 4-bulb viscometer data obtained at 200-600 sec^{-1} and projected to 5 sec^{-1} by means of the Carreau model.

Turbidimetry Measurements [7]

Calcium chloride solutions were prepared gravimetrically and the concentrations verified by refractive index measurements. Polymer solutions ranging from 1.5 to 5.0 g/liter were prepared by dissolving the appropriate amount of polymer in deionized water. Salt concentrations were varied by addition of the appropriate amounts of solid salt (for higher salt concentrations) or known amounts of salt solution (for lower salt concentrations). The weight of the solution was determined both before and after each measurement, and water lost by evaporation was replaced.

A phototurbidimeter was used for the phase behavior measurements. The sample of polymer solution (30-36 ml) was stirred by a magnetic stirrer, and heated slowly ($<1^{o}C$/minute) by an air-heating system. A thermometer was used to record the temperature to within $\pm 0.1^{o}C$. The decrease in photoelectric current caused by a decrease in transmittance was used to determine the onset of precipitation. The cloud points (critical temperatures) were taken as the temperature at which precipitation was first observed. The process is reversible with temperature; however, two slightly different critical temperatures were observed depending upon whether the solution was cooled or heated. The average of the two observed temperatures was taken as the cloud point temperature, T_c.

Potentiometry Measurements

All measurements of pH were made using a Corning 130 pH-mV meter with an Orion pH electrode. The meter was standardized using a two-point calibration method. All measurements were conducted at $25 \pm 0.05^{o}C$.

Copolymer concentrations ranged from 0.5 to 1.5 g/l. Two titrations were performed on each sample: one with adjustment of ionic strength to 0.36M using potassium chloride and one with no ionic strength adjustment. Acid solutions less than 0.1 M were prepared and standardized using sodium carbonate. The titrations were conducted under nitrogen atmosphere.

The degree of ionization α, defined as the fraction of acid groups dissociated, was determined for each addition of titrant. For observed pH values between 4.5 and 8.5, no correction for free acid was needed, and α was calculated as C_{A^-}/C_{HA}, where C_{A^-} is the concentration of the dissociated carboxylic acid and C_{HA} is the total concentration of acid groups in the sample [8]. For pH values below 4.5 or above 8.5, corrections for free acid groups were calculated and found to be negligible. Values of the

dissociation constant (pKa) were calculated using the Henderson-Hasselbalch equation [9]:

$$pKa = pH - \log(\alpha/1-\alpha) \quad (1)$$

Because no corrections for free energy, etc. were made, all pKa values reported are apparent pKa values. Plots of pH vs. log (α/1-α) were made as well to determine pK and n values for each sample titration using the modified Henderson-Hasselbalch equation [10-11]:

$$pH = pK' + n \log(\alpha/1-\alpha) \quad (2)$$

These results are shown in Table III.

RESULTS AND DISCUSSION

Aging Effects

In order to properly assess the effects of temperature, added electrolytes, copolymer composition, and pH on the solution behavior of the AM-NaAMB polymers, aging studies were first conducted. For aqueous solutions of many water-soluble polymers, the effects of aging are seen in an initial increase in measured viscosity during dissolution followed by a gradual viscosity decrease. Such an aging effect has been observed for polyacrylamide [12-13] and partially hydrolyzed polyacrylamide [14-15], and may be attributed to changes in inter- and intrachain hydrogen bonding in aqueous solutions.

The aging effects for the AM-NaAMB copolymers, as well as the NaAMB homopolymer, were studied utilizing a size 100 Cannon-Fenske capillary viscometer at 30°C. The polymer concentrations in 0.257 M NaCl solutions were 0.15 g/dl, while the polymer concentrations in pure water were 0.05 g/dl. Figure 1 shows the aging effect for the NaAMB polymers in salt solutions. The reduced viscosities decrease slightly (about 1-6%) over the 30 day aging period. Figure 2 shows the aging effect on the polymers in water. The viscosity loss in pure water is slightly higher for the copolymers (about 5-9%); however, the NaAMB homopolymer undergoes a severe aging effect (about 44% reduction in reduced viscosity) over the 30 day aging period. Apparently the NaAMB homopolymer exhibits major conformational and/or hydrogen bonding

changes leading to a diminished hydrodynamic volume as a function of time.

Effects of Added Electrolytes on Intrinsic Viscosity

The effects of added sodium chloride on the zero-shear intrinsic viscosities of AM-NaAMB copolymers are shown in Figures 3 and 4. Since the copolymers of AM with NaAMB are polyelectrolytes, the expected viscosity decrease, due to shielding of ionic charges by increasing NaCl concentration, was observed. AMB-10-2, which contains about 8 mole % NaAMB, showed the greatest degree of salt tolerance with a viscosity decrease of about 24% in going from 0.043 M to 0.514 M NaCl. AMB, the homopolymer, had the greatest salt sensitivity exhibiting a viscosity decrease of about 63% in going from 0.043 M to 0.514 M NaCl. A comparable copolymer containing 9.5% of NaAMPS lost 53% of its intrinsic viscosity over the same range of salt concentrations. Since the NaAMB and NaAMPS copolymers differ only in the substitution of the carboxylate for the sulfonate group, the difference in salt response must reflect differing degrees of chain stiffness caused by hydrogen bonding effects. The calculated copolymer microstructures in terms of monomer sequence lengths are nearly identical (Table I) [25].

Effects of Copolymer Composition

The effects of copolymer composition on the zero-shear intrinsic viscosities of the AM-NaAMB copolymers in 0.514M NaCl and on the apparent viscosities of the polymers in pure water are shown in Figures 5 and 6, respectively. The zero-shear intrinsic viscosities of the polymers in 0.514 M NaCl decrease with increasing NaAMB content. Since the molecular weights of the copolymers are similar, the viscosity decrease can be attributed to composition and microstructure. The copolymer containing about 20 mole % NaAMB has a slightly lower intrinsic viscosity than expected; this may be due to a more compact coil conformation owing to its specific microstructure and local interactions. It should be noted that the copolymer with about 8 mole % NaAMB, which exhibits the highest viscosity, has a mean sequence length ratio of 10.7 AM units per NaAMB unit.

It is not possible to obtain intrinsic viscosities for the AM-NaAMB copolymers in pure water by extrapolation to zero shear rate due to the overwhelming polyelectrolyte effects. Thus, a comparison of apparent viscosities at 100 sec^{-1} can be made. There are no significant differences in the viscosities of the AM-NaAMB copolymers under these conditions; therefore, it can be concluded that in pure water the viscosities are controlled by polyelectrolyte effects rather than compositional effects.

Effects of Temperature

The effects of temperature on the intrinsic viscosities of representative AM-NaAMB copolymers in 0.257 M NaCl are shown in Figure 7, while the effects of temperature on the apparent viscosities of these same polymers in water are shown in Figure 8. The zero-shear intrinsic viscosities in 0.257 M NaCl and the apparent viscosities in water decrease with increasing temperature. The decreases in viscosities with increasing temperature indicate a decrease in the hydrodynamic volume of the polymer molecules, which in turn, indicates conformational and solvent associational changes.

Effects of pH

Since the copolymers of AM with NaAMB contain the charged salt of a weak acid, the effects of pH on the zero-shear intrinsic viscosities should be quite evident. Table IV illustrates the dependence of the viscosity on pH for the AM-NaAMB copolymers, as well as the NaAMB homopolymer. The zero-shear intrinsic viscosities increase as the pH increases, corresponding to an increasing degree of ionization of the carboxylate groups leading to more extended chain structures due to electrostatic repulsions. The homopolymer, AMB, precipitates at a pH of about 5.4 since enough of the carboxylate groups are in the acid form to render the polymer insoluble. The pH studies were conducted in 0.514 M NaCl to ensure total counterion shielding of charged carboxylate units.

Effects of Shear Rate

The copolymers of AM with NaAMB exhibit high viscosities and pseudoplastic behavior in deionized water. Addition of increasing amounts of sodium chloride lowers both viscosity and pseudoplasticity. Figure 9 illustrates the effect of shear rate on a typical copolymer (AMB-40-2) in the low shear region obtained by a Contraves Low Shear Viscometer. It should be noted that essentially Newtonian behavior is observed at a relatively high salt concentration and low polymer concentration.

Turbidimetry

Many polymers and copolymers containing carboxylate and sulfonate groups in their side chains are known to undergo phase separation in the presence of divalent salts such as calcium chloride, magnesium chloride, or barium chloride [16-21]. No phase separation was found to occur for copolymers of AM and

NaAMB, even those containing up to 63 mole % NaAMB units; however, the NaAMB homopolymer did undergo phase separation. The critical temperature was found to decrease with increasing calcium chloride concentration as shown in Figure 10. The phase separation curve is found at temperatures 20-25°C higher than the curves for acrylamide-sodium acrylate copolymers, suggesting that even the NaAMB homopolymer is more stable toward calcium ion binding than sodium acrylate copolymers. In copolymers of acrylamide with sodium-2-acrylamido-2-methyl propanesulfonate (NaAMPS), the strong acidity (and weak ion-binding) of the sulfonate group is thought to be the reason for lack of phase separation. However, in NaAMB copolymers, the geometry of the chain is also important, since the NaAMB carboxylate groups are known to be weaker acids.

Potentiometry

The apparent pKa values calculated for the NaAMB polymers using the Henderson-Hasselbalch and the modified Henderson-Hasselbalch equation are shown in Tables II and III.

The potentiometric titrations were conducted in water and in 0.36M KCl to observe conformational and pKa differences in the different solvents. Several differences in the pKa values were observed: (1) The KCl solutions give lower pKa values than the water solutions. This may be explained by the slight acidity of the KCl solutions (pH = 5.8 - 6.4 for a 5% KCl solution) and the greater stability of the anionic groups of the copolymers caused by association with the potassium cations. Furthermore, the polymer chains are much more tightly coiled in an electrolyte solution and, thus, more hydrogen bonding is possible between the carboxylate groups and acrylamide units in the chain due to their closer proximity. (2) The ΔpKa values shown in Table II are greatly decreased in the salt solutions. This results from the decreased electrostatic repulsion of the charges on the polymer chains due to the shielding effects of the potassium cations. The pKa vs. α curves in Figure 11, for several of the NaAMB series in 0.36 M KCl, demonstrate a much flatter profile than the same copolymers in water due to the removal of charge-charge effects in the salt solutions.

The pKa values in pure water show the greater conformational changes in the absence of constant ionic strength. At low α when there is little charge-charge repulsion, the polymers and copolymers appear to be in a compact, random coil conformation. As α increases, the repulsion between charges increases and the conformation of the chains changes to an extended, almost rod-like molecule with the maximum size coming at $\alpha=1$ (complete dissociation). The viscosity data show that at pH > 8 ($\alpha=1$), the viscosity is much higher due to this extended chain conformation; furthermore, the viscosities decrease as the pH decrease. Of

course, these conformational changes are greatly diminished in salt water since the added electrolyte shields the charges on the chain, resulting in a compact random coil.

It can be observed as well from Tables II and III that the pKa values tend to increase with increasing NaAMB content in the copolymers. This behavior is expected for two reasons [22]. First, the increased electrostatic repulsion with increasing NaAMB content causes decreased stability of the ionic groups, thereby raising the pKa. Secondly, the less NaAMB present, the more the acrylamide units are available for hydrogen bonding which will further stabilize the anion and lower the pKa. This can be observed in Table II by comparing the copolymer sequence distributions shown where A is an acrylamide group and B is a NaAMB unit. Greater amounts of ABA will give lower pKa values, while increased BBB triads will cause greater charge-charge interaction and thus give higher pKa values. The sequences shown are calculated statistically based on reactivity ratios, run number, and copolymer composition [23].

The slope and intercept from plots of pH vs. $\log(\alpha/1-\alpha)$ were made from the modified Henderson-Hasselbalch (equation 2). The n value, which is the slope of the line, is a measure of the average electrostatic repulsion between charges on the chain. The pK value, which is the intercept of the line, is another means of calculating the apparent pKa. The two pKa values show good correlation with one another. The results are shown in Table III. Note that in water the n values are higher, indicating that the pKa values in this medium are more affected by interactions between charges when compared to those in 0.36 M KCl. Notice also that the n values increase in water with increasing carboxylate group content. This again is a result of greater charge-charge repulsion due to a higher charge density on the chains.

CONCLUSIONS

Copolymers of AM-NaAMB have been shown to have high viscosities, good salt stability and surprising resistance to divalent ion binding. AMB-10-2 showed the greatest salt tolerance, while the NaAMB homopolymer showed the least salt tolerance. All of the NaAMB polymers exhibited viscosity decreases with increasing temperature and decreasing pH. Additionally, all of the NaAMB copolymers showed slight viscosity decreases as a function of time, while the NaAMB homopolymer exhibited a large decrease in viscosity (44% decrease) in pure water due to aging effects. The copolymers of NaAMB exhibit pKa values which are similar to hydrolyzed polyacrylamides. These values decrease with decreasing NaAMB content, a result which may be due to hydrogen bonding with acrylamide units.

The observed viscosities for the different copolymers is likely to be a function of the different microstructures of the copolymers. The copolymer sequence distributions suggest that lower pKa values occur when greater quantities of acrylamide units are present, and a similar relationship may be responsible for the higher salt tolerance of AMB-10-2. The viscosity, salt tolerance, divalent ion binding, and apparent pKa data suggest the importance of local interactions specified by copolymer microstructure. These include hydrogen bonding, hydrophobic, and steric interactions along the macromolecular chain.

TABLE I

Structural Data for the Copolymers of Acrylamide (AM) with Sodium-3-Acrylamido-3-Methylbutanoate (NaAMB)

Sample Number	Composition (mol%)[a]		Blockiness (mol%)[b]		Alternation (mol%)[b]	Mean Sequence Length	
	AM	NaAMB	AM-AM	NaAMB-NaAMB	AM-AMB	μ_{AM}	μ_{NaAMB}
AMB-5-1	94.01	5.99	88.2	0.2	11.6	23.8	1.0
AMB-10-1	91.96	8.04	84.3	0.4	15.3	11.8	1.1
AMB-25-1	79.73	20.27	62.2	2.8	35.0	4.6	1.2
AMB-33-1	73.01	26.99	51.2	5.2	43.6	3.4	1.2
AMB-40-1	68.77	31.23	44.8	7.2	48.0	2.8	1.3
AMB-60-1	51.61	48.39	23.1	19.9	57.0	1.8	1.7
AMB-75-1	36.89	63.11	10.6	36.8	52.6	1.4	2.4

[a]from elemental analysis; [b]statistically calculated using reactivity ratios

TABLE II

Correlation Between pKa and Copolymer Sequence Distribution

Sample	pKa (H_2O)	ΔpKa	pKa (0.36 M KCl)	ΔpKa	P_{ABA}	P_{BBB}	$P_{BBA-ABB}$
AMB-10-2	5.23±0.05	0.08	4.79±0.06	0.10	0.946	0.001	0.053
AMB-25-2	5.31±0.06	0.22	4.74±0.05	0.10	0.754	0.018	0.228
AMB-40-2	5.75±0.08	0.28	4.90±0.04	0.05	0.615	0.047	0.338
AMB-60-2	5.88±0.05	0.55	5.01±0.04	0.12	0.339	0.175	0.486
AMB-75-2	6.19±0.06	0.46	5.10±0.05	0.12	0.205	0.299	0.495
AMB	6.86±0.07	0.41	5.49±0.05	0.20			

TABLE III

Acid Strength (pKa) of Acrylamide-NaAMB Copolymers

Sample	H_2O				0.36 M KCl			
	pKa_{app}	n	pK'	Corr. Coeff.	pKa_{app}	n	pK'	Corr. Coeff.
AMB-10-2	5.23	1.1	5.23	0.99	4.79	1.1	4.71	0.99
AMB-25-2	5.31	1.4	5.29	0.99	4.74	1.1	4.69	0.99
AMB-40-2	5.75	1.5	5.74	0.99	4.90	1.1	4.82	0.99
AMB-60-2	5.89	1.8	5.96	0.99	5.01	1.1	5.03	0.99
AMB-75-2	6.19	1.7	6.19	0.99	5.10	1.0	5.18	0.98

TABLE IV

Zero Shear Intrinsic Viscosity Data for Copolymers of Acrylamide (AM) with Sodium-3-Acrylamido-3-Methylbutanoate (NaAMB) in 0.514 M NaCl Solutions of Various pH values at 30°C

Sample	Mole % NaAMB	pH	$[\eta]_0$ (dl/g)
AMB-10-2	8.37	4	23.8
		7	26.0
		9	39.5
AMB-40-2	31.41	4	15.4
		7	16.2
		9	35.4
AMB-60-2	49.77	4	11.1
		7	11.9
		9	27.9
AMB-75-2	63.58	4	5.7
		7	23.4
		9	26.8
AMB	100	7	3.8
		9	5.4

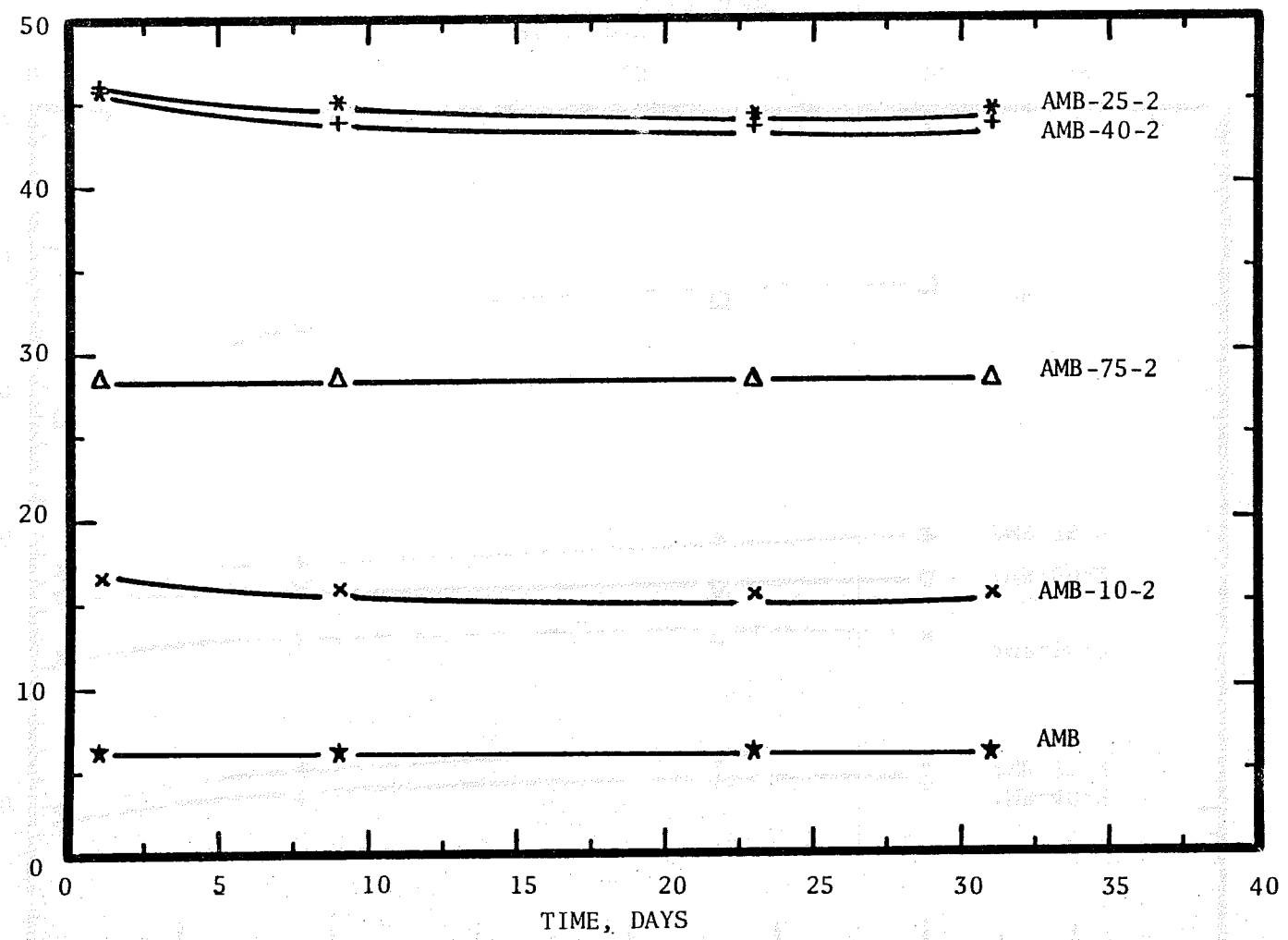

FIGURE 1. Aging of AM-NaAMB copolymers and NaAMB homopolymer in 0.257 M NaCl (aq.) at 30°C

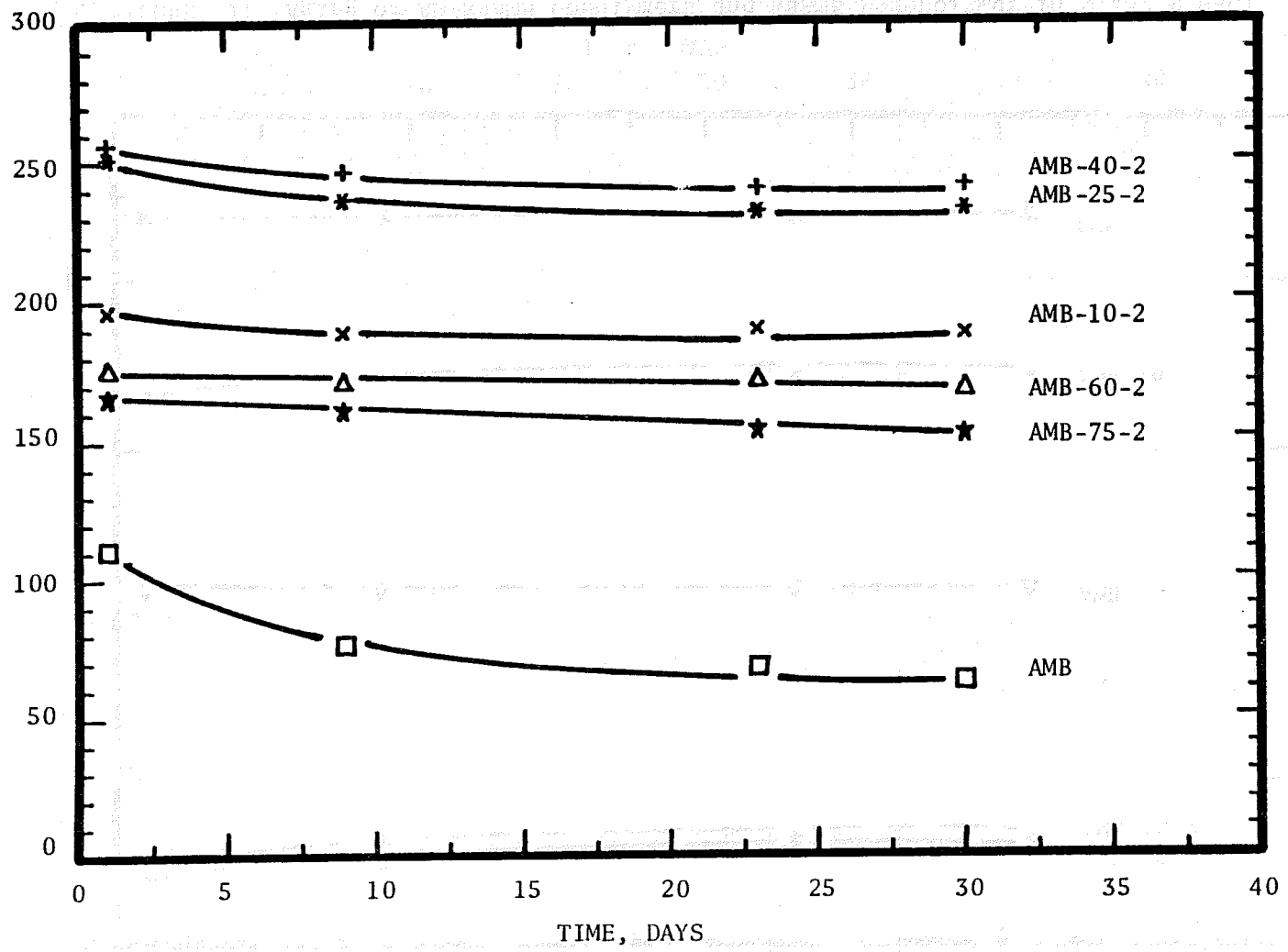

FIGURE 2. Aging of AM-NaAMB copolymers and NaAMB homopolymer in deionized water at 30°C.

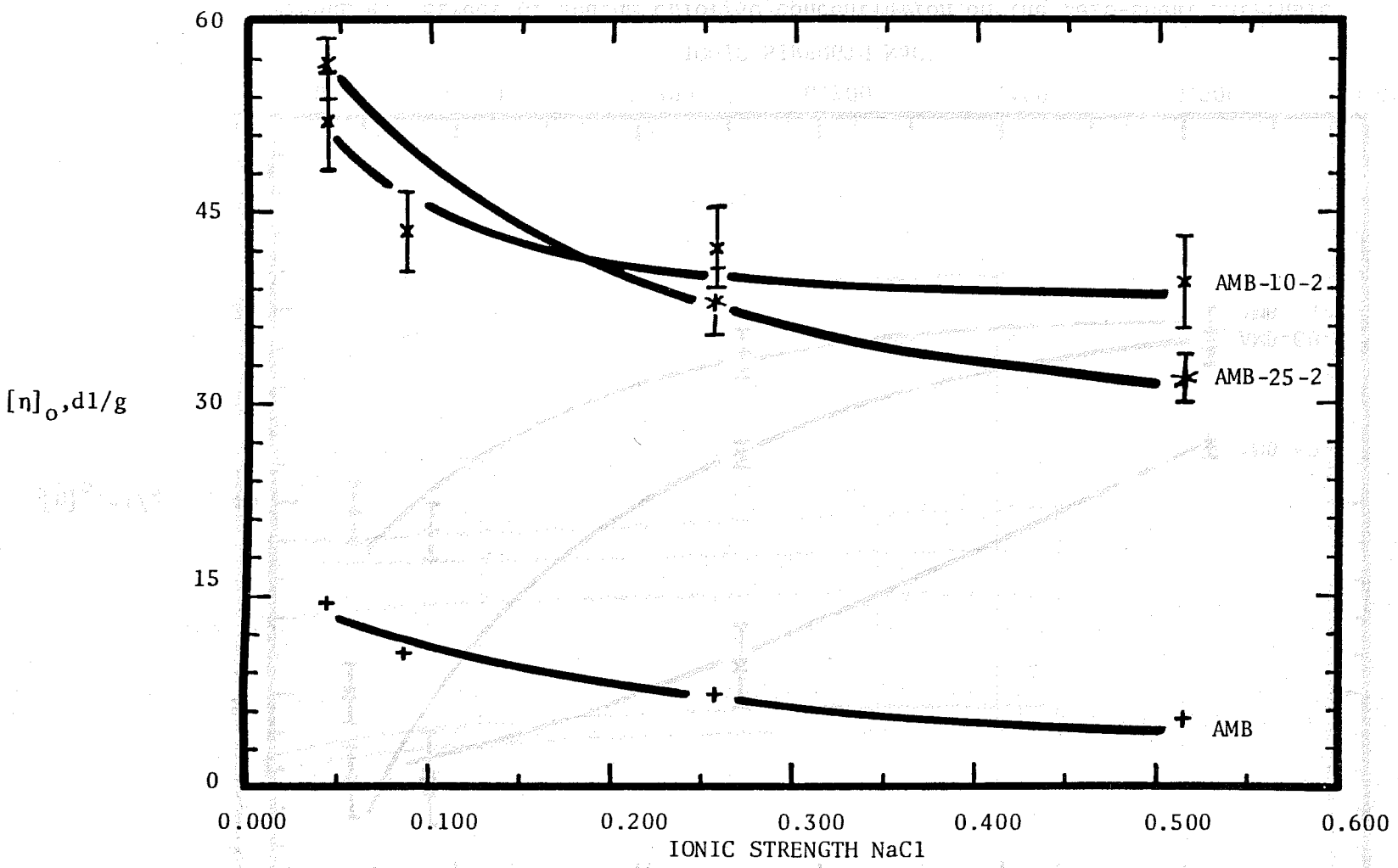

FIGURE 3. Effect of sodium chloride concentration on the zero-shear intrinsic viscosities of AM-NaAMB copolymers and NaAMB homopolymer at 30°C.

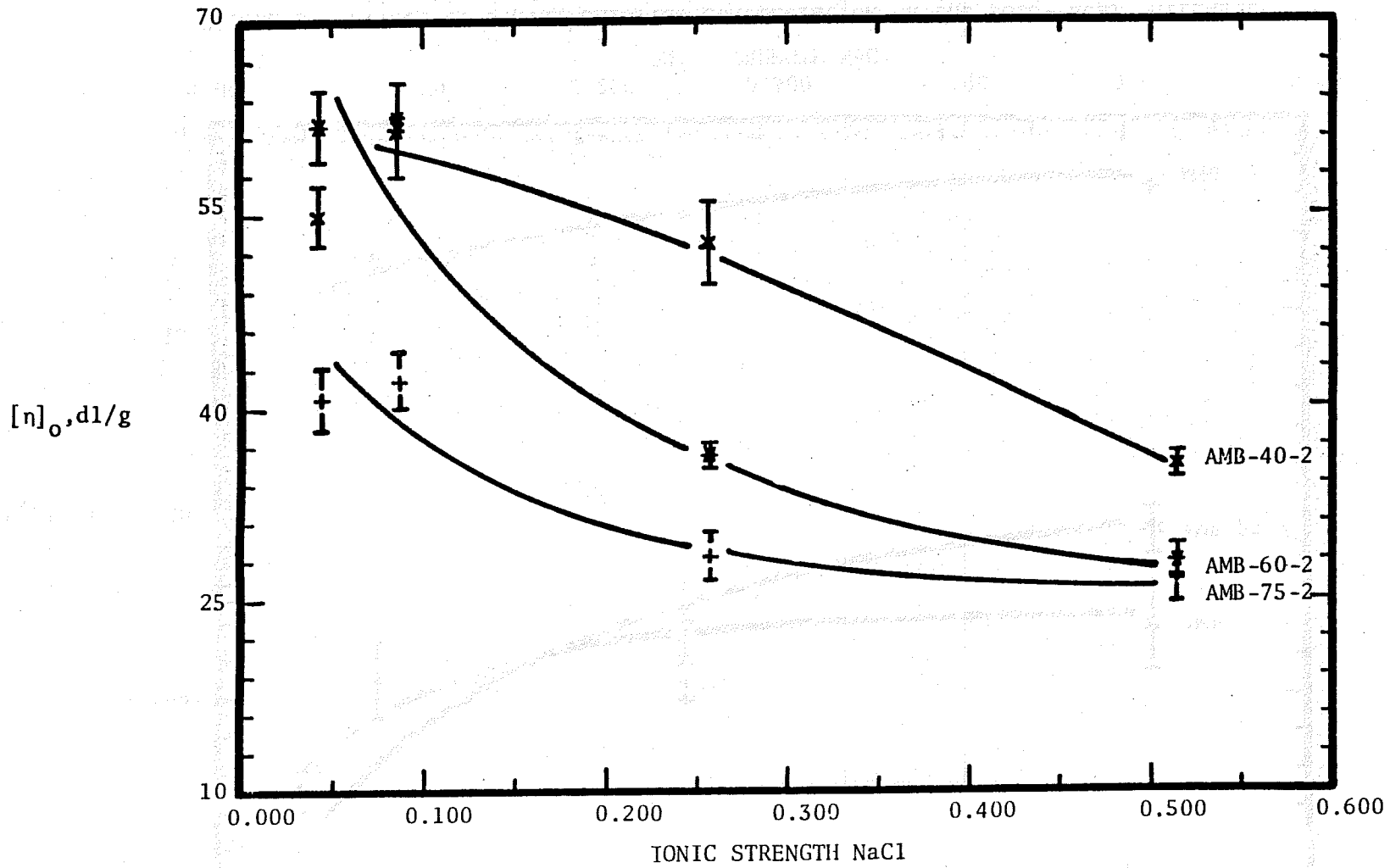

FIGURE 4. Effect of sodium chloride concentration on the zero-shear intrinsic viscosities of AM-NaAMB copolymers at 30°C.

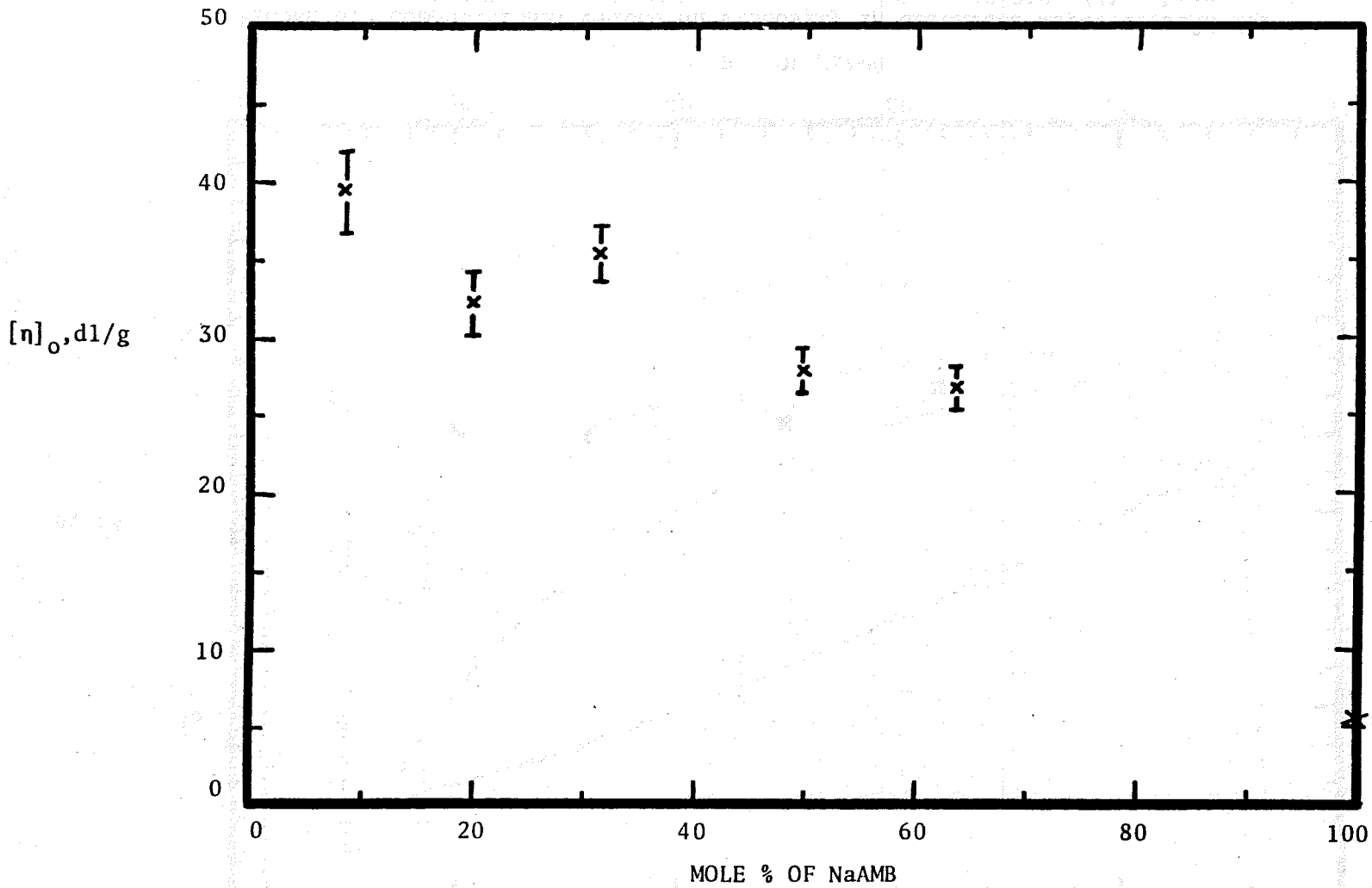

FIGURE 5. Compositional effect on zero-shear intrinsic viscosity in 0.514 M NaCl (aq.) at 30°C for AM-NaAMB copolymers.

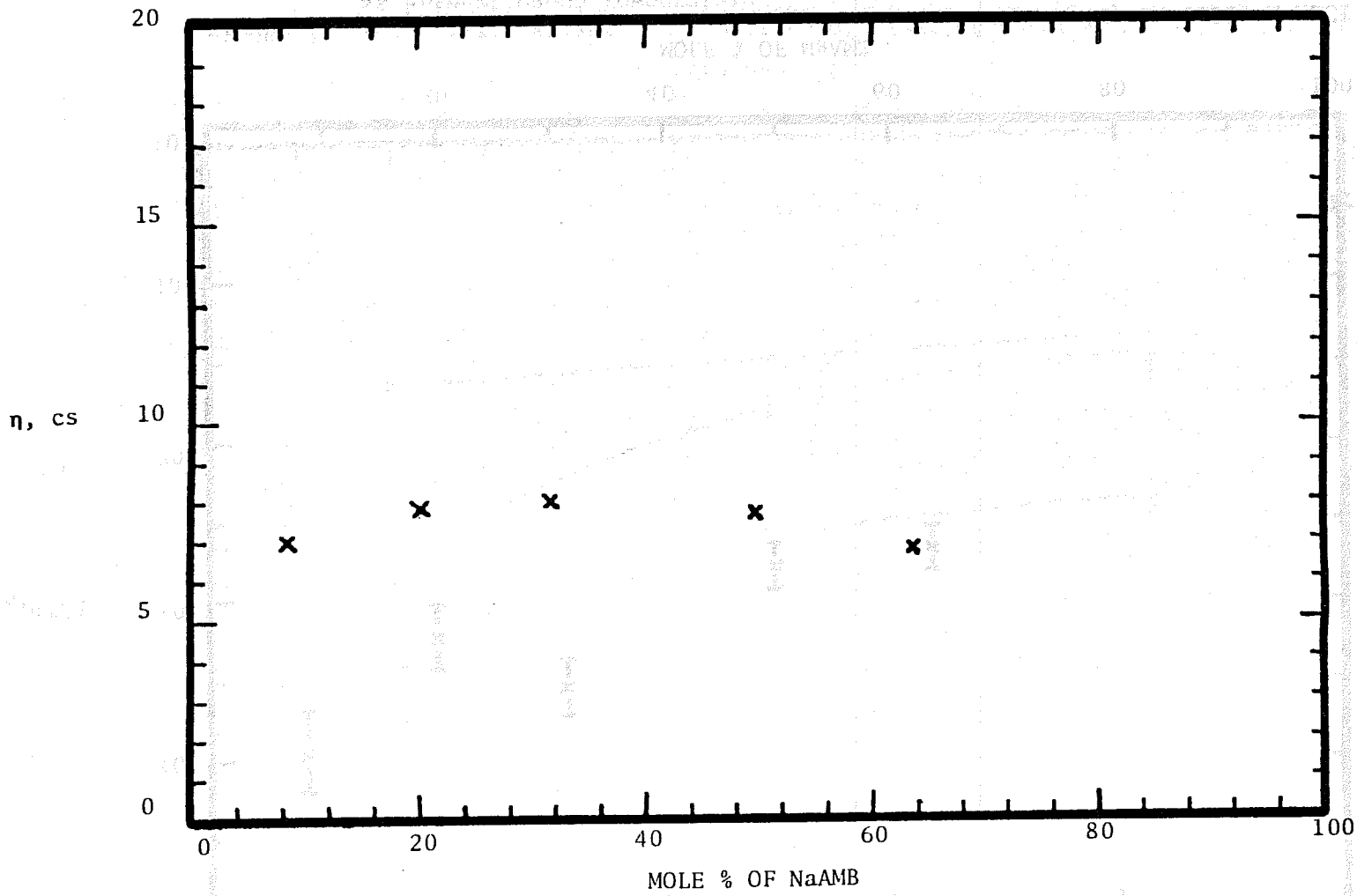

FIGURE 6. Compositional effect on viscosity in deionized water at 30°C for AM-NaAMB copolymers (polymer concentration = 0.019 g/dl, shear rate = 100 sec^{-1}).

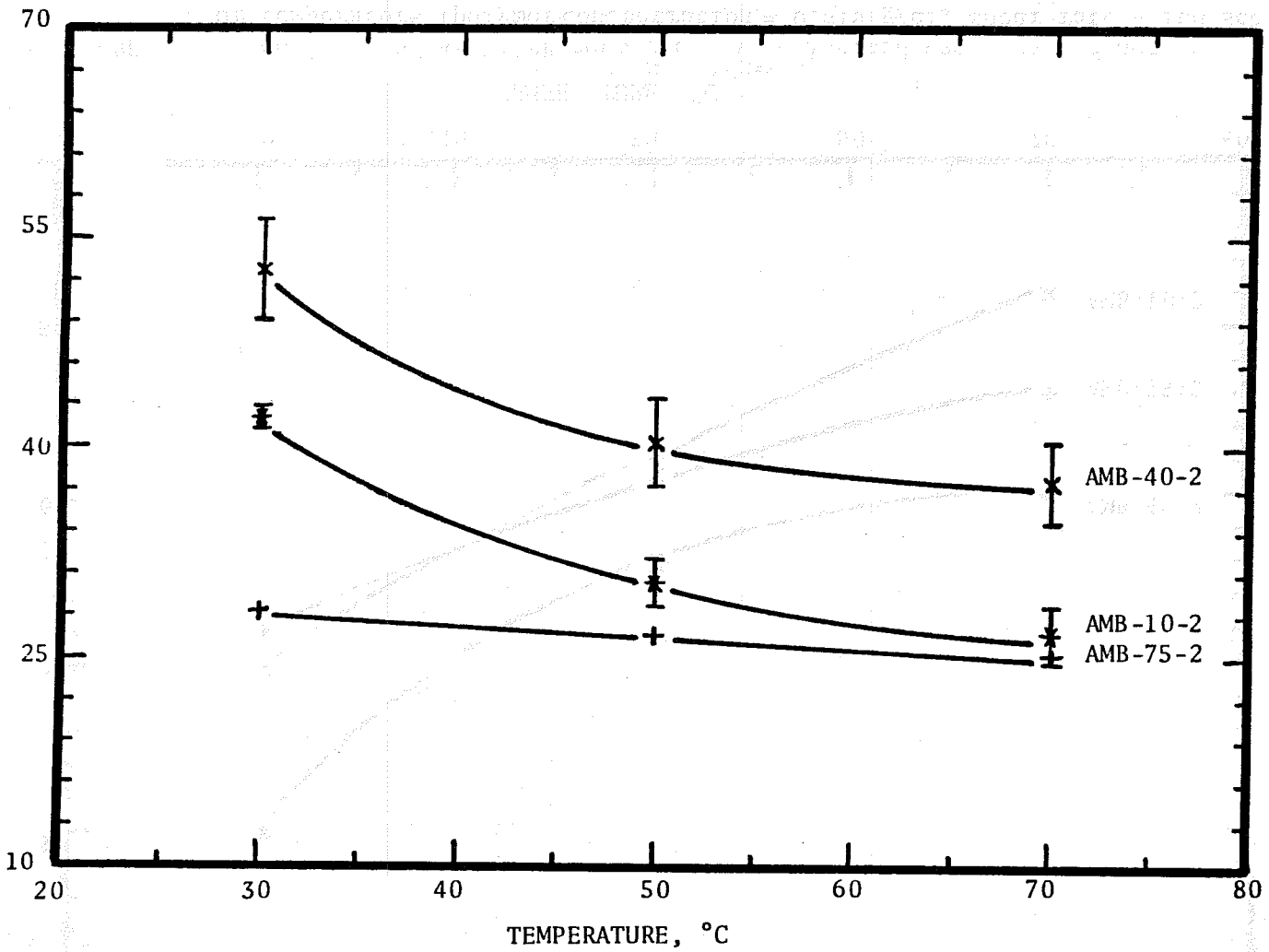

FIGURE 7. Zero-shear intrinsic viscosities of AM-NaAMB copolymers in 0.257 M $NaCl_{(aq.)}$ as a function of temperature.

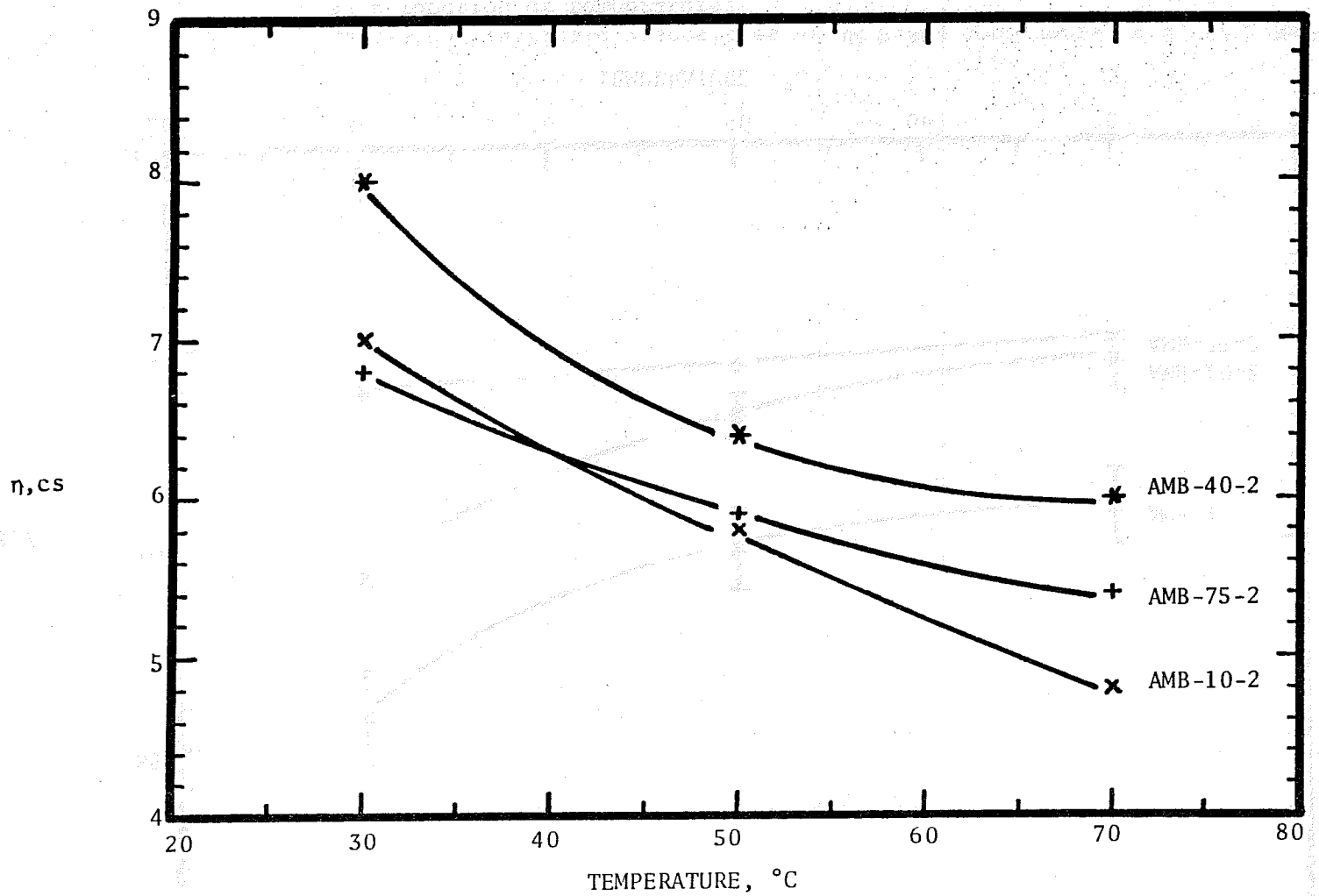

FIGURE 8. Viscosities of AM-NaAMB copolymers in deionized water as a function of temperature (polymer concentration = 0.019 g/dl, shear rate = 100 sec^{-1}).

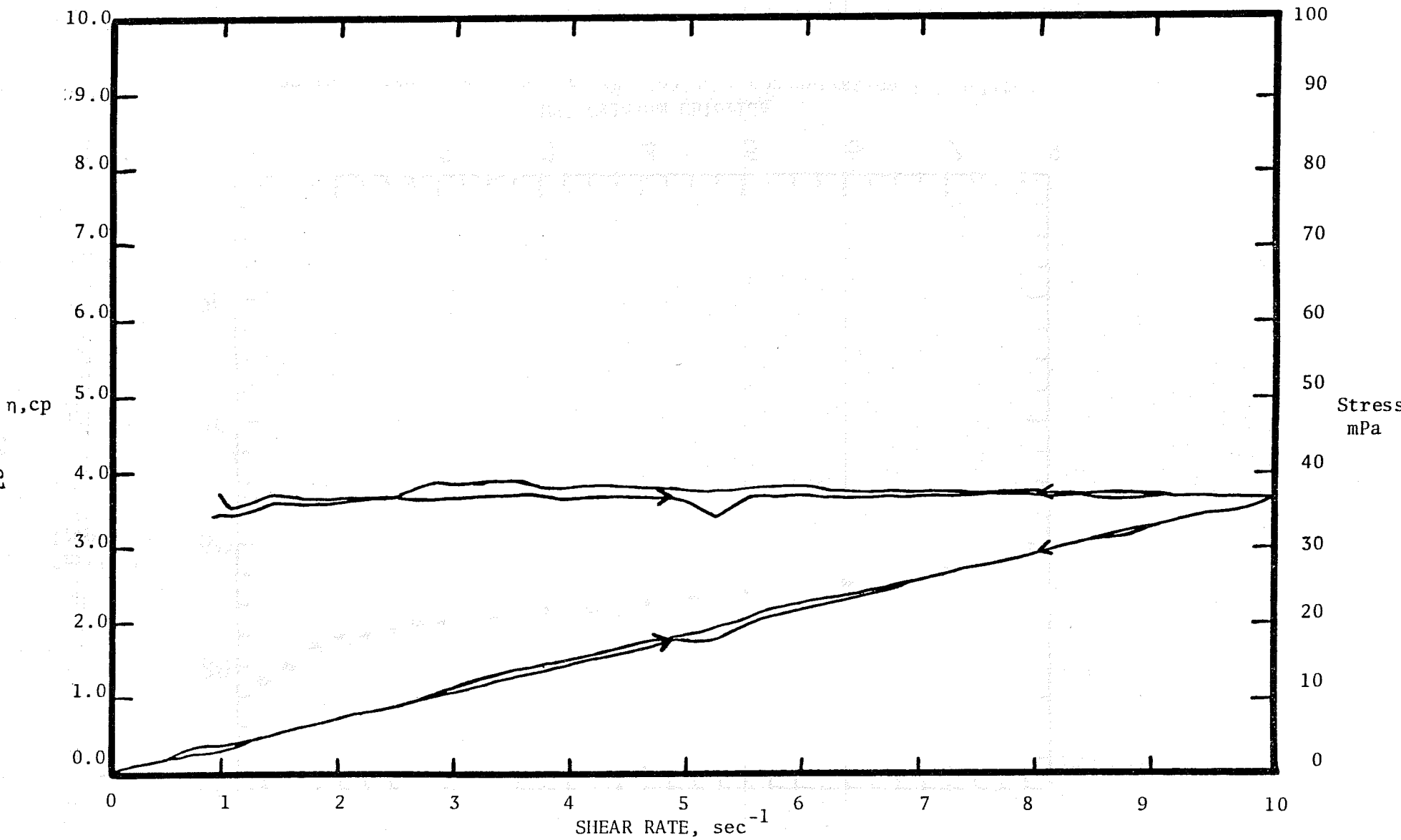

FIGURE 9. Viscosity of AMB-40-2 as a function of shear rate in the low shear region in 0.514 M NaCl (aq.) at 25°C (polymer concentration = 0.05 g/dl).

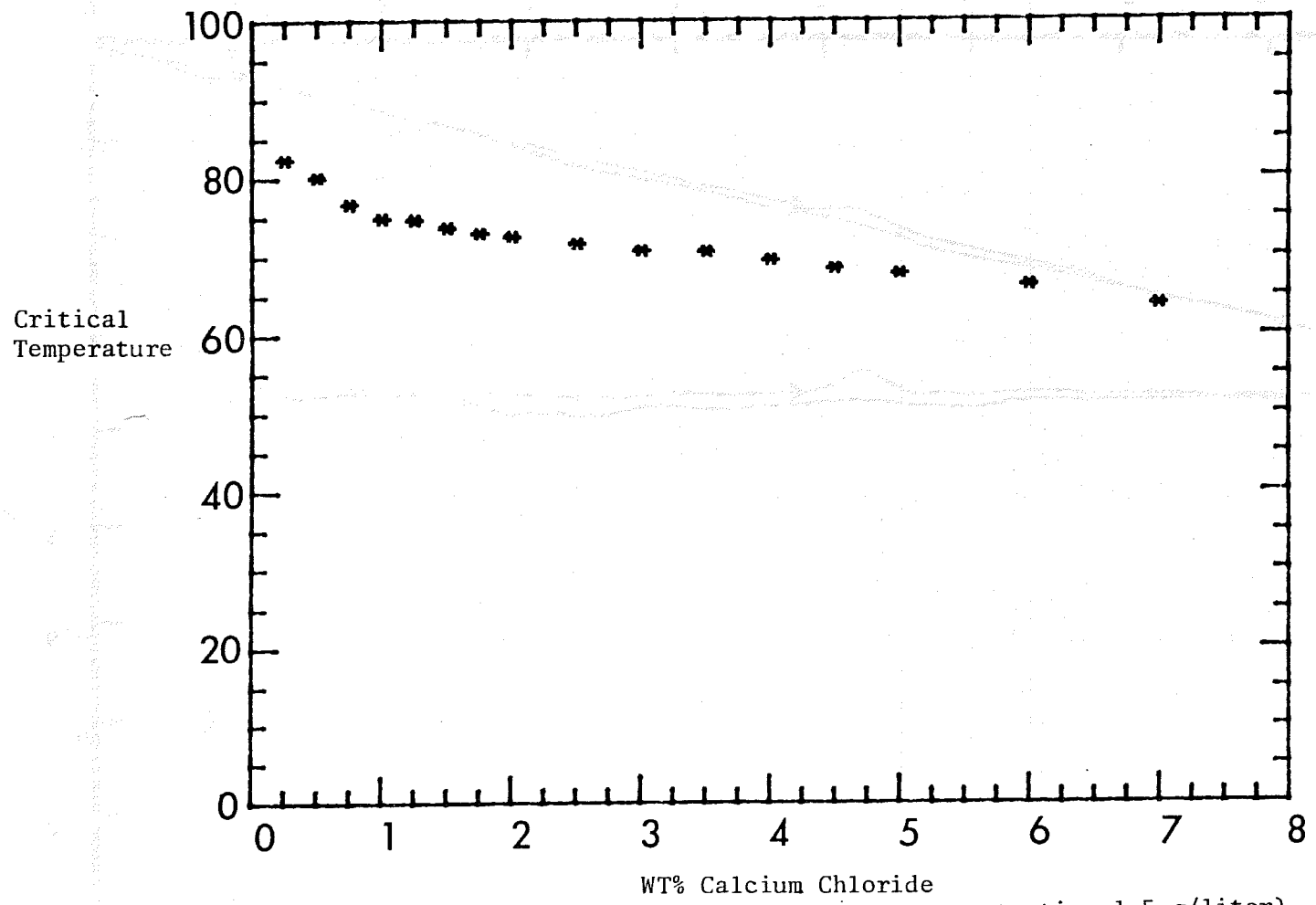

FIGURE 10. Phase separation of AMB. (polymer concentration 1.5 g/liter)

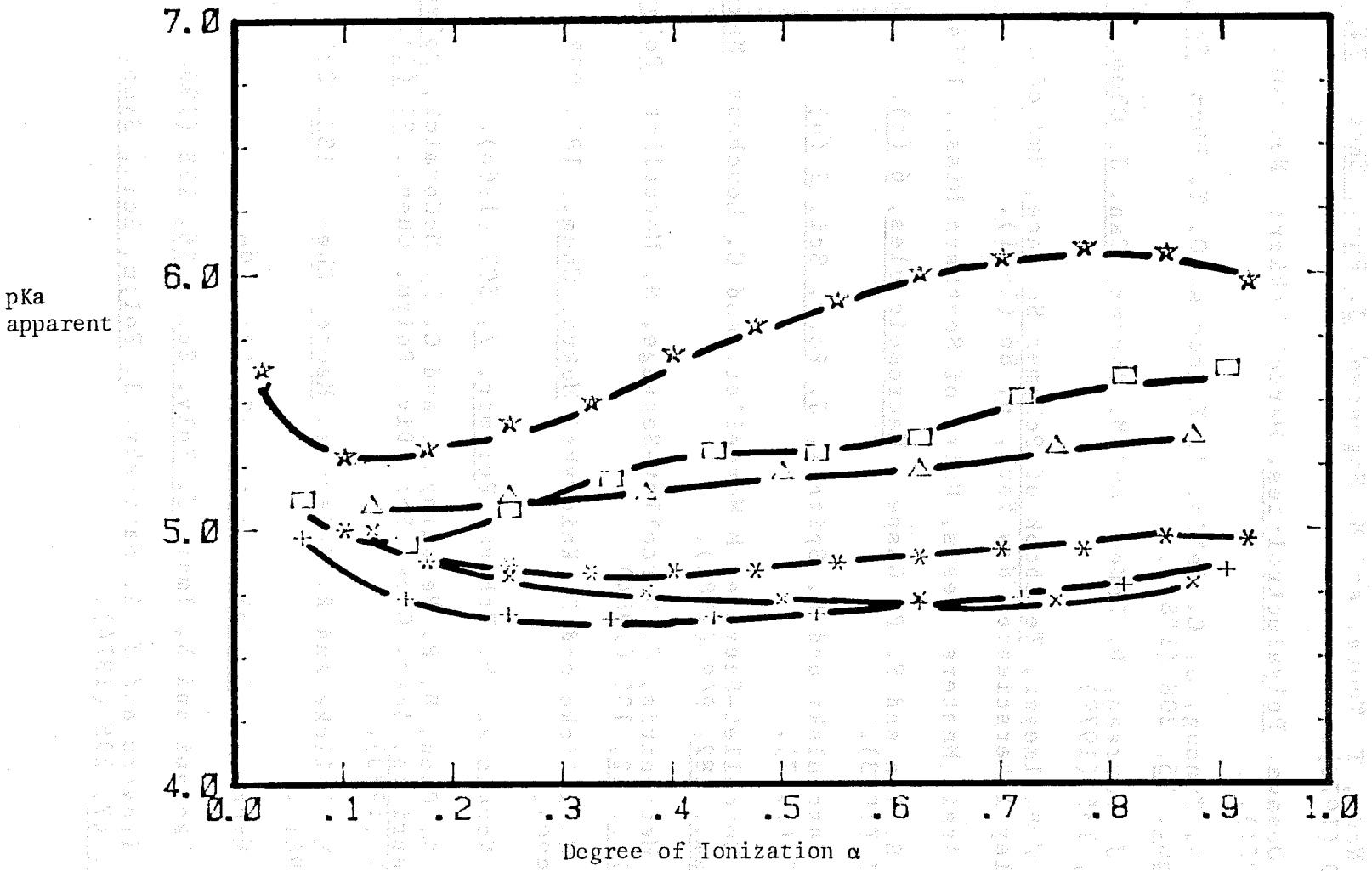

FIGURE 11. Potentiometric titration of AM-NaAMB copolymers - pKa vs. α +-AMB-10+2 in 0.36 M KCl; x-AMB-25-2 in 0.36 M KCl; *-AMB-40-2 in 0.36 M KCl; Δ-AMB-10-2 in H_2O; □-AMB-25-2 in H_2O; ☆-AMB-40-2 in H_2O.

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CHAPTER IV

POTENTIOMETRIC AND TURBIDIMETRIC STUDIES OF WATER-SOLUBLE COPOLYMERS OF ACRYLAMIDE: COMPARISON OF NaA, NaAMB, and NaAMPS COPOLYMERS

C. L. McCormick and D. L. Elliott

SYNOPSIS

Comparisons of copolymers of acrylamide (AM) with sodium acrylate (NaA), sodium 3-acrylamido-3-methylbutanoate (NaAMB), and sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS) were made with respect to their phase separation behavior in aqueous solutions and their potentiometric properties. Copolymers of N,N-dimethyl acrylamide (DMAM) with NaA, NaAMB, and NaAMPS were synthesized and compared to each other and to the acrylamide series concerning the same properties. Phase separation in the presence of calcium ions is found to be a function of the length of the side chain, the acidity of the ionic group, and the local microstructure of the copolymers. Copolymers of NaAMPS and NaAMB with AM and DMAM are found to remain soluble in aqueous calcium chloride solutions up to 100°C.

Correlations between copolymer sequence distributions and pKa values suggest that hydrogen bonding with acrylamide units in the copolymer lowers the pKa value by stabilizing the charged groups. This hydrogen bonding and the length of the side chain of the NaAMB and NaAMPS monomers appear to explain the observed phase behavior and pKa values.

INTRODUCTION

In previous studies in our laboratories, copolymers of acrylamide (AM) with sodium acrylate (NaA), sodium 3-acrylamido-3-methylbutanoate (NaAMB), and sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS) have been found to be useful as viscosity-modifying agents in enhanced oil recovery (1). Further experimentation involving phase separation behavior studies and potentiometric titrations has been performed in an effort to relate local ionic effects, copolymer sequence distribution, and other molecular interactions (such as hydrogen bonding) to the macromolecular

properties such as viscosity and salt sensitivity previously observed.

The purpose of this research is to compare the phase behavior of the three AM copolymer series and the three DMAM series in terms of the nature of the anion-containing side group, the hydrogen bonding of the anion with AM units in the copolymer, and the local microstructure of the copolymers. The observed phase behavior is correlated to the acidities of the AM and DMAM series as determined from the potentiometric studies.

EXPERIMENTAL

Materials

Poly(acrylamide-co-sodium acrylates) were prepared by alkaline hydrolysis of polyacrylamide (Molecular weight=5 million)(HPAM series) and free radical polymerization of the two monomers (NaA series). The synthetic copolymers had molecular weights (Mn) ranging from 300,000 to 800,000 (1a). Copolymer composition was determined by elemental analysis (1a) and C-13 NMR.

Poly(acrylamide-co-sodium 3-acrylamido-3-methyl-butanoates)(NaAMB series) were prepared by free radical polymerization and characterized as reported previously (2-3). Their molecular weights (Mn) ranged from 500,000 to 1.5 million.

Poly(acrylamide-co-sodium 2-acrylamido-2-methylpropane sulfonates)(NaAMPS series) were prepared by free radical polymerization and characterized as reported elsewhere (1a). Their Mn values were found to be from 600,000 to 1 million (1a). The compositional data for these copolymers are shown in Table 1.

N,N-dimethyl acrylamide (DMAM) monomer was obtained from Aldrich Chemical Co. and distilled at 35°C and 10mm Hg. Acrylic acid monomer from Aldrich Chemical Co. was also distilled at 35°C and 10mm Hg. NaAMB and NaAMPS monomers were recrystallized and neutralized as previously reported (1a).

Synthesis

Copolymers of N,N-dimethyl acrylamide with NaA, NaAMB, and NaAMPS were prepared by free-radical polymerization at 30°C using potassium persulfate initiator. Copolymer composition was determined by C-13 NMR quantitative analysis using the method of Hutchinson (3). The copolymers were precipitated twice in methyl ethyl ketone and then freeze-dried. Polymerization times ranged from 1-3 hours. The results are summarized in Table 2. Aliquots were taken at low conversions, analyzed, and compared to compositions at the higher conversions shown. No compositional drift was found to occur. The reactivity ratios were calculated using the methods of Kelen and Tudos (9) and Fineman and Ross (10). The reactivity ratios are shown in Table 3.

Turbidimetry Measurements (4)

Calcium chloride solutions were prepared gravimetrically and the concentrations verified by refractive index measurements. Polymer solutions ranging from 1.5 to 5.0 g/liter were prepared by dissolving the appropriate amount of polymer in deionized water. Salt concentrations were prepared by addition of the appropriate amounts of solid salt (for higher salt concentrations) or appropriate amounts of salt solution (for lower salt concentrations). The weight of the solution was determined both before and after each measurement, and water lost by evaporation was replaced.

A phototurbidimeter was used for the phase behavior measurements. The sample of polymer solution (30-36 ml) was stirred by a magnetic stirrer, and heated slowly (<1°C/minute) by an air-heating system. A thermometer was used to record the temperature (minimum reading: 0.1°C). The decrease in photoelectric current caused by a decrease in transmittance was used to determine the onset of precipitation. The cloud point (critical temperature) was taken as the temperature at which precipitation was first observed. The process is reversible with temperature; however, two slightly different critical temperatures were observed depending upon whether the solution was cooled or heated. The average of the two observed temperatures was taken as the cloud point temperature, T_c.

Potentiometry Measurements

All measurements of pH were made using a Corning 130 pH-mv meter with an Orion pH electrode and an Orion double-junction reference electrode. The meter was standardized using a two-point calibration method. All measurements were conducted at 25±.05°C.

Copolymer concentrations ranged from 0.5 to 1.5 g/liter. Two titrations were performed on each sample: one with adjustment of ionic strength to 0.36M using potassium chloride and one with no ionic strength adjustment. Acid solutions less than 0.1M were prepared and standardized using sodium carbonate. The titrations were conducted under nitrogen atmosphere.

The degree of ionization α, defined as the fraction of acid groups dissociated, was determined for each addition of titrant. For observed pH values between 4.5 and 8.5, no correction was needed, and α was calculated as C_{A^-}/C_{HA}, where C_{A^-} is the concentration of the dissociated acid groups and C_{HA} is the total concentration of acid groups in the sample (5). For pH values below 4.5 or above 8.5, correction for free acid groups was found to be negligible. Values of the dissociation constant (pKa) were calculated using the Henderson-Hasselbalch equation (6):

$$pKa = pH - \log(\alpha/1-\alpha)$$

Because no corrections for free energy, etc. were made, all pKa values reported are apparent pka values. Plots of pH vs. $\log(\alpha/1-\alpha)$ were made as well to determine pK' and n values for each sample titration using the modified Henderson-Hasselbalch equation (7-8):

$$pH = pK' + n \log(\alpha/1-\alpha)$$

These results are shown in Table 6.

Results and Discussion

It is believed that local hydrogen bonding between anionic groups along a polymer chain and neighboring acrylamide units may account for the observed properties. Therefore, three analogous copolymer series containing N,N-dimethyl acrylamide (DMAM) with NaA, NaAMB, and NaAMPS were

synthesized to compare with the acrylamide-based copolymers. The AM copolymers contain amide hydrogens available for hydrogen bonding while the DMAM copolymers contain no amide hydrogens. The structures of the three series of copolymers of AM and the three series of DMAM are shown in Figure 1.

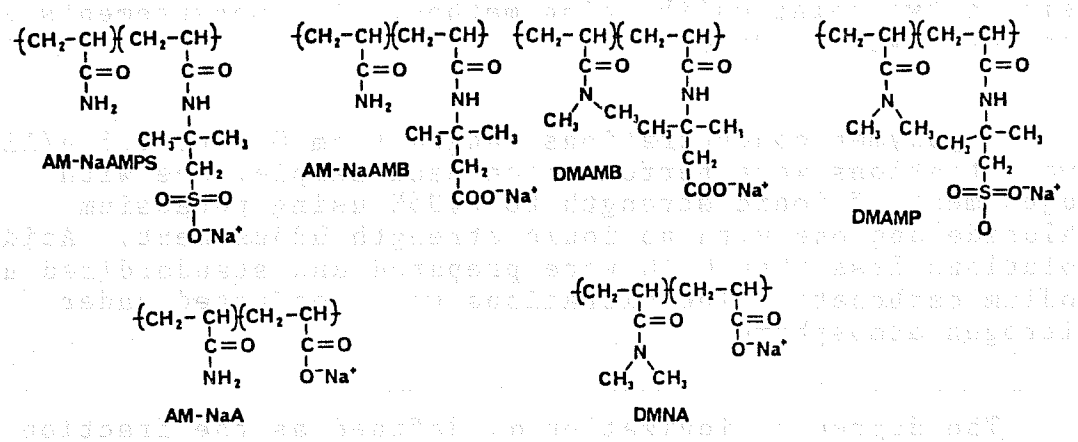

Figure 1. Structures of Copolymers

The NaAMPS copolymers were originally prepared as models for viscosity modification in enhanced oil recovery. The NaAMB series was subsequently made as a carboxylated analog to the NaAMPS and to the NaA series in order to compare their respective viscosities, salt sensitivities, and phase behavior. The NaAMB series was found to exhibit unusual phase behavior in the presence of divalent salts, and in order to investigate this further a study of these systems using potentiometric titrations was undertaken in order to correlate structure, functional group properties, and ionic effects to the observed phase behavior.

TURBIDIMETRY

Temperature and Salt Concentration

All copolymers were tested for phase separation in aqueous calcium chloride solutions as a function of temperature and calcium chloride concentration. Table 1 gives representative data for each copolymer series. The NaA series exhibited phase separation when the copolymer contained more than 25% sodium acrylate units, while the HPAM series exhibited phase separation when the copolymer contained more than 15% sodium acrylate units. The difference in critical NaA content is due to the HPAM series having a much higher molecular weight. Examples of these phase

diagrams showing all the data are given in Figures 2 and 3. Previous reports have verified these results (11-13).

It might be expected that the NaAMB copolymers would show phase separation behavior in the presence of calcium chloride as a function of temperature. However, they were found to be fully soluble up to 100°C and in all salt concentrations studied. Even the copolymer containing 63 mole percent NaAMB did not precipitate. The homopolymer of NaAMB did show phase separation, but at much higher temperatures than copolymers of the NaA and HPAM series.

Previous work in these laboratories (4) has shown no precipitation in the presence of calcium chloride for the NaAMPS copolymers and the NaAMPS homopolymer. Other sulfonated polymers and copolymers such as poly(sodium vinyl sulfonate), which is comparable to the NaA polymers, do exhibit phase separation in the presence of divalent salts (14-15). Polymers such as poly(styrene sulfonate) exhibit phase separation under certain conditions (16), but under the conditions used here no phase separation is observed.

The copolymers containing N,N-dimethyl acrylamide also showed no phase separation, with the exception of DMNA-40, which contained about 24% NaA groups.

A mechanism of precipitation of anionic polymers in the presence of divalent cations has been proposed (13,15). The temperature increase appears to "activate" both the polymer and the ion by increasing the mobility of each. When a divalent ion binds two carboxylate groups or sulfonate groups, an insoluble salt forms. These salt bonds may be intrachain or interchain (i.e. an ionic crosslink). When the number of insoluble bonds reaches a critical concentration, the polymer becomes insoluble and precipitation occurs. The polymer-solvent interaction, which is affected by the molecular weight will also be a factor in the polymer's phase behavior (e.g., the observed difference between the NaA and the HPAM series). Thus, different polymer and copolymer systems will show different phase behaviors based on these properties.

In addition, the microstructure of the polymers and copolymers may be an important factor. The copolymer sequence distributions and the tacticity (of the homopolymers) as well as the configurational differences in the copolymers affect the properties of the ionic groups and thereby alter the ability to bind divalent ions (12-13).

Effect of Side Chain Length

It appears that, in the case of the NaA copolymers which precipitate in the presence of divalent ions, and the NaAMB copolymers which do not precipitate, the length of the NaAMB side chain causes decreased salt sensitivity and the decreased divalent ion binding. We can rationalize that two adjacent sodium acrylate units might easily bind a divalent ion due to their close proximity. Two adjacent NaAMB units, on the other hand, have a much greater number of conformational states possible and thus are less likely to form insoluble ionic bonds. Copolymers containing acrylamide units separating the NaAMB units would increase the distance between charges, thus making them even less likely to bind calcium ions and form ionic bonds. This explanation is aided by the fact that model compounds of the repeat units of NaA and NaAMB show little difference in their pKa values (17). Thus there is little difference in the binding strengths of the individual NaA and NaAMB carboxyl groups, and this small difference in ion binding ability does not explain the observed differences in phase behavior for polymers and copolymers of these two monomers.

The above theory of the mechanism of precipitation does not specify that the ionic bonds formed be intrachain or interchain. Furthermore, it can be assumed that either intrachain bonds between adjacent groups, or intrachain bonds involving two separate units of the same chain (two nonadjacent groups), or two groups on different chains are equally able to form insoluble ionic bonds which can account for the phase behavior of these polymers.

In the similar comparison between poly(vinyl sulfonate) and the NaAMPS series, the same argument can be used when explaining the precipitation of the former and the lack of phase separation of the NaAMPS series. However, both of these systems contain sulfonate groups which are known to bind divalent ions more weakly, as potentiometric results indicate. Poly(sodium styrene sulfonate) was found not to exhibit phase separation in our studies using calcium chloride. This further illustrates the conclusion that moving the anionic site away from the polymer backbone suppresses or prevents precipitation by divalent cations. Using other conditions, poly(sodium styrene sulfonate) has been found to undergo phase separation in the presence of barium ions (15-16).

The apparent pKa values are shown in Table 4 for the three copolymer series containing acrylamide and the three series containing N,N-dimethyl acrylamide. The pKa values at constant ionic strength show several trends. The measured pKa values of the NaA and NaAMB copolymers are found to be very similar, with the NaAMB series having slightly higher values. This may be due to the distance from the backbone of the acid group and the destabilization due to the hydrophobic geminal dimethyl groups on the side chain of the NaAMB units. But the differences in pKa values do not account for the observed differences in their phase behavior.

Effect of Copolymer Composition

It is observed that within each series the pKa values change depending on the number of charged groups in the copolymer. The NaA and NaAMB series show trends of increasing pKa values for their acid groups with increasing NaA or NaAMB content in the copolymer. The NaAMPS series shows the opposite trend, with decreasing pKa values observed with increasing NaAMPS content. The pKa is expected to increase as the charge density increases due to increased charge-charge interactions which will destabilize the anionic groups.

Another reason for this trend may be due to the changing acrylamide availability. At lower acid-group content, the greater frequency of acrylamide units on the chain increases the availability of hydrogen bonding of the anion with a neighboring hydrogen, leading to greater stability from the increase in nearest neighbor interactions. This is illustrated by Table 5 where statistical copolymer sequence distributions (18) are compared to pKa values in water and in 0.36M KCl solutions. The pKa values are observed to be inversely proportional to the content of ABA triads present in the copolymer. In addition, the copolymer sequence data suggest a general trend of increasing pKa values with increasing BBB triads. This is expected since a charged NaA or NaAMB unit between two acrylamide units can be stabilized by the amide hydrogens on its nearest neighbors, while a charged group between two other charged groups will be destabilized by the lack of nearest-neighbor hydrogen bonding and the repulsion of the neighboring charges. The hydrogen bonding between the charged monomers and acrylamide is a stabilizing factor on the anionic groups, making them weaker bases and consequently resulting in lower pKa values.

Effect of Ionic Strength

Comparisons of the observed pKa values in water and in 0.36M KCl shown in Table 5 show that the pKa values are lower in salt water than in water. This is due to several factors: a.) the slight acidity of the KCl solutions, b.) the stabilization of the anions through shielding of the charge-charge interactions by the potassium counterions, and c.) the increase in neighboring-group effects due to the random-coil nature of the polymer chains in salt water.

The ΔpKa values are also lower in the KCl solutions than in water. This is likely due to the lack of conformational change occuring as a function of the degree of ionization α. In other words, the charge-charge interactions are greatly diminished in salt solutions as compared to pure water. The polymers in pure water are much more extended (almost rod-like) due to charge-charge repulsion and are much more sensitive to pH changes. Greater conformational changes apparently are responsible for the wider pKa range (greater Δ pKa values) observed.

The NaAMPS copolymers, which contain sulfonate groups, are expected to show much lower pKa values. As mentioned above, the pKa values decrease with increasing acid content (Table 4). This suggests that the main factor affecting the acidity of these copolymers is the number of NaAMPS groups per chain. The sulfonate anion is not destabilized by the charge-charge interactions to the extent observed in the carboxylated series because of the strong stabilization of the NaAMPS sulfonate anion in solution. This is further evidenced by the pKa values when compared in salt water and in pure water. Little or no change is observed, thus showing the lack of sensitivity of the local environment due to the sulfonate group's stability.

It can be concluded after studying the potentiometric properties of these three model systems that the phase behavior characteristics of each cannot be fully explained by the acidity of the ionic group, the extent of hydrogen bonding, or the ion-binding strengths of the ionic groups. Instead, the length of the side chain appears to be the dominant factor and must be studied in conjunction with ionic effects to fully understand the differences in phase behavior.

Effect of Charge-Charge Interactions

Further understanding of the role of charge-charge interactions can be obtained by observing the charge-charge repulsion using the modified Henderson-Hasselbalch equation (11,19). Here an n value has been placed in the equation, and can be calculated by plotting the pH of the solution vs. $\log(\alpha/1-\alpha)$ as shown in equation 2. The n value will be the slope of the line, and the intercept will be the apparent pKa. The n value is a measure of the electrostatic interactions where n=1 is the value given to a nonpolymeric monoacid (8,20). In polymers, electrostatic repulsion between charged groups along the chain give values of $n>1$. For NaA and NaAMB copolymers, n increases with increasing charges per chain in pure water (Table 6). In 0.36M KCl, values of n=1 are observed. This is due to the decreased interaction between charges in electrolyte solutions, causing each charge to act similar to a monoacid (n=1). The NaAMPS copolymers give values of $n<1$, indicating little or no interaction between groups. This suggests again that the sulfonate groups are not affected by added salt.

Effect of Hydrogen Bonding

The N,N-dimethyl acrylamide copolymers show many of the same trends as the acrylamide copolymers, but the absence of any available amide hydrogens causes the pKa values to be higher; the anionic groups cannot be stabilized by hydrogen bonding (20). The NaAMPS copolymers again are not affected by the number of acid groups per chain. This suggests that the neighboring-group effects such as acrylamide hydrogen-bonding are not factors in the stability of the NaAMPS anionic groups. The n values from the modified Henderson-Hasselbalch equation show the same trends as in the acrylamide copolymers. Therefore, increased electrostatic repulsion causes higher pKa values.

The similar phase behavior of the AM and the DMAM copolymers again suggests that the length of the side chain must be considered as well as the binding ability of the ionic group. The absence of hydrogen bonding in the DMAM copolymers affects the pKa values of the ionic groups but does not affect the phase behavior of the system. The DMAM units in the chain act as spacer units; the longer side chains of the NaAMB and NaAMPS units again prevent the formation of insoluble bonds which cause phase separation.

CONCLUSIONS

The phase separation behavior of a polymer is dependent on several factors, ranging from molecular weight and solubility on a macromolecular scale to local ionic effects and microstructure on a much more localized scale. In the systems discussed here, phase separation is most affected by the geometry of the anion. The NaAMB and NaAMPS repeat units, whose side chains are longer, contain charged groups which are several bonds removed from the backbone, giving the charged group more mobility and conformational freedom, and thus making it more difficult for insoluble ionic bonds to form. These longer side chains give NaAMB and NaAMPS copolymers more stability from precipitation and thus they are characterized by a lack of phase separation behavior in electrolyte solutions.

Another example of the effect of the side chain length is seen by studying the homopolymers of NaAMPS and sodium vinyl sulfonate. The latter undergoes phase separation due to the close proximity of the ionic groups to the backbone. The observed difference in phase behavior is similar to that observed in the carboxylated analogs.

The phase separation behavior is also affected by the basicity of the anion. Copolymers such as those of the NaA and NaAMB series will be stronger bases and are expected to bind with divalent salts more readily than the NaAMPS copolymers, whose charged groups are much more stable in the anionic form (weaker bases). The NaAMPS homopolymer does not precipitate in calcium chloride solutions, while the NaAMB homopolymer does. This behavior is readily explained by the difference in acidity of the two polymers, with the NaAMPS homopolymer being much more stable in the anionic form and therefore much less likely to bind the divalent salt.

Acrylamide units in the copolymer chain appear to be excellent sites for hydrogen bonding by anionic groups in the chain. Thus local microstructure will directly affect the pKa of a copolymer. A charged group between two acrylamide units will be more stable than one between a charged group and an acrylamide unit or between two charged groups because of the availability of the neighboring acrylamide units for forming stabilizing hydrogen bonds. Thus copolymer composition, copolymer sequence distributions, and linear charge density in the chain will affect pKa values.

The effect of hydrogen bonding can be shown by comparing copolymers of acrylamide and of N,N-dimethyl acrylamide. The DMAM copolymers, which have no amide hydrogens available for hydrogen bonding, show larger pKa values, meaning the anionic groups are less stabilized through hydrogen bonding than in the AM copolymers.

Further understanding of phase behavior is needed on carefully tailored models. Ongoing work includes potentiometric titrations using calcium-sensitive electrodes and conductrimetric titrations to compare the ion-binding ability of the ionic groups in different microstructural environments. Model compound studies have been utilized in an effort to clearly correlate structural and geometric information to the observed phenomena.

TABLE 1

Compositional Data and Observed Phase Behavior of Acrylamide Copolymers

Sample:	% charged groups	Critical Temperature (°C) 0.25%$CaCl_2$	1%$CaCl_2$	3%$CaCl_2$
NaA-10	6	*	*	*
NaA-20	14	*	*	*
NaA-35	25	*	94.3	98.0
NaA-50	30	65.5	48.6	62.9
NaA-65	48	25.1	<RT	<RT
HPAM-823	15	74.9	45.6	59.7
HPAM-309	36	60.4	41.0	58.1
HPAM-301	48	26.2	<RT	<RT
HPAM-305	65	<RT	<RT	<RT
NaAMB-10	8	*	*	*
NaAMB-25	20	*	*	*
NaAMB-40	31	*	*	*
NaAMB-60	48	*	*	*
NaAMB-75	63	*	*	*
NaAMB-hom	100	82.3	74.9	70.8
NaAMPS-15	14	*	*	*
NaAMPS-20	17	*	*	*
NaAMPS-35	29	*	*	*
NaAMPS-hom	100	*	*	*

* No phase separation observed up to 100°C.

TABLE 2

Synthesis of Copolymers of N,N-dimethylacrylamide (DMAM)

Sample:	Feed Ratio	Copolymer: $\%M_1$	$\%M_2$	Copolymer Conversion(%)	Initiator Ratio: $K_2S_2O_8$
M_2=NaAMB					
DMAMB-10	90:10	90.72	9.28	35	1:1000
DMAMB-20	80:20	81.78	18.22	36	1:1000
DMAMB-40	60:40	65.91	34.09	40	1:1000
DMAMB-60	40:60	54.23	45.77	35	1:1000
M_2=NaAMPS					
DMAMP-5	95:5	95.23	4.77	29	1:500
DMAMP-15	85:15	89.12	10.88	30	1:1000
DMAMP-30	70:30	76.65	23.35	33	1:1000
DMAMP-50	50:50	56.52	43.48	34	1:1000
M_2=NaA					
DMNA-25	75:25	89.53	10.47	26	1:1000
DMNA-40	60:40	75.73	24.27	32	1:1000

TABLE 3

Reactivity Ratios of DMAMB and DMAMP Series

	r_{DMAM}	r_{NaAMB} or NaAMPS
DMAMB Series		
Fineman-Ross	1.02	0.91
Kelen-Tudos	1.18	0.99
DMAMP Series		
Fineman-Ross	1.26	0.68
Kelen-Tudos	1.18	0.92

TABLE 4

Dissociation Constants of Acrylamide and N,N-dimethyl-acrylamide Copolymers in 0.36M KCl

Sample:	pKa:	Δ pKa:	Sample:	pKa:	ΔpKa:
AM-NaAMB			DMAM-NaAMB		
NaAMB-10	4.79 ±.06	0.10	DMAMB-10	5.15±.06	0.08
NaAMB-25	4.74 ±.05	0.10	DMAMB-20	5.07±.06	0.14
NaAMB-40	4.90 ±.04	0.05	DMAMB-40	5.09±.05	0.17
NaAMB-60	5.01 ±.04	0.12	DMAMB-60	5.23±.06	0.10
NaAMB-75	5.10 ±.05	0.12			
NaAMB-hom	5.49 ±.05	0.20			
AM-NaA			DMAM-NaA		
NaA-10	4.60 ±.04	0.12	DMNA-25	5.93±.05	0.14
NaA-20	4.53 ±.04	0.14	DMNA-40	5.82±.04	0.14
NaA-35	4.48 ±.05	0.12			
NaA-50	4.63 ±.04	0.14			
NaA-65	4.74 ±.04	0.14			
AM-NaAMPS			DMAM-NaAMPS		
NaAMPS-15	3.64 ±.06	0.28	DMAMP-5	4.22±.06	0.16
NaAMPS-20	3.57 ±.06	0.32	DMAMP-15	3.48±.06	0.19
NaAMPS-35	3.30 ±.05	0.33	DMAMP-30	3.22±.06	0.25
NaAMPS-hom	2.79 ±.06	0.27	DMAMP-50	3.10±.06	0.14

TABLE 5

Correlation Between pKa and Copolymer Sequence Distribution

Sample:	pKa (H_2O)	ΔpKa	pKa (0.36M KCl)	ΔpKa	P_{ABA}	P_{BBB}	P_{ABB}
NaAMB-10	5.23±.05	0.08	4.79±.06	0.10	0.946	0.001	0.053
NaAMB-25	5.31±.06	0.22	4.74±.05	0.10	0.754	0.018	0.228
NaAMB-40	5.75±.08	0.28	4.90±.04	0.05	0.615	0.047	0.338
NaAMB-60	5.88±.05	0.55	5.01±.04	0.12	0.339	0.175	0.486
NaAMB-75	6.19±.06	0.46	5.10±.05	0.12	0.205	0.299	0.495
NaAMB-hom	6.86±.07	0.41	5.49±.05	0.20			
NaA-10	5.28±.04	0.09	4.60±.04	0.12	0.901	0.003	0.095
NaA-20	5.05±.05	0.21	4.53±.04	0.14	0.597	0.052	0.351
NaA-35	5.39±.06	0.23	4.48±.05	0.12	0.483	0.093	0.424
NaA-50	5.61±.06	0.31	4.63±.04	0.14	0.530	0.074	0.396
NaA-65	5.83±.06	0.38	4.74±.04	0.14	0.277	0.224	0.499
NaA-hom	6.39±.06	0.40					

TABLE 6

Analysis of Electrostatic Interactions Using the Modified Henderson-Hasselbalch Equation

Sample:	0.36M KCl				H_2O			
	pKa	n	pK'	C.C.	pKa	n	pK'	C.C.
NaA-10	4.60	0.9	4.62	0.97	5.28	0.9	5.28	0.99
NaA-20	4.53	1.0	4.49	0.99	5.05	1.3	5.05	0.99
NaA-35	4.48	1.0	4.48	0.98	5.39	1.3	5.43	0.99
NaA-50	4.63	1.2	4.55	0.99	5.61	1.5	5.60	0.99
NaA-65	4.74	1.2	4.74	0.99	5.83	1.6	5.83	0.99
NaAMB-10	4.79	1.1	4.71	0.99	5.23	1.1	5.23	0.99
NaAMB-25	4.74	1.1	4.69	0.99	5.31	1.4	5.29	0.99
NaAMB-40	4.90	1.1	4.82	0.99	5.75	1.5	5.74	0.99
NaAMB-60	5.01	1.1	5.03	0.99	5.88	1.8	5.96	0.99
NaAMB-75	5.10	1.0	5.18	0.98	6.19	1.7	6.19	0.99
NaAMPS-15	3.64	0.8	3.63	0.97	3.45	0.6	3.49	0.99
NaAMPS-35	3.30	0.7	3.34	0.97	3.31	0.5	3.31	0.96
NaAMPS-hom	2.79	0.6	2.85	0.96	2.86	0.7	2.91	0.97
DMNA-25	5.93	0.9	5.95	0.98	6.61	0.9	6.61	0.97
DMNA-40	5.82	0.9	5.82	0.99	6.58	1.0	6.56	0.99
DMAMB-10	5.15	1.1	5.21	0.99	5.70	1.2	5.71	0.99
DMAMB-20	5.07	1.2	5.07	0.99	5.72	1.5	5.70	0.99
DMAMB-40	5.09	1.3	5.13	0.99	5.99	1.7	5.96	0.99
DMAMB-60	5.23	1.0	5.24	0.99	6.02	1.7	5.93	0.99
DMAMP-30	3.22	0.9	3.29	0.90	3.14	0.6	3.14	0.96
DMAMP-50	3.10	0.8	3.14	0.95	3.04	0.5	3.04	0.97

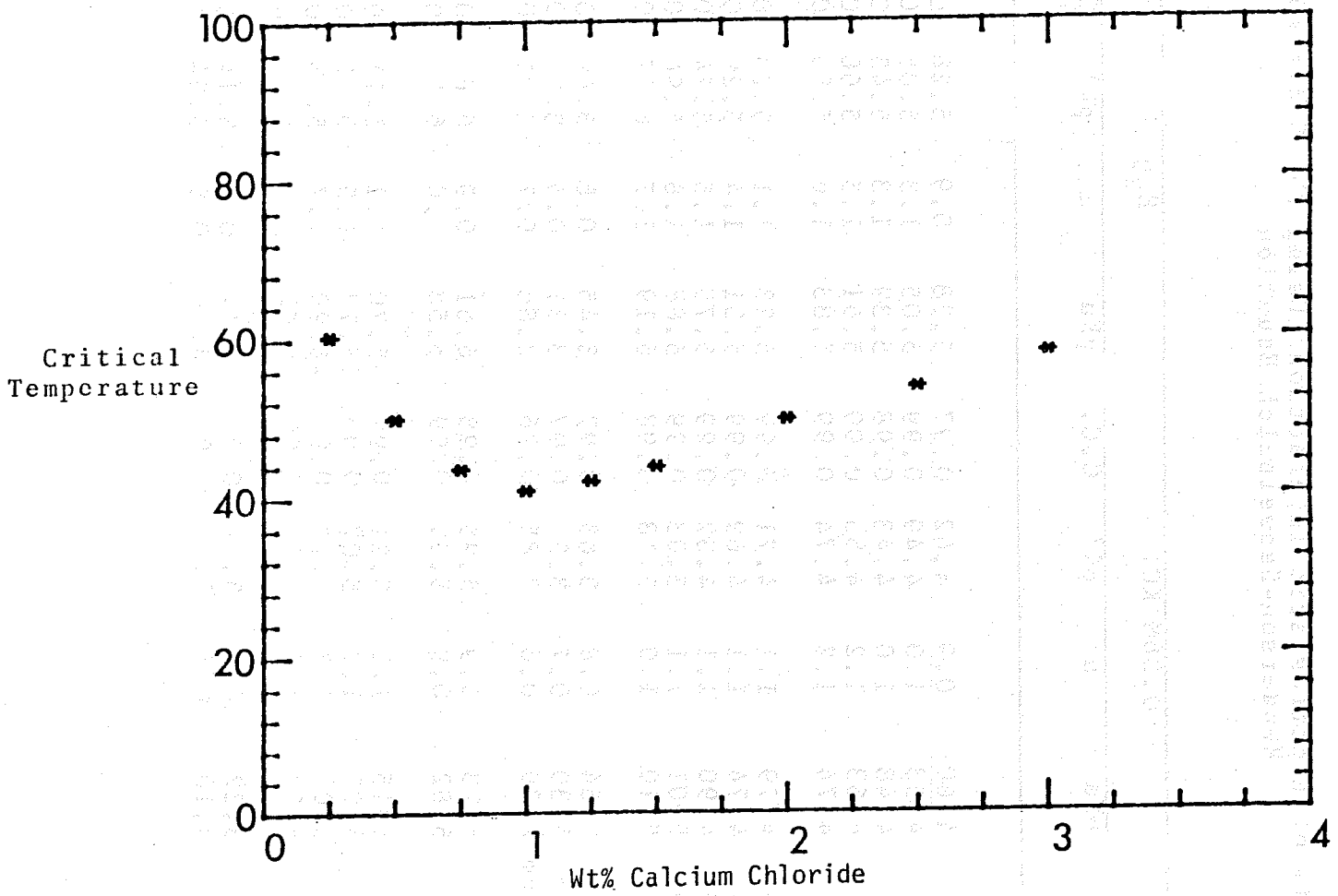

Figure 2. Phase Separation of HPAM-309

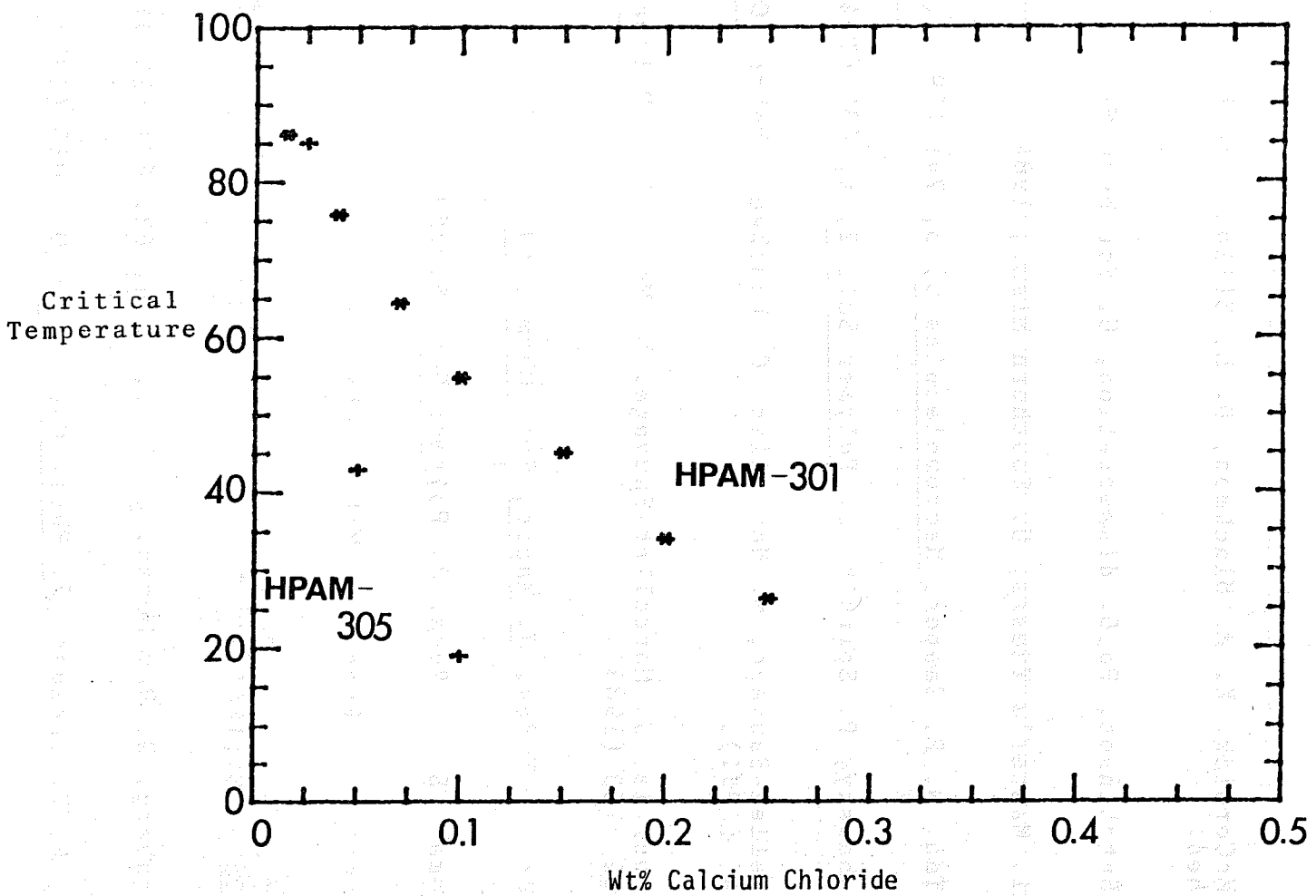

Figure 3. Phase Separation of HPAM-301 & 305

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CHAPTER V

WATER SOLUBLE COPOLYMERS: STUDIES OF RANDOM COPOLYMERS OF ACRYLAMIDE WITH NaAMPS AND DAAM BY CARBON-13 NMR

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SYNOPSIS

Quantitative analysis using ^{13}C NMR has been used to determine copolymer and terpolymer composition for copolymers of acrylamide and sodium-2-acrylamide-2-methylpropanesulfonate, (NaAMPS) copolymers of acrylamide with N(1,1 dimethyl-3—oxobutyl) acrylamide (DAAM), and terpolymers of acrylamide, NaAMPS and DAAM. In addition, the NMR analyses are unaffected by bound water, are relatively fast, require little sample preparation, and are non-destructive. The method involves the accumulation of spectra using pulse repetition which allow for retention times greater than $5T_1$s, as well as the use of gated decoupling to remove NOE effects. NOE and T_1 data are reported for the polymer systems studied here, and a justification of the parameters utilized is given. Comparisons of the compositional data with elemental analysis data are made and found to be in agreement.

INTRODUCTION

In recent years the use of acrylamide-based copolymers in applications including mobility control, viscosity modification, and flocculation has increased. Since the ultimate performance of these polymers is based on composition, analytical techniques for accurate, rapid analysis have been sought.

Compositional analyses of acrylamide copolymers have traditionally been based on elemental nitrogen analysis (1-5), potentiometric titration (6-8), and more recently on thermogravimetric analysis (9). However, the hygroscopic nature of these polymers can result in errors in weight determination; additionally, extensive drying can result in covalent or associative cross-linking preventing subsequent dissolution (10).

Only recently has the tacticity of polyacrylamide been elucidated (11, 12). McCormick, Chen, and Hutchinson have demonstrated the utility of ^{13}C NMR quantitative determination of copolymer compositions by comparing the results with IR spectroscopy and elemental analysis techniques (13).

The determination of copolymer composition by proton NMR has been well documented (14-16); however, acrylamide-based copolymers are soluble in few solvents suitable for proton analysis. These copolymers are, fortunately, very soluble in water, an ideal solvent for ^{13}C NMR due to the absence of interfering resonances.

Quantitative analysis of polymers by ^{13}C NMR has been addressed in a number of reviews (17-19). In general two major conditions must be met when attempting to extract quantitative information. When using 90° pulse angles, pulse repetitions of greater than five times the spin-lattice relaxation time, T_1, should be employed. This time period allows for the reestablishment of the Boltzmann distribution of nuclei.

Some allowance must also be made for the possible inequality of the nuclear Overhauser enhancement (NOE) (20) of the observed resonances. The equalization of the NOE's can be accomplished by the addition of a paramagnetic impurity (21); however, this practice often results in excessive broadening of the carbon peaks. Freeman, Hill, and Kaptein (22) suggested using a gated decoupling technique in which the NOE's were eliminated by cycling the decoupler on only during signal acquisition. This process results in completely decoupled spectra with no NOE.

The intention of this study is to demonstrate the utility of quantitative ^{13}C NMR for determining the copolymer composition of a series of water-soluble, acrylamide-based copolymers. Random copolymers of acrylamide (AM) with sodium-2-acrylamido-2-methylpropanesulfonate (AMPS) and N(1,1-dimethyl-3-oxobutyl) acrylamide (DAAM) have been studied as well as a terpolymer series of the three monomers. Consideration has been given to the molecular motion of the copolymers in solution as it pertains to the quantitative procedure.

EXPERIMENTAL

The syntheses of the random copolymers have been described previously (23). Before use the polymers were dried at $40^{o}C$ under vacuum. Polymer solutions were prepared by weighing a known amount of dried polymer and adding it to 2 ml of D_2O in a 10mm

O.D. NMR tube. The polymer concentration used for this study was kept at 5% w/v to alleviate viscosity problems. Dissolution was usually acomplished in a 2-day period.

All NMR spectra were obtained on a JEOL FX 90Q spectrometer operating at a carbon-13 NMR frequency of 22.5 MHz. A 5000 Hz window was employed with exponential weighting. The spectra were referenced to either an external or an internal DSS standard. The probe temperature was maintained at 32 $\pm$ 2°C.

The spin-lattice relaxation times were determined through either an inversion recovery method (24) or a fast inversion recovery method (25). Peak intensity/pulse interval data were analyzed by utilizing a three-parameter fit proposed by Sass and Zeissow (26). The procedure involves a Newton iteration of the error-analyzed equation utilizing a computer program written for this purpose. These methods have been reported to yield accurate T_1 values in the least amount of time (27). The relaxation times are reported within $\pm$ 15% due largely to low signal/noise ratios of these high molecular weight and highly viscous sample solutions.

Determinations of NOE values were performed for a number of polymer samples in order to justify the use of gated decoupling. Alternate NMR studies were conducted with and without gated decoupling. A pulse interval of ten times the longest observed T_1 values was used to eliminate the error as outlined by Canet (28). The peaks for each spectrum were integrated under identical conditions and the NOE values determined. A maximum error of 0.2 NOE units is reported.

Evaluations of copolymer composition were performed utilizing a 90° pulse angle, gated decupling, and pulse repetitions $\geq 5T_1$ values. Well-resolved representative peaks were chosen from each monomer and multiple integrations were carried out. The maximum estimated error for the determinations is $\pm$ 10 %. Typically 5000-10,000 transients were accumulated.

RESULTS AND DISCUSSION

Monomers used in synthesis of copolymers analyzed in this study are illustrated below. In this section assignments of ^{13}C resonances are made and relaxation times given. Additionally comparisons of copolymer compositions are discussed in relation to those determined by other methods.

Figure 1 illustrates the completely decoupled carbon-13 NMR spectrum of NaAMPS-3, a copolymer of acrylamide (AM) with sodium-2-acrylamido-2-methylpropanesulfonate (NaAMPS). With the aid of off-resonance decoupling and comparison to model compounds, all of the peaks were assigned as shown in Figure 1. The relative chemical shifts change very little throughout the series of copolymers. Therefore, all of the peaks with the exception of the backbone carbons which are broad and overlapping have the potential to be used for determination of the copolymer composition.

The use of gated decoupling to equalize NOE values is necessary when the observed NOE values are different for different carbons. Evaluation of these NOE values is then justified. Rapidly reorienting carbons which relax through a dipole-dipole mechanism often exhibit a maximum NOE value of 2.9. However, some large biomolecules and synthetic polymers exhibit reduced NOE values due to an apparent violation of the extreme narrowing condition (29). Table I shows the measured NOE values for the NaAMPS series. It is obvious that these polymers are, in fact, violating the extreme narrowing condition since most of the carbons are relaxed predominantly through dipole-dipole relaxation.

The data are also indicative of the presence of copolymers rather than a mixture of two homopolymers. In general the NOE values decrease with the amount of NaAMPS in the copolymer. The successive introduction of AMPS in the copolymer has the effect of stiffening the polymer chain possibly through bulky side group interactions. This results in changes in the effective correlation time and further decreases the polymer motion. Consequently these data indicate the need for gated decoupling to eliminate the NOE for quantitative analysis.

Table II lists the measured spin lattice relaxation times for the NaAMPS series. The longest T_1's are those of the carboxyl and the quaternary carbons which are a result of the absence of bonded hydrogens. Since the quantitative process requires the use of the AM carboxyl, pulse repetition times are long. The values for the backbone carbons are only apparent values since resonances from each monomer overlap. However, the bulk-measured T_1 is a good approximation due to the similarity in the individual carbon T_1's (30). For the backbone carbons, a factor of two difference is noted in measured T_1. This is due to the bonded proton dependence of the two carbons (2 protons on one to only one proton on the other). This dependence on bonded protons is evidence that they are undergoing isotropic motion only. Increased segmental motion in the side chain is observed through the methylene resonances. Additionally the mechanism of spin-rotation relaxation is observed for the side chain methylene groups resulting in T_1 values on the order of 0.2 seconds.

Copolymer compositions were calculated using the acrylamide carbonyl and the carbonyl and methyl resonances of the NaAMPS monomer. Equation 1 was utilized for the calculations. I_{AMPS} represents the NaAMPS monomer peak integral and I_{AM} the acrylamide carbonyl inegral.

$$\frac{I_{AMPS}}{I_{AMPS}+I_{AM}} \times 100 = \text{mole \% AMPS} \qquad (1)$$

Comparisons of these values to those from elemental analyses are shown in Table III.

Figure 2 represents the completely proton decoupled carbon-13 NMR spectrum of DAAM-41, a copolymer of acrylamide with N(1,1-dimethyl-3-oxobutyl)acrylamide, DAAM. Distinct peaks can be seen for individual carbons in the polymer with the exception of the backbone carbons. Copolymer compositions were determined as previously discussed utilizing the individual amide carbonyl peaks as well as the quaternary, methylene and methyl resonances of the DAAM side chain.

Table IV contains the measured spin-lattice relaxation times of the DAAM series. Once again a general tendency is noted for the T_1 values to decrease with the successive introduction of the bulky monomer into the chain. The NOE data in Table 5 show the same trend indicative of the slow rotation of these polymers in solution again resulting in extreme narrowing condition violations.

By using pulse repetitions greater than 6 seconds, analysis of copolymer from this series agreed well with elemental analysis data as shown in Table 6. No effort was made to include the Keto carbonyl resonance due to its relatively long T_1 (> 2 seconds) and due to its proximity to the outer edge of the 5000 Hz window which is used in these spectral determinations. Additionally, the peak integrated poorly due to uneven excitation in this area.

Carbon-13 NMR quantitative analysis techniques can also be applied to terpolymers with relative ease. By comparison, elemental analysis equations for determining compositions are often quite complicated. Figure 3 is the completely decoupled NMR spectrum of T-12 which consists of AM, NaAMPS and DAAM. Individual peaks indicative of each monomer are readily discernable. The peak at 177 ppm contains the overlapped carbonyl resonances for the DAAM and AMPS monomers. Relaxation time data for these polymers indicate that the longest T_1 of a usable peak is about 1.5 seconds necessitating an eight-second pulse repetition. Typically 10,000 transients were accumulated. The terpolymer

compositions were determined utilizing the two carbonyl resonances at 182 and 177 ppm and the NaAMPS methylene side chain carbon peak at 61 ppm according to equations 3,4 and 5.

$$X_{AMPS} = \frac{I_{61}}{I_{182} + I_{178}} \times 100 \quad (3)$$

$$X_{DAAM} = \frac{I_{178} - I_{61}}{I_{182} + I_{178}} \times 100 \quad (4)$$

$$X_{AM} = \frac{I \quad I_{182}}{I_{182} + I_{178}} \times 100 \quad (5)$$

The calculated data are given in Table VII. The values are generally in excellent agreement with those predicted by elemental analysis.

CONCLUSIONS

Quantitative ^{13}C NMR has been used little previously in determining copolymer compositions, especially for water-soluble polymers. It represents, however, a relatively simple and facile means of obtaining composition data. The analyses are not affected by bound water, or other impurities such as residual precipitating solvent. Little sample preparation is required, and the analyses are non-destructive. Additionally, information on microviscosity effects can be obtained from T_1 values to correct for NOE effects and relaxation differences. Spectra have been obtained and analyzed for copolymers of acrylamide and NaAMPS, copolymers of acrylamide and DAAM, and terpolymers of acrylamide, NaAMPS, and DAAM. The quantitative analysis data from NMR were in excellent agreement with elemental analysis data.

Further efforts are underway presently to decrease the required analysis times and to improve the signal-to-noise ratios of the spectra by incorporation of the Ernst equation (31) as suggested by Visintainer (32). These efforts to further speed up the NMR analysis have also been applied to other random and graft copolymer systems (33).

TABLE I

Nuclear Overhauser Enhancements[b] for the NaAMPS Series

Sample	3[c]	4	5	6	7
AMPS[a]	-	1.7	-	2.3	1.6
1	2.3	1.8	2.5	1.9	2.5
2	1.8	2.1	2.4	1.9	2.5
3	1.2	1.2	1.3	1.8	1.8
7	1.2	1.2	1.4	1.8	1.4

[a]Homopolymer

[b]$\pm$.2 Units

[c]From Figure 1

TABLE II

Spin-Lattice Relaxation Times[a] for the NaAMPS Series

Sample	Carbon No.[c] 1	2	3	4	5	6	7
AMPS[b]	0.03	0.06	-	0.83	0.80	0.15	0.04
1.	0.05	0.09	1.23	1.09	0.95	0.22	0.04
2	0.04	0.08	1.12	1.03	1.07	0.16	0.06
3	-	0.08	1.03	0.97	0.90	0.17	0.05
7	-	-	0.70	0.80	0.76	0.16	0.05

[a]Estimated accuracy ± 15% (sec.)

[b]Homopolymer

[c]From Fig. 1

TABLE III

Material Specifications for the NaAMPS Series

Sample	%N[a]	%S[a]	Mole % AMPS	
			Elemental Analysis[a]	^{13}C NMR
1	14.03	3.05	9.51	10.7
2	12.15	5.28	19.01	17.3
3	10.65	6.78	27.85	27.2
7	6.94	10.43	65.75	69.5

[a]Reference (33)

TABLE IV

Spin-Lattice Relaxation Times[a] for Copolymers of Acrylamide with N(1,1-dimethyl-3-oxobutyl)acrylamide (DAAM)

Sample	Carbon No.[b]								
	1	2	3	4	5	6	7	8	9
11	0.04	0.08	1.22	1.10	1.04	0.22	0.06	2.22	0.9
21	0.03	0.08	1.02	0.96	1.16	0.21	0.07	2.20	0.9
31	0.03	0.06	0.93	0.84	0.91	0.19	0.06	1.75	0.8
41	0.03	0.06	1.01	0.94	0.82	0.19	0.06	1.55	0.9

[a] ± 10% estimated accuracy (sec.)

[b] From Fig. 2

TABLE V

NOE Values[a] for DAAM Copolymers

Sample	Carbon No.[b] 1	2	3	4	5	6	7	8	9
11	1.8	2.1	1.8	1.9	-	2.6	2.0	-	1.9
41	-	1.7	1.5	1.6	-	2.1	1.7	-	1.9

[a] ± 0.2 units

[b] From Fig. 2

TABLE VI

Material Specifications for the DAAM Series

Sample	%C[a]	%N[a]	Mole % DAAM	
			Elemental Analysis[a]	^{13}C NMR[b]
11	53.10	16.90	11.1	10.5
21	56.60	14.85	22.8	21.7
31	57.09	13.64	31.4	31.3
41	58.57	12.49	41.2	38.8
BH-DA-31	53.20	12.76	31.1	31.4
BH-DA-21	-	-	-	22.7

[a]Reference (33)

[b]±10% estimated accuracy

TABLE-VII

Material Specifications for the Terpolymer Series of AM-DAAM-NaAMPS

Sample	%C[a]	%N[a]	%S[a]	Mole %					
				AM		DAAM		NaAMPS	
				EA	^{13}C	EA	^{13}C	EA	^{13}C
11	46.89	13.55	2.99	79.5	82.2	10.6	6.9	9.6	10.8
12	45.69	12.34	4.44	72.7	74.9	11.3	12.4	15.7	12.5
13	43.11	9.83	6.88	54.5	56.2	14.7	12.3	30.5	31.8
14	39.67	7.13	9.45	22.5	26.8	19.4	17.5	57.8	55.7

[a]Reference (33)

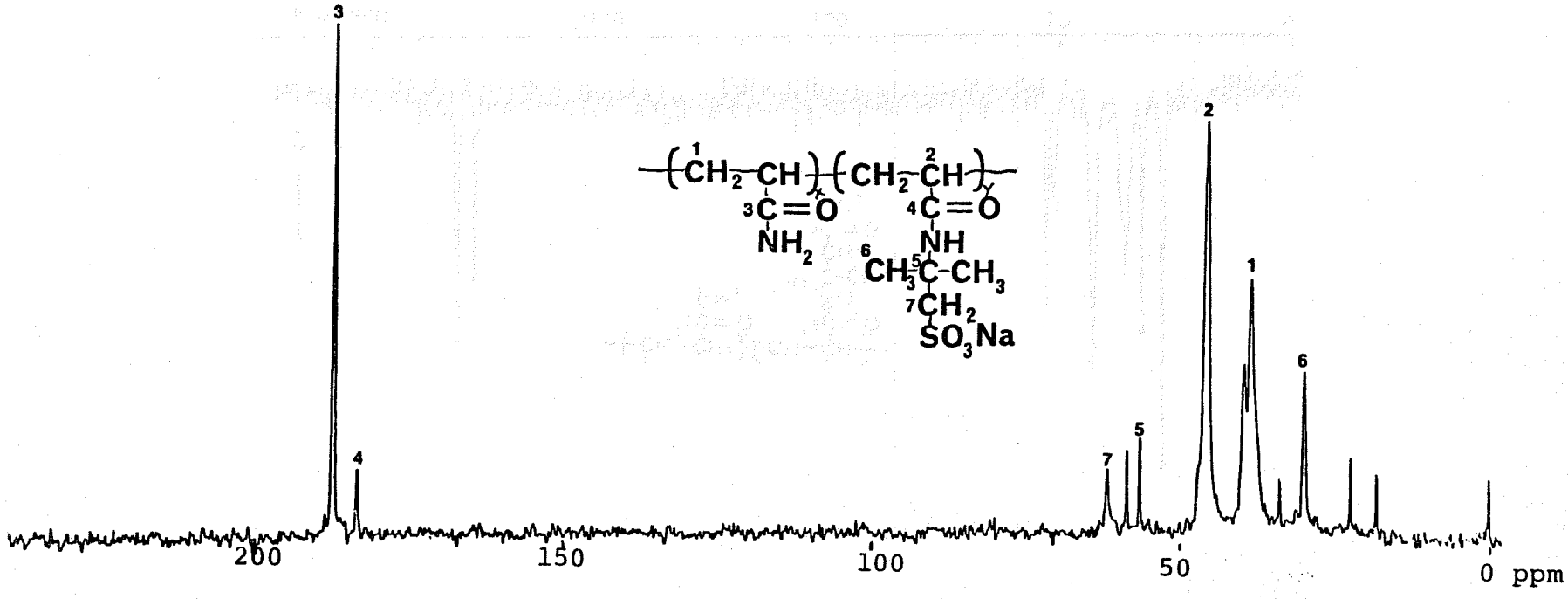

Figure 1. Gated decoupled FT carbon-13 NMR spectrum of a 5% w/v solution of AMPS-3 in D_2O with an 8 second pulse repetition, a 90° pulse angle, 7500 transients, and 32°C.

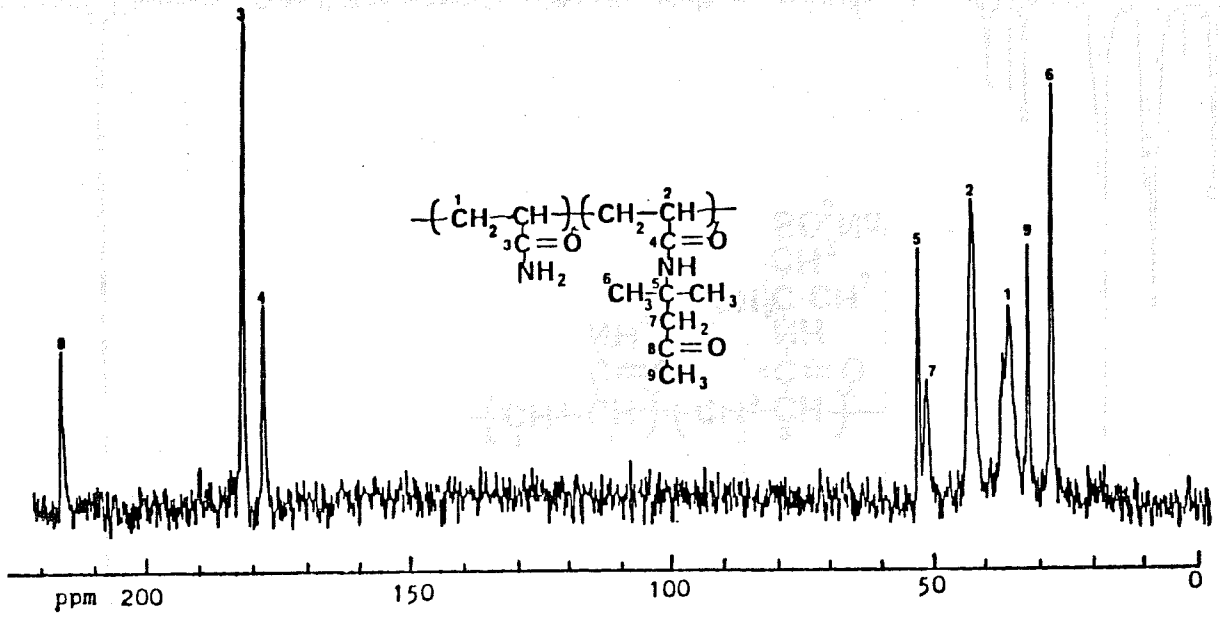

Figure 2. Gated decoupled FT carbon-13 NMR spectrum of a 5% w/v solution of DAAM-31 in D_2O with a 6 second pulse repetition, a 90° pulse angle, 7500 transients, and 32°C.

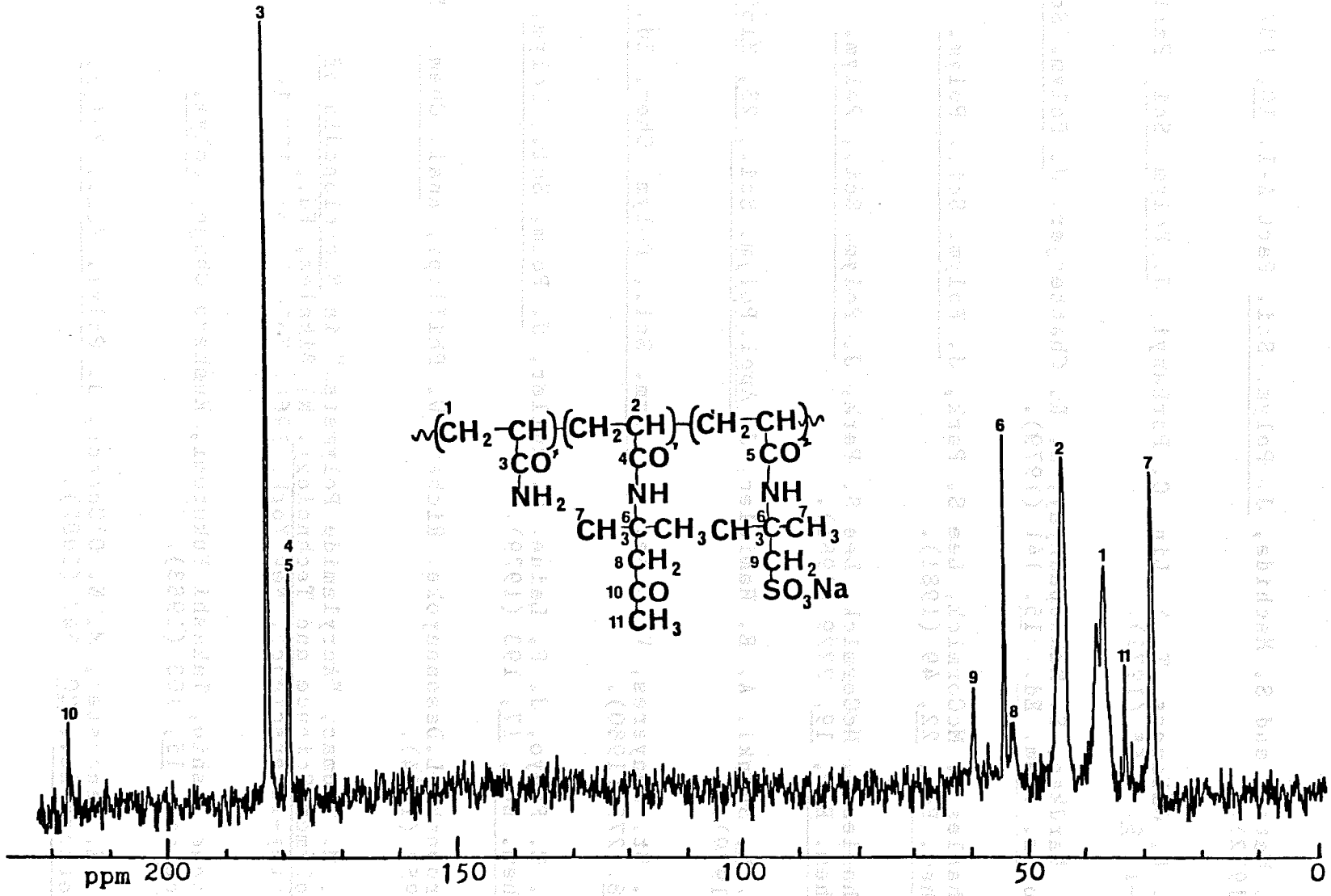

Figure 3. Gated decoupled FT carbon-13 NMR spectrum of a 5% w/v solution of T-12 in D_2O with an 8 second pulse repetition, a 90° pulse angle, 7500 transients, and 32°C

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CHAPTER VI

CHARACTERIZATION OF LARGE WATER-SOLUBLE MACROMOLECULES BY SIZE EXCLUSION CHROMATOGRAPHY

Charles E. Lundy and Roger D. Hester

SYNOPSIS

A method for characterizing EOR polymers by size exclusion chromatography (SEC) has been developed. Sephacryl S1000 packing material, a precision syringe pump, and an eluent pressure detector have been utilized to produce highly accurate chromatograms of water-soluble polymers having molecular hydrodynamic diameters up to 280 nm. Previous SEC analysis has been limited to hydrodynamic diameters of less than 120 nm. Thus the new method has doubled the range of SEC analysis for enhanced oil recovery type polymers.

INTRODUCTION

Characterization of EOR polymers for size distribution is extremely important. During polymer flooding, macromolecules that are too large can shear degrade to smaller molecules during injection into the reservoir and/or can plug the well head. However smaller polymer molecules are ineffective in mobility control. Usually a specific polymer size and size distribution is optimum for efficient polymer flooding.

Characterization of macromolecules for their size distribution can be accomplished by using size exclusion chromatography (SEC). This separation is accomplished using a flow of solvent to force a polymer sample into solution through columns with porous packing material. Smaller polymer molecules in the sample are retained within the packing for a longer time because they can access more fluid volume than larger molecules. Thus polymer molecules are separated according to their hydrodynamic size. Larger molecules will elute from the packing before smaller molecules. Some type of detector is used to measure the polymer present in the fluid stream leaving the packing. Plots of detector signal versus the mass or volume of fluid that has passed through the packing after injection of the polymer sample are

chromatograms and can be used to measure the size distribution of a polymer sample.

Several major problems have prevented effective SEC analysis of large water soluble polymers, i.e., macromolecules having hydrodynamic sizes greater than 100 nm. These problems are 1) the lack of efficient, large pore-size packing material, 2) the adsorption and/or entrapment of the macromolecules, 3) shear degradation of larger molecules, 4) the poor ability to detect the presence of polymer in the eluent stream and 5) packing calibration difficulties due to the lack of well-characterized, large water-soluble polymer standards.

This paper describes an SEC system which has overcome many of the above problems. The major components of the system are a large pore size gel packing material, a low flow-high precision syringe pump and an eluent pressure detector. It will be demonstrated that this SEC system can be used to separate macromolecules having hydrodynamic sizes up to 280 nm (10 million in molecular weight).

EXPERIMENTAL

Overall Aqueous SEC System Features

As shown by Figure 1 and Table I, the SEC system is constructed by placing several elements in series with respect to the solvent flow stream. The flow or carrier stream used was a 1.0 molar NaCl aqueous solution. A syringe pump was designed and constructed to consistently force the carrier stream through the system at low volumetric flow rates, usually 0.15 ml/min. Low flow was necessary to prevent fluid pressure deformation of the packing as well as to allow sufficient time for larger macromolecules to diffuse into and out of the pores present in the packing. Also, low flow rates prevent high fluid shear stress which could shear degrade larger polymer molecules. Thus low flow rates are absolutely necessary for good separation efficiency.

The packing, Sephacryl S1000, was slurry packed into a 1.9 I.D. X 42 cm long stainless steel column. The column was capped with 10 micron end fittings.

The carrier stream or eluent leaving the packed column was analyzed for polymer by both an eluent capillary pressure (CP) detector and a refractive index (RI) detector. Total eluent volume was monitored with respect to time elapsed from sample

injection using a Mettler PC400 balance interfaced to a microcomputer. A data logger interfaced to the computer was used to record detector signals. The SEC computer and data logger subsystem have been previously described [1]. Usually data from all sources (balance, CP and RI detectors) were measured every three seconds for 45 seconds. The average of each signal taken during each 45 second time interval was calculated, recorded, and thereafter used to construct various chromatograms.

Syringe Pump

Not only low flow rates, but also very consistent noise free flow rates are required for efficient SEC analysis of very large macromolecules. Conventional dual piston SEC pumps are not capable of satisfying these flow rate requirements. Therefore a syringe pump was designed and constructed to meet the stringent flow conditions. Our pump design was based upon a recent recommendation [2]. A schematic of the pump is shown in Figure 2. The syringe pump is simply a piston which moves to displace fluid from a cylinder. Piston movement is extremely slow and uniform because of a large gear ratio, 12000 to 1, between motor and piston screw shaft. A motor controller is incorporated so that final piston movement translates to volumetric flow rates between 0.02 and 1.0 ml/min.

To gravity feed fluid into the cylinder, the piston is placed in the "up" position and a vent through the cylinder is opened. This procedure was necessary to eliminate all air from the cylinder. Air in the flow stream caused false signals in the capillary pressure detector. In the piston "up" position, the full cylinder contained approximately 250 ml of fluid. This fluid quantity was sufficient for about 24 hours of SEC operation at the usual flow rate, 0.15 ml/min.

Packing Material

Sephacryl S1000 has recently been used in aqueous SEC for separation of phospholized vesicles [3] and hydrolyzed polyacrylamides [4]. This packing, manufactured by Pharmacia Fine Chemical, consists of cross linked gel particles of allyl Dextran and bis-acrylamide which have diameters betweeen 40 and 105 microns. This packing material has several inherent advantages for use in SEC analysis of large water-soluble polymer molecules.

Not only do the packing particles have large pores (up to 400 nm), but these larger pores are unusually numerous. This high volume percentage of larger size pores is responsible for the excellent separation capability when analyzing very large

macromolecules, as is shown by the calibration curve in Figure 3. The packing calibration curve uses the "Southern" calibration technique [16]. Note the linear nature of the calibration curve and the high range of separation capability.

In addition, the large packing particle size is responsible for lower fluid shear and elongational forces. If present, large forces could lead to macromolecular chain rupture [5]. Also past work in this laboratory has shown that for large polymers physical entrapment occurs when the packing particles are smaller than 30 microns [6]. Lastly, it will be shown in this paper that typical EOR type polymers do not permanently adsorb onto this packing material.

Capillary Pressure Detector

The capillary pressure (CP) detector senses the eluent pressure drop developed when it flows through a 0.05 cm inside diameter capillary which is 25 cm long. A Validyne model DP-15 differential pressure transducer equipped with a number 20 diaphragm was used to measure the pressure drop.

As shown by Figure 4, the syringe pump maintains an extemely noise-free CP signal in comparison to the CP signal when using a dual piston pump. When used in conjunction with the precision syringe pump, the capillary pressure detector is capable of measuring extremely small changes in eluent viscosities. For example, the drift or decrease in the capillary pressure signal, shown in the bottom curve of Figure 4, is attributed to a 0.3°C increase in the eluent (water) temperature. This produced a viscosity decrease of only 2% which in turn translates to only 0.05 cm of water pressure! This very small pressure decrease is easily detected and demonstrates the high sensitivity possible with this type detector. Commercial pressure detectors have recently become available with even higher sensitivity [10,11].

The capillary pressure detector can be used to sense the presence of polymer in the eluent. As previously reported [12], when polymer is present in the eluent, the solution pressure drop, P, is greater than the pressure drop of pure solvent, P_o. The larger the volume fraction of polymer in the fluid, the larger the pressure drop. This increase can be used to determine the specific viscosity of the eluent, V_{sp} The specific viscosity is directly proportional via a constant, k, to volume fraction polymer,f, in the eluent.

$$V_{sp} = (P - P_o)/P_o \quad (1)$$

$$V_{sp} = kf \quad (2)$$

A plot of eluent specific viscosity versus elution volume was defined as a specific viscosity chromatogram. It was also shown that the intrinsic viscosity of a polymer sample is simply the area within its specific viscosity chromatogram divided by the total mass of polymer sample injected [12]. Larger molecules, due to their larger intrinsic viscosities, will have larger specific viscosity chromatograms. This detection characteristic gives an advantage to the CP detector over refractive index (RI) detectors when dealing with high molecular weight polymers. Since an RI detector's signal is proportional to the mass of sample injected and since the concentration of polymer must be decreased as the molecular weight increases (to insure dilute solution conditions), an RI signal must decrease as the molecular weight increases. In contrast, because the specific viscosity increases with molecular weight, the CP detector signal also increases with increasing molecular weight.

SPECIFIC VISCOSITY CHROMATOGRAMS OF EOR POLYMERS

Previous work in this laboratory expermimentally demonstrated that the specific viscosity chromatograms of small polymer molecules can be used to accurately predict polymer intrinsic viscosities. See Figure 5. Also it was shown that the non-Newtonian or shear thinning behavior of these polymers did not significantly affect the specific viscosity chromatograms. It was expected, however, that shear thinning would affect the specific viscosity chromatograms of larger polymer molecules.

To confirm this expectation we developed specific viscosity chromatograms for several high molecular weight polymers. Figure 6 shows four specific viscosity chromatograms. The PN samples are graft copolymers which were synthesized by McCormick's EOR research group [13]. They are cerium-initiated grafts of acrylamide onto Dextran. The T500 sample is pure Dextran with a weight average molecular weight of about 500,000.

As indicated on the table included in Figure 6, these four polymers have average molecular diameters that range from 30 to 300 nm. These average diameters were measured using dynamic scattering techniques [14]. First, note the excellent size separation performance of the SEC system. Each polymer has a well defined distribution that lies between the void volume, 30 ml, and the total volume, 80 ml. Secondly, note that, because all chromatograms are normalized to 10 mg of polymer sample, the area

under each chromatogram is proportional to the polymer's intrinsic viscosity. As expected, as the polymer molecules increase in size, they elute sooner and also have larger chromatograms because larger polymer molecules have larger intrinsic viscosities.

At a carrier fluid volumetric flow rate of 0.15 ml/min, the shear rate in the pressure detector capillary is 300 sec^{-1}. All fluid viscosities are measured at this shear rate and the intrinsic viscosity from the chromatograms therefore reflect the intrinsic viscosity of the polymer sample when measurements were made at 300 sec^{-1}. If polymer shear thinning is occurring at this shear rate, then the intrinsic viscosities measured by the chromatograms should be smaller than those which would be measured if the fluid shear rate were lower. This is exactly what was observed when chromatogram intrinsics were compared to intrinsics measured by a Contraves rheometer operating at lower shear rates. See details in Chapter VI. Also as expected, the difference in intrinsics decrease as the polymer samples decrease in molecular size. No difference between intrinsics existed for the smaller Dextran T500 polymer, but up to a 30% difference existed between the intrinsics measured for larger macromolecules such as PN10. However, as shown by the table in Figure 6, chromatogram intrinsics were equal to Contraves intrinsics when both measurements were made at the same shear rate, 300 sec^{-1}.

To confirm the above results an additional series of large random copolymers were also analyzed by SEC. These polymers were also obtained from McCormick's EOR research group. The AMB polymers are copolymers of sodium-2-acrylamido-2-methylpropane carboxylate and acrylamide and the DMAM polymers are copolymers of acrylamide and dimethyl acrylamide [15]. Specific viscosity chromatograms for these polymers are shown in Figure 7. These random copolymers were also easily separated by the SEC system. In addition, as shown by the table in Figure 6, chromatogram intrinsics were equal to Contraves intrinsics measured at the 300 sec^{-1} shear rate. Thus both series of EOR polymers can be separated and their intrinsics can be measured from specific viscosity chromatograms. This is shown by Figure 8, a plot comparing intrinsic viscosities.

If intrinsic viscosities from the CP detector were less than the intrinsic viscosities from the rheometer, then this would indicate possible adsorption or entrapment of macromolecules within the SEC packing. Since this was not the case, we can conclude that adsorption or entrapment did not occur with these polymers.

CONCLUSIONS

Sephacryl packing, a precision syringe pump and an eluent pressure detector were combined to construct an aqueous size exclusion chromatographic system which can analyze extremely large water soluble polymers. The combination of this equipment has a synergistic effect that enhances SEC analysis separation range and sensitivity. Typical EOR water-soluble molecules, having molecular weight up to 10 million, were separated without difficulty. The combination of low elution flow rates and large packing volume produced SEC analysis times of about four hours. It is expected that future SEC system optimization will reduce the analysis time to less than two hours.

Because of the stable eluent volumetric flow rates produced by a syringe pump, use of a capillary pressure detector was possible. For large water soluble macromolecules, this detector was found to have polymer detection sensitivity superior to a conventional refractive index detector. This superiority is due to the fact that a pressure detector senses the volume fraction of polymer present in eluent rather than its concentration. This detector does not sense the presence of small molecular weight impurities which, in contrast, can produce false signals from a refractive index detector.

Specifiy viscosity chromatograms were constructed from pressure detector signals. A specific viscosity chromatogram indicates the volume fraction distribution of macromolecules within a polymer sample. The area envelope within a polymer's specific viscosity chromatogram when normalized for total mass of polymer injected was shown to be equal to the polymer's intrinsic viscosity. A comparison of intrinsic viscosities can be used to confirm the presence of polymer adsorption or entrapment within the packing material.

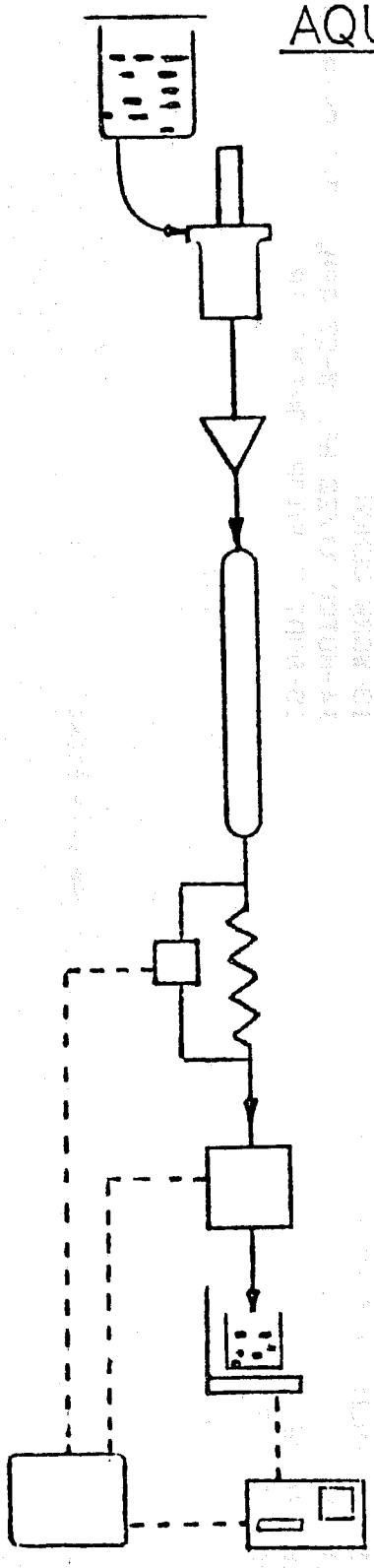
TABLE I

System Equipment Description and Operating Conditions

System/Equipment	Details and Conditions
Polymers	All random and graft copolymers were dissolved in a filtered 1M NaCl solution containing 0.01% NaN_3 as a biocide. Dextran polymers were purchased from Pharmacia and dissolved in deionized water containing 0.01% NaN_3. Sodium Polystyrene Sulfonate polymers were purchased from Pressure Chemical Co., and were dissolved in 0.2m NaCl with 0.02% Triton-40-5L added as a surfactant and 0.01% NaN_3. All solvents used were filtered through a 0.45 micron filter and vacuum degassed at 40°C.
Pump	Constructed of 316 guage stainless steel having a fluid capacity of 250 ml. The flow rate was maintained at 0.15 ml/min.
Injector	A Rheodyne Model 7010 injector with a 1.0 ml sample loop. The sample injections were 1.0 ml.
Packing Material	Sephacryl S1000 was purchased from Pharmacia Fine Chemicals. The column was made of 316 stainless steel having a 1.9 cm ID X 40 cm length. The packing material was slurry packed according to available Pharmacia literature. Approximately 300 ml of a 50% slurry was used to pack the column. The column was capped with 10 micron frits.
Capillary Pressure Detector	A capillary of .05 cm ID X 25 cm length was connected to the column outlet tubing and pressure transducer by Upchurch Scientific 3-way tees. The pressure transducer was a Validyne DP-15 with a Model CD15 Sine Wave Demodulator. A no. 20 diaphragm was used in all experiments.
Refractive Index Detector	A Waters Model 500 Differential Refractive Index detector having a cell volume of 10 microliters was connected downstream of the CP detector.
Balance	A Mettler Model PC-400 balance was used to monitor elution volume. The balance was enclosed to prevent disturbances from air currents.
Data Logger and Computer	The Data Logger is a Hewlett-Packard Model 4397A Acquisition/Control unit. The computer is a Hewlett-Packard Model 85A microcomputer.

FIGURE 1

AQUEOUS SEC SYSTEM



1 M NaCl flow stream

Syringe pump(0.15 ml/min)

Rheodyne 7010 Injector
with 1 ml sample loop

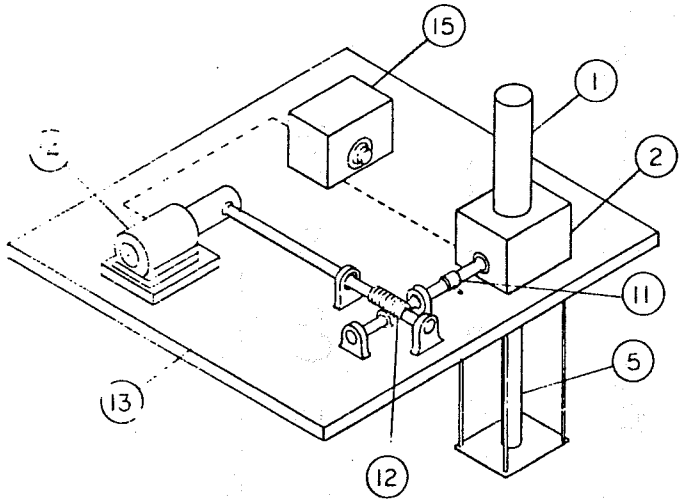
Sephacryl S1000 packing in
1.9 ID X 42 cm column

Pressure Detector(Validyne
DP15 & #20 Diaphragm)
0.05 ID X 25 cm Capillary

Waters 500 Refractometer

Mettler PC400 Balance

HP3497A A/D Converter
HP85 Microcomputer



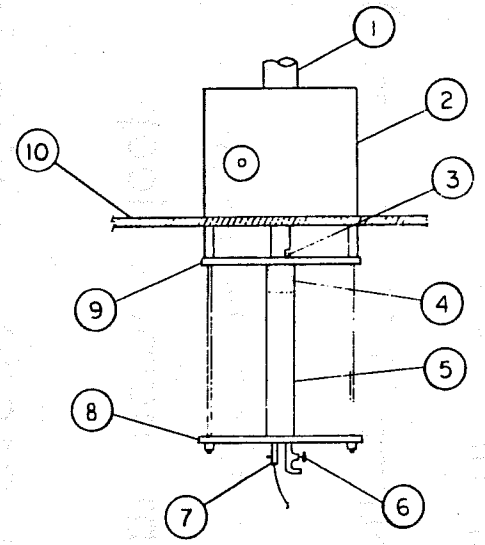


FIGURE 2 : SYRINGE PUMP DETAILS

1-SCREW COVER (SCREW 1 1/4 INCH. DIA., 12 TPI)
2-GEAR BOX (6 PITCH, 20:1 RATIO)
3-CYLINDER VENT VALVE
4-PISTON (FLUID SEAL BY 'O' RINGS)
5-CYLINDER (1 1/2 INCH ID X 10 1/4 INCHES)
6-FLUID INLET VALVE
7-FLUID OUTLET VALVE
8-LOWER SUPPORT PLATE
9-UPPER SUPPORT PLATE
10-BENCH TOP
11-COUPLING AND 1/8 INCH. DIA. ALUM SHEAR PIN)
12-WORM GEAR (8 PITCH, 20:1 RATIO)
13-WORK BENCH
14-MOTOR (1/20 HP, 0-57 RPM, 30:1 GEAR RATIO)
15-BODINE MOTOR CONTROLLER

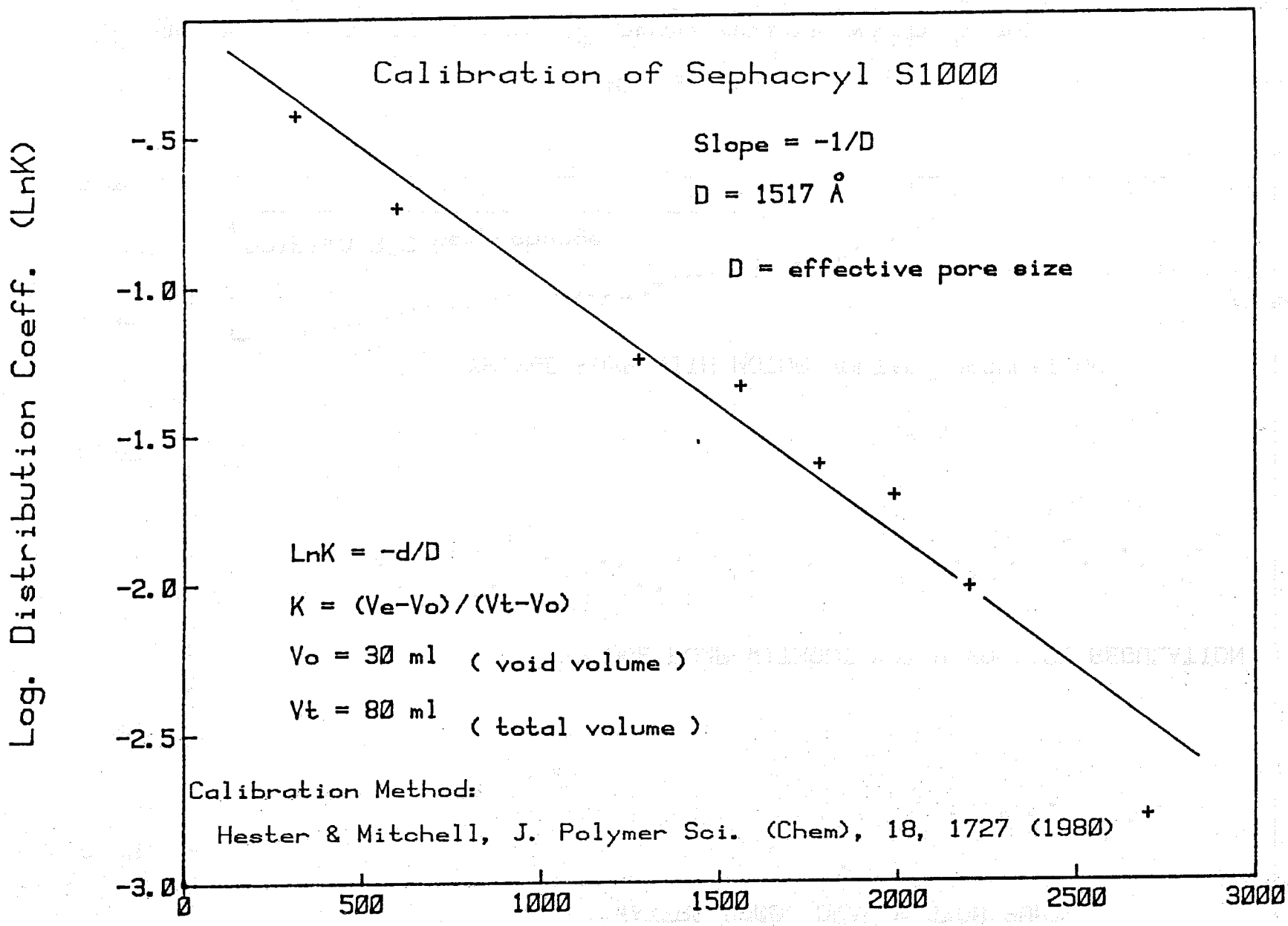

Calibration of Sephacryl S1000
Slope = -1/D
D = 1517 Å
D = effective pore size
LnK = -d/D
K = (Ve-Vo)/(Vt-Vo)
Vo = 30 ml (void volume)
Vt = 80 ml (total volume)
Calibration Method:
Hester & Mitchell, J. Polymer Sci. (Chem), 18, 1727 (1980)
Log. Distribution Coeff. (LnK)
-.5
-1.0
-1.5
-2.0
-2.5
-3.0
0
500
1000
1500
2000
2500
3000
Hydrodynamic Diameter (Å)

Figure 3

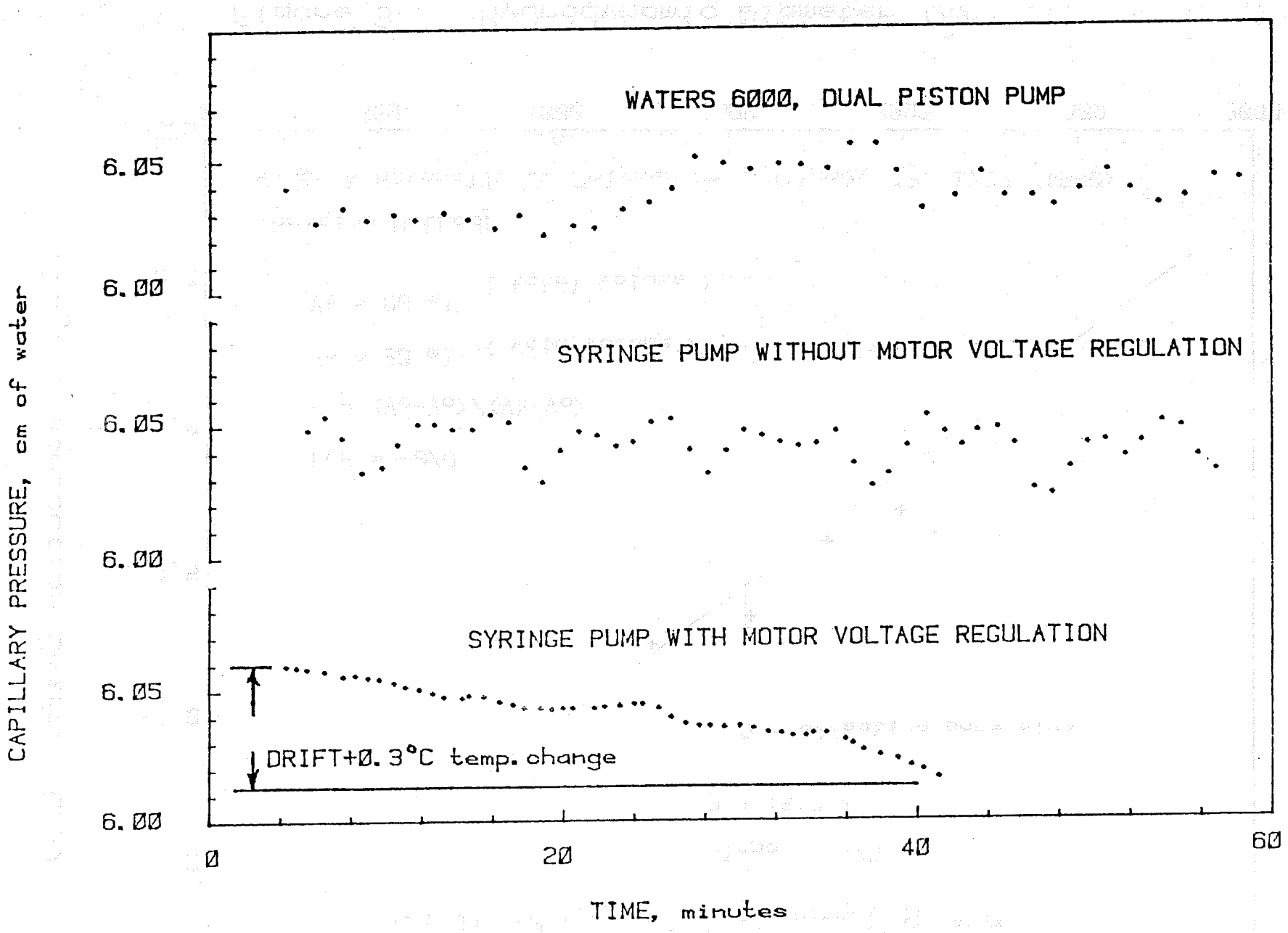


Figure 4 Comparison of pump noise with time

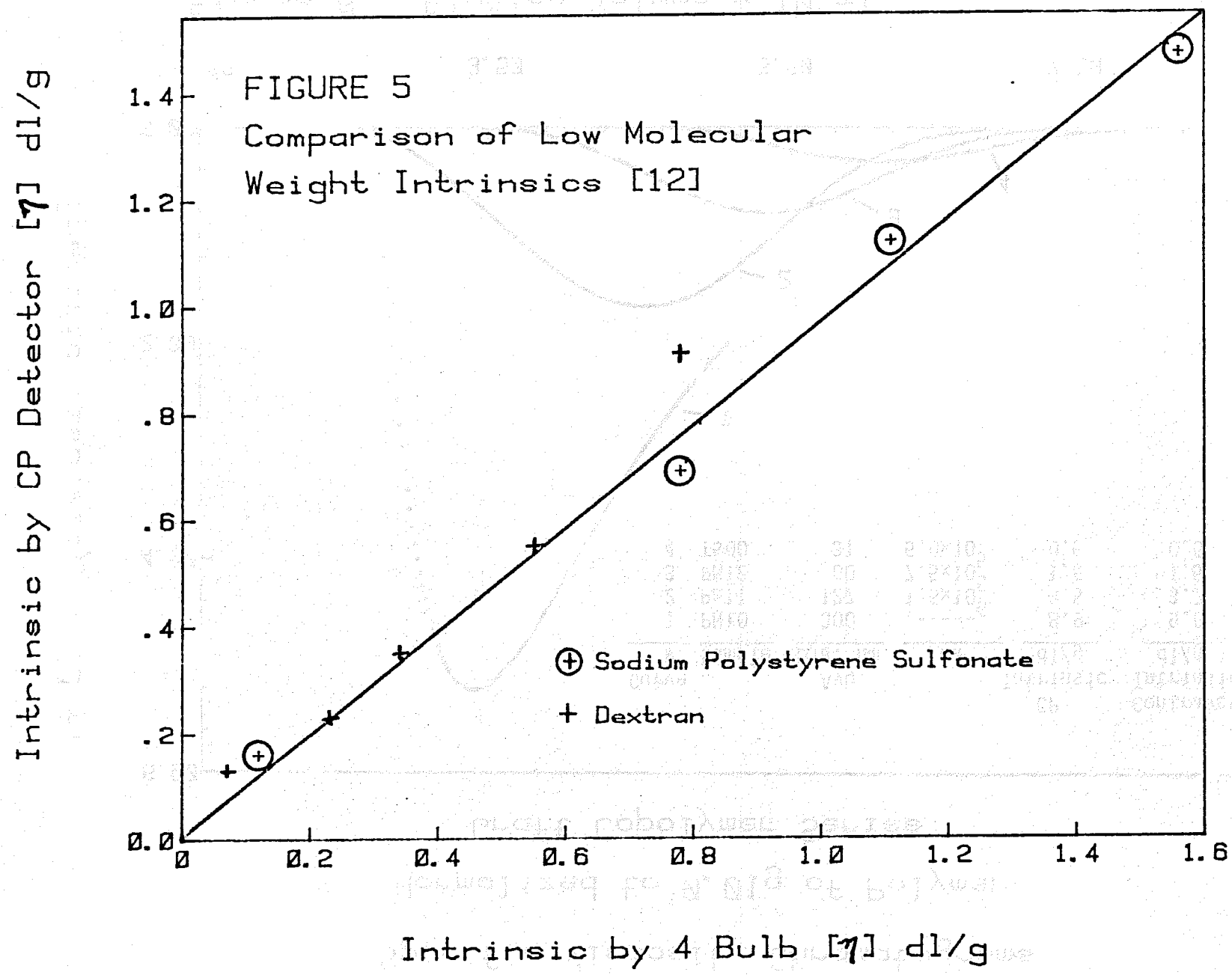
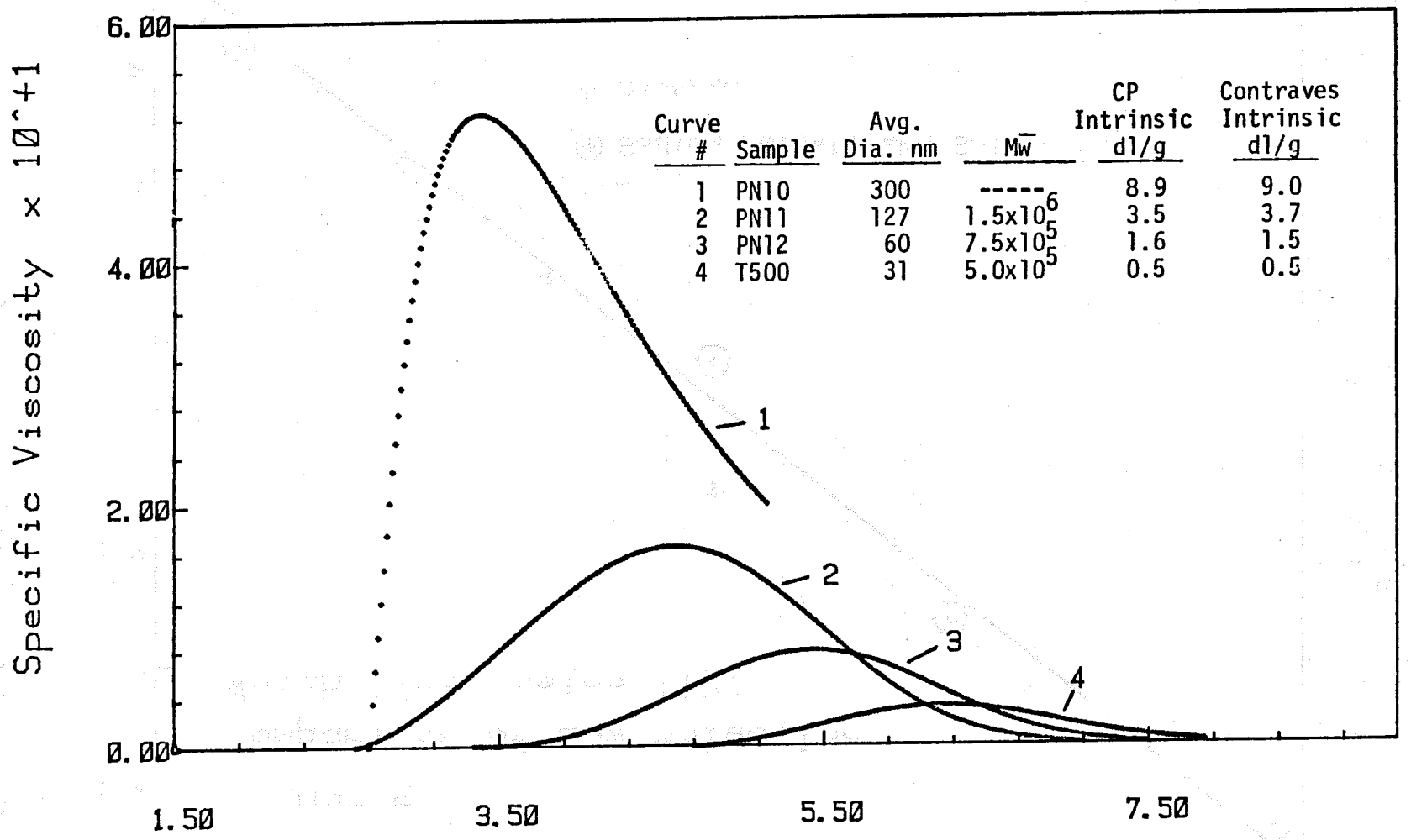


FIGURE 5
Comparison of Low Molecular
Weight Intrinsics [12]
Sodium Polystyrene Sulfonate
Dextran
Intrinsic by CP Detector [η] dl/g
Intrinsic by 4 Bulb [η] dl/g
0.0
.2
.4
.6
.8
1.0
1.2
1.4
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6

Specific Viscosity Chromatograms

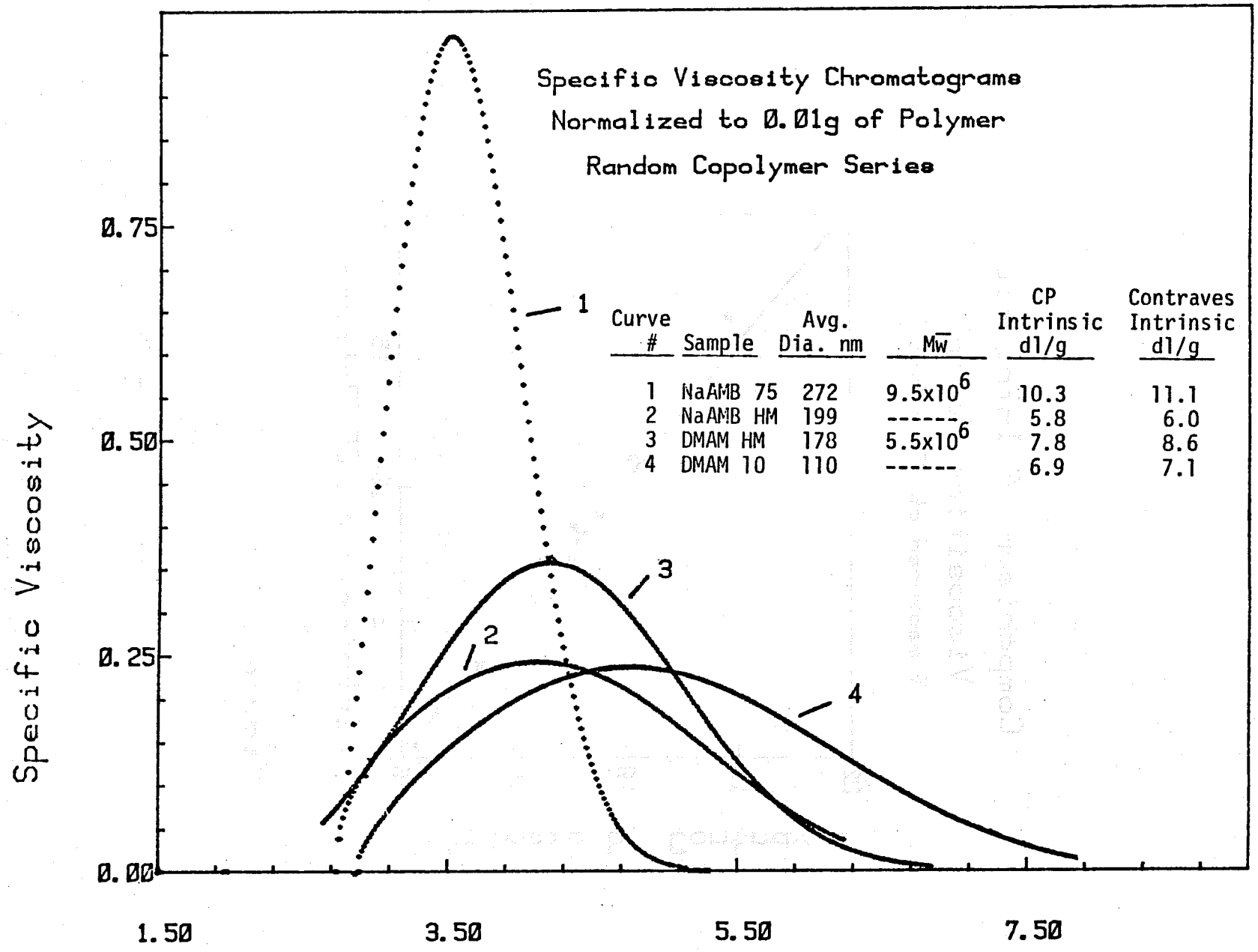
Normalized to 0.01g of Polymer

Graft Copolymer Series



Curve #	Sample	Avg. Dia. nm	$\overline{Mw}$	CP Intrinsic dl/g	Contraves Intrinsic dl/g
1	PN10	300	-----	8.9	9.0
2	PN11	127	1.5×10^6	3.5	3.7
3	PN12	60	7.5×10^5	1.6	1.5
4	T500	31	5.0×10^5	0.5	0.5

Figure 6 Elution Volume x 10^-1



Curve #	Sample	Avg. Dia. nm	$\overline{Mw}$	CP Intrinsic dl/g	Contraves Intrinsic dl/g
1	NaAMB 75	272	9.5×10^6	10.3	11.1
2	NaAMB HM	199	------	5.8	6.0
3	DMAM HM	178	5.5×10^6	7.8	8.6
4	DMAM 10	110	------	6.9	7.1

Figure 7 Elution Volume x 10^-1

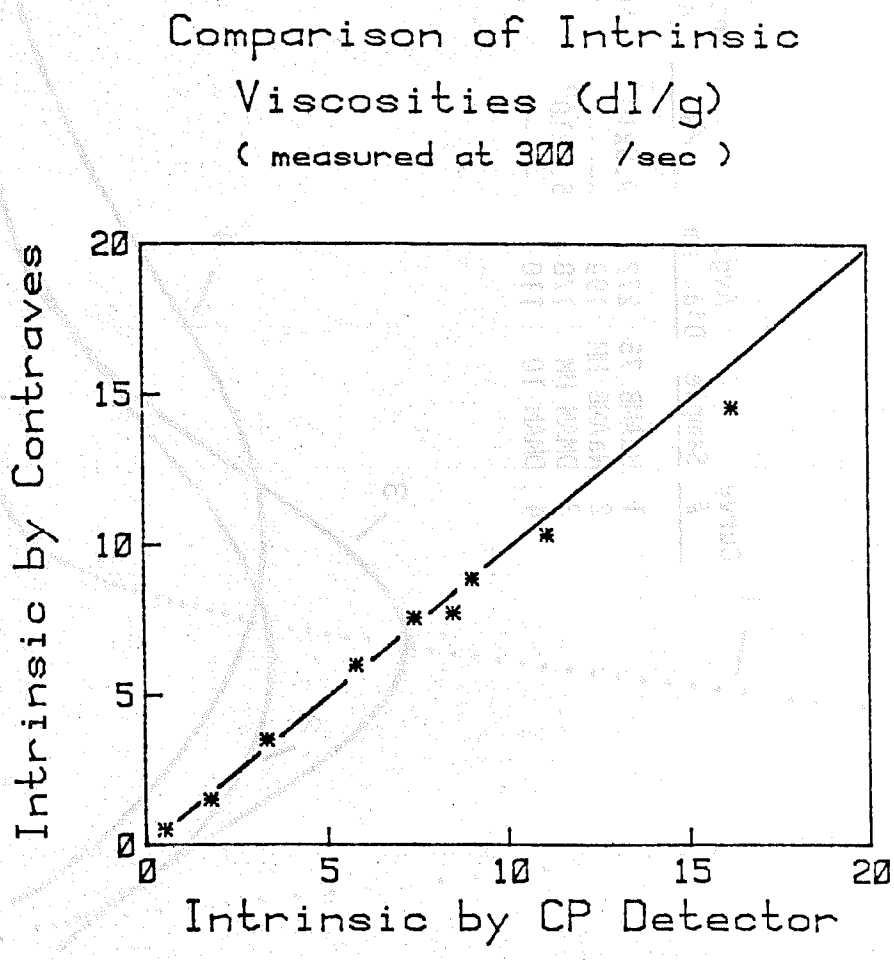

Comparison of Intrinsic
Viscosities (dl/g)
(measured at 300 /sec)
Intrinsic by Contraves
20
15
10
5
0
0
5
10
15
20
Intrinsic by CP Detector

Figure 8.

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CHAPTER VII

DETERMINATION OF INTRINSIC VISCOSITIES: A COMPARISON OF THE CONTRAVES RHEOMETER, CAPILLARY PRESSURE DETECTOR AND FOUR-BULB CAPILLARY VISCOMETER

C. E. Lundy, R. A. Campbell, R. D. Hester

SYNOPSIS

Intrinsic viscosities determined from a Contraves rotational rheometer were compared to intrinsic viscosities determined from both a 4-Bulb capillary viscometer and a Capillary Pressure Detector. For polymer solutions having small pseudoplastic or shear thinning behavior, all three instruments give comparable results. For polymer solutions having high pseudoplastic behavior and for polymers which associate, the Contraves rotational rheometer was found to be superior. The precision of the Contraves has been improved through a low cost data acquisition system which minimizes operator error. The Contraves rotational viscometer is shown to be excellent in measuring the simple shear rheological behavior of typical EOR polymer solutions at low shear rates.

INTRODUCTION

The effects of fluid shear forces on high molecular weight polymers are widely known. These forces cause elongation of polymer chains along the direction of flow producing a lowering of the apparent solution viscosity. This shear thinning, or pseudoplastic, phenomenon produces error in measuring the value of the intrinsic viscosity, which is defined as the average volume that an unperturbed polymer chain occupies per unit molecular weight. Streamlining of a polymer chain due to shear forces in a fluid flow field lowers molecular drag (viscosity). However at very low shear rates, the molecule is unperturbed and the solution viscosity is larger. The Newtonian region, existing at low shear rates, is important since this region describes the unperturbed dimensions of the polymer and it is in this region that many of the EOR applications of high molecular weight water-soluble polymers exist. In order to correct for high shear rates a "zero"

shear viscosity or Newtonian viscosity must be determined. This "zero" shear value may be determined using several rheological techniques [1].

The most common and least expensive instrument for determining the shear dependence of polymers is a four bulb capillary viscometer. Unfortunately, the shear rates in this viscometer are many times too high to effectively extrapolate to a "zero" shear viscosity. Therefore a Contraves rotational rheometer has recently been utilized to determine the "zero" shear viscosities of water-soluble polymers synthesized for potential EOR applications.

A data acquisition system was developed to eliminate several operator errors inherent with this rheometer and to improve its precision of measurement. It will be shown in this paper that for polymer solutions which exhibit little or no shear thinning, the 4-bulb and Contraves extrapolated "zero" shear viscosities agree. However, for many high molecular weight polymers having large shear thinning behavior or polymers which associate, a 4-bulb viscometer gives lower solution viscosities than those obtained from the Contraves rheometer. This discrepancy illustrates the necessity of using a rotational rheometer in determining the intrinsic viscosity for many water-soluble polymers.

COMPARISON OF CAPILLARY VISCOMETER AND CONTRAVES RHEOMETER

Two types of instruments are generally used to measure viscosities. These are the 4-bulb capillary viscometer and the concentric cylinder rheometer. The major difference between the two instruments is that the capillary viscometer does not maintain a constant shear rate from sample to sample. In the capillary viscometer there is a radial shear gradient and the shear rate reported is only an average shear rate. Also there are only 4 shear rates available. The shear rate in a capillary is not controllable but is inversely proportional to the efflux time for the sample to pass through the capillary viscometer bulbs. This efflux time is dependent on the sample viscosity. Thus two samples with different viscosities are then measured at different shear rates.

The capillary viscometer has a gradient of shear rates in the radial direction from the center line of the capillary to the wall. Thus individual molecules are exposed to varying shear rates depending on the instantaneous position of the molecule in the capillary. The average shear rate is reported as the apparent shear rate.

For a given polymer sample concentration, four shear rates are available with the capillary viscometer. The capillary viscometers used were Cannon Instruments shear dilution 4-bulb viscometers, size 50 and 100. These shear rates are plotted versus reduced viscosities to determine the "zero" shear reduced viscosity at each concentration. Generally, the data points are non-linear due to shear thinning and must be extrapolated to "zero" shear or the 1st Newtonian shear region. With only four data points, linear extrapolation can have considerable error.

Therefore, a function which closely describes the behavior of shear thinning polymers is desirable. The Carreau model, which relates the apparent viscosity to the shear rate, has been found to be an excellent function to describe the rheological behavior of many high molecular weight polymers. The Carreau function [2] is described by equation (1):

$$V = V_s + [V_o - V_s]\,[1 + (TD)^2]^{(M-1)/2} \qquad (1)$$

The polymer solution viscosity, V, is related to the shear rate, D, and pure solvent viscosity, V_s, through three parameters: the "zero" shear viscosity, a molecular relaxation time, T, and a flow index, M.

By fitting apparent viscosity versus shear rate data to equation (1), the parameter values can be determined. Thus the "zero" shear viscosity can be extrapolated from viscosity data taken at higher shear rates. This non-linear fitting was done by the method of Marquardt [3].

The Contraves rheometer has a shear rate distribution narrow enough to assume a uniform shear rate throughout the fluid sample [4]. This allows all the sample solution to be exposed to the same shear rate. Also, the shear rate is controllable. Thus the shear rate can be made constant from sample to sample. There are 30 available shear rates on the Contraves. These shear rates are lower than the lowest possible shear rate of the four-bulb viscometer, about 50 sec^{-1}. This allows for a more accurate extrapolation to the "zero shear" viscosity [5].

The Contraves Low Shear 30 Rheometer (LS30) is a rotational rheometer based on the Couette principle. The fluid to be measured is placed in a gap between two concentric cylinders. The cylinder set used in this study was the low shear measuring set MS-LS 2T-2T. The outer cylinder of the LS30 is driven by a speed-controlled motor having thirty (30) fixed speeds, in a geometric progression ranging from 0.02 to 130 sec^{-1}.

The outer cylinder, or cup, of the coaxial measuring system, which is rotating at accurately defined speed, exerts through the fluid a torque on the inner cylinder, or bob. This bob is suspended on a torsion wire. The applied torque causes a mirror attached to the torsion wire to undergo a deflection. This deflection, in turn, is measured by a photo-electric system in the LS30 measuring head. This deflection is proportional to the torque and to the fluid viscosity.

In its basic form, the LS 30, with appropriate measuring systems, can evaluate fluids with viscosities in the range of 1.5 X 10^{-3} to 6 X 10^{6} CP. Depending on the measuring system, the shear rate ranges from 3.5 X 10^{-3} to 2.5 X 10^{2} sec $^{-1}$ and the shear stress ranges from 20 X 10^{-6} to 0.1 Pa. The system requires less than 1.5 ml of sample volume. Signal output of the basic unit is a digital display of the torque, which is converted to a viscosity value by use of the appropriate factor from a table corresponding to the geometry of the particular cylinder set measuring system.

DATA ACQUISITION

Inherent in the operation accuracy of the LS30 is a degree of operator dependency. This operator dependency is due to zeroing the instrument, centering the measuring bob, and reading the torque indication. Suitable torque zeroing can be accomplished with a deviation of ± 0.05% on torque ranges 3 through 5. However, ranges 1 and 2, the more sensitive ranges, require more effort to zero. Centering of the measuring bob is done by adjusting the levelling feet on the measuring head until the cup is suspended concentrically in the bob. The torque indication is a digital readout from 0 to 100 with 1 decimal precision. Generally the torque readout fluctuates between a maximum and a minimum value and these readouts must be averaged to get a suitable torque value. These fluctuations reflect centering problems. Other sources of error can be due to inadequate bob or cup cleaning procedures and/or failure to remove air bubbles from the fluid sample. Also, due to the high sensitivity of the instrument, even small dust particles can produce torque disturbances.

Several of the problems of operator dependency have been removed or at least reduced with the addition of an inexpensive data acquisition system to the Contraves. The problems associated with centering the bob and reading the torque indication have been removed since the acquisition system averages many torque signals for an adequate length of time. The acquisition system consists of an analog-to-digital interface, a handheld calculator, and an

interface loop to connect the interface to the calculator. Software has been developed to control the acquisition of data from the Contraves. See Figure 1.

The interface is an ADC 41, built by Interface Instruments of Corvallis, Oregon. The ADC 41 is an 8 channel, 4 1/2 digit analog-to-digital computer interface. The calculator is a Hewlett-Packard HP-41CX. The calculator has a built-in timer, allowing variable scan intervals so that a minimum of 1 complete revolution on the Contraves is always measured. The HP-41CX has enough memory to store the data from several fluid viscosity determinations. A Hewlett-Packard interface loop module connects the calculator to the interface. The interface loop allows connection of the calculator to a Hewlett-Packard HP-85 microcomputer. This facilitates data transfer for analysis by the HP-85 [6].

Software has been developed to control the acquisition of data [7]. See Figure 2. The instrument operator imputs the torque range and motor setting (shear rate). The program then determines the appropriate scan time interval (minimum 1 sec/scan), allows the Contraves to equilibriate, and samples the torque for a number of scans to allow a minimum of one cup revolution. The sampled torque scans are then averaged. The shear rate, average viscosity, and standard deviation of the viscosity are output by the program. Detailed program documentation and program code is available upon request.

DISCUSSION

The intrinsic viscosities of several water-soluble polymers were compared by 4-bulb, CP detector, and Contraves viscometers. The results are given in Table I. In all cases the intrinsic viscosity was determined by extrapolating the reduced viscosity to zero polymer concentration.

For large molecular weight water-soluble polymers the intrinsic viscosity is highly shear dependent. Due to this shear dependence the Carreau rheological equation was used to determine the "zero" shear viscosity from data obtained by a 4-bulb viscometer. Figures 3 and 4 show the accuracy with which the Carreau equation fits experimental data. The lowest curve in Figure 3, corresponding to the lowest concentration, is a spline fit to the data. This was necessary because of the inability of the Carreau model to fit data at extremely low polymer concentrations.

As Table I shows, there is good agreement between the intrinsic viscosities determined by the three methods. The polymers used to construct Table I were, in general, Newtonian in behavior. Therefore, in the absence of shear thinning behavior, viscosities determined at different shear rates agree very well.

Table II lists the intrinsic viscosities of several diacetone acrylamide/acrylamide copolymers determined by 4-bulb, Contraves, and CP viscometers. These polymers are associative in nature and are highly shear dependent. As the table shows there is poor agreement between viscosity measurements. The CP detector which operates at a shear rate of 300 sec^{-1} is not expected to accurately estimate the zero shear viscosity of these polymers due to their extreme shear sensitivity.

In these polymers, shear forces do not merely elongate the polymer coils, as in the case of unassociated high molecular weight polymers, but also disassociate clusters of polymer molecules. Consequently, the Carreau model, which seems to accurately describe the shear thinning behavior of high molecular weight water-soluble polymers and polyelectrolytes, is unable to describe the association/disassociation process simultaneously occurring in these polymers. Therefore, the CP detector and 4-bulb viscometers, which operate at fairly high shear rates, act to break up the associations, and are unable to effectively describe the nature of these polymers. Thus these measurements give lower viscosity values than expected.

The Contraves viscometer, capable of operating at extremely low shear rates, can more accurately describe the viscous nature of these polymers in an unperturbed state. Figure 5 shows the effect of shear rate on the viscosity of DAAM-25 as determined from a 4-bulb and Contraves viscometer. As shown, the viscosity measurements between instruments show a large discontinuity at a shear rate of 100 sec^{-1}. This difference may be due to the radial gradient of shear rates always existing in a 4-bulb capillary viscometer [8]. This shear rate gradient would produce a different degree of polymer association than would exist in the same fluid measured by the Contraves where no shear rate gradient exists. Also it should be noted that associative polymers have viscous behavior which is history dependent. Each viscometer is measuring the same fluid, but the same fluid has experienced a different shear history in each viscometer.

CONCLUSIONS

The instrument used to measure viscosities is dependent on the sample being tested. For non-associating polymers and polymers with a low shear dependency, the less expensive 4-bulb capillary viscometer can provide reasonable viscosity values. However, for all associating polymers and polymers with a high shear dependency, the 4-bulb viscometer is not acceptable due to a large shear gradient and high shear rates in the capillary.

For associating polymers and polymers with a high shear dependency, the Contraves concentric cylinder rheometer can be used. Comparison of the Contraves rheometer and the 4-bulb viscometer data shows a discrepancy in the measured viscosities. This difference can possibly be attributed to the shear history experienced by a sample in the instruments. Several sources of possible operator error and the precision of the Contraves have been improved with the addition of an inexpensive data acquisition unit to the rheometer system.

In future work, an intensive study of the effects of shear history on potential EOR polymers will be performed using the Contraves rheometer. Also, improvements in the data acquisition system will be made. Of special importance are improvements in the analysis of data taken at extremely low shear rates and polymer concentrations.

TABLE I

Comparison of Intrinsic Viscosities

Polymer Sample ID	Intrinsic Viscosity, dl/g		
	Four Bulb+	Pressure Detector*	Contraves Rheometer*
T-500	0.51	0.53	0.52
PN12	1.7	1.6	1.8
PN11	3.6	3.5	3.4
PN10	7.0	8.9	9.0
NaAMBHM	5.5	5.8	6.0
NaAMB75	---	10.3	11.1

\+ Variable shear rates

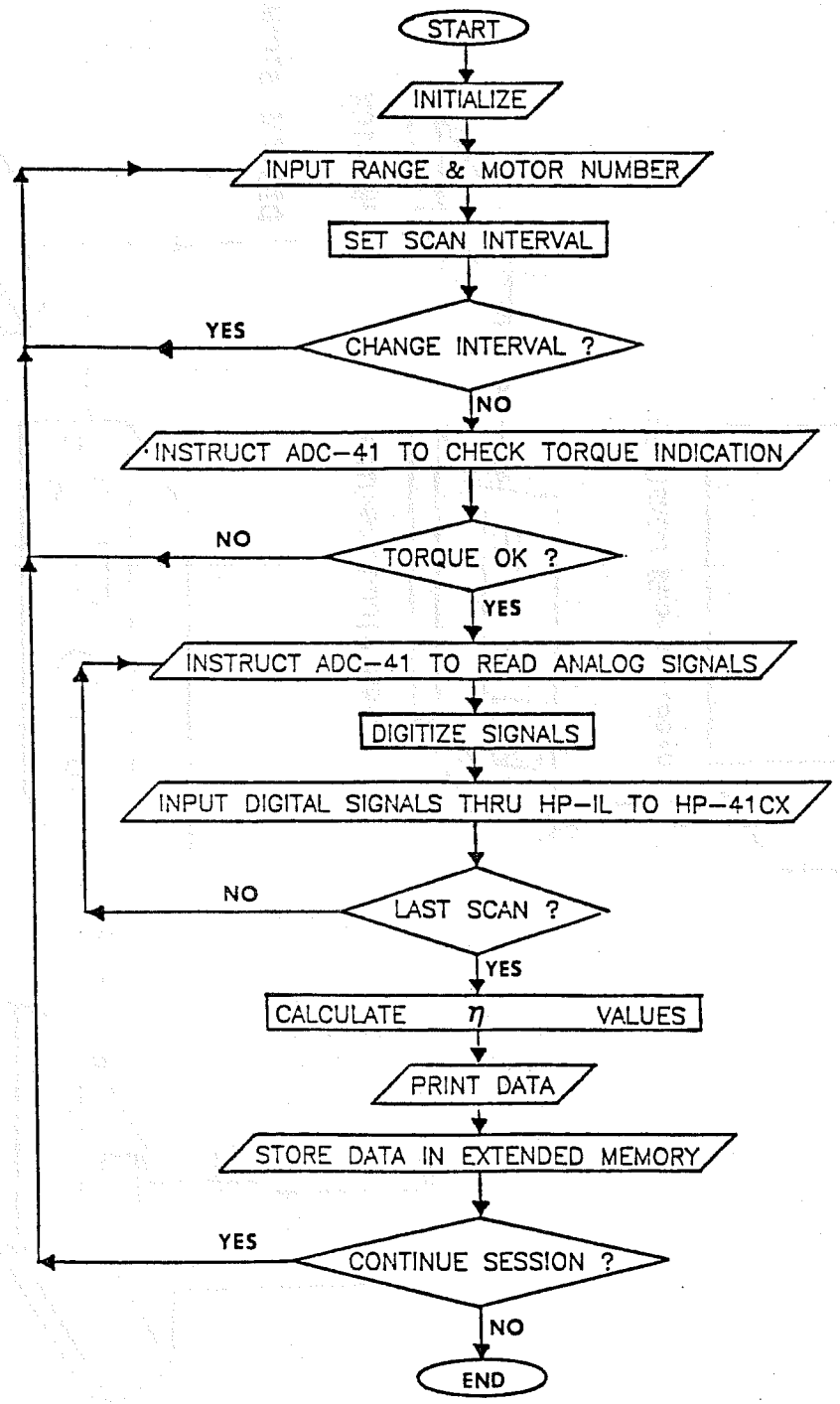
* Shear rate of 300 sec^{-1}

TABLE II

Comparison of Diacetone Acrylamide/Acrylamide Copolymers

Polymer Sample	Intrinsic Viscosity (dl/g)		
	Four Bulb	CP Detector	Contraves
DAAM-25	7.2	14.6	23.4
DAAM-2L	4.0	7.57	15.1
DAAM-3L	4.0	6.05	12.4

FIG. 1 FLOW DIAGRAM OF CONTRAVES ACQUISITION PROGRAM



CONTRAVES RHEOMETER SYSTEM SCHEMATIC DIAGRAM

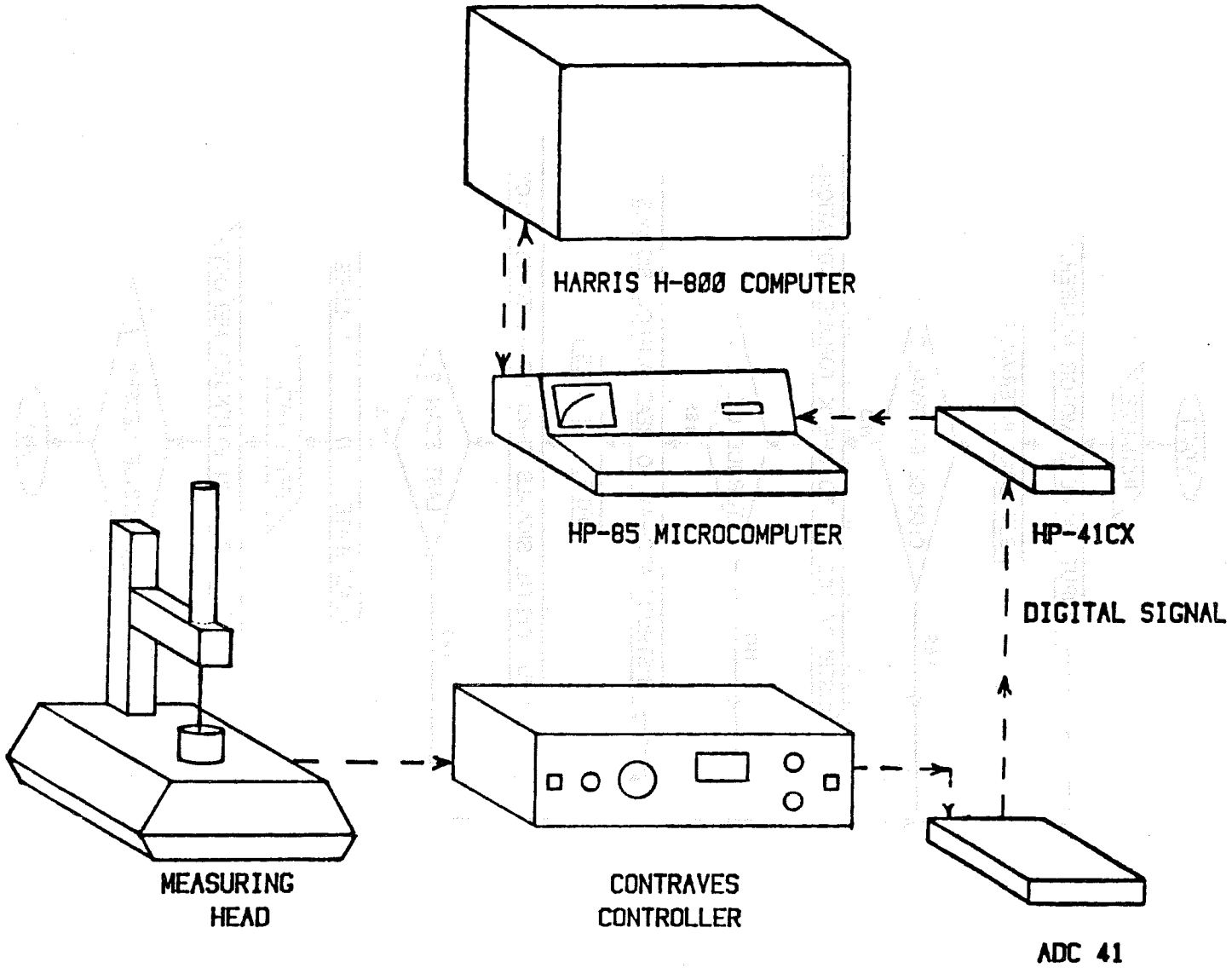


Figure 2

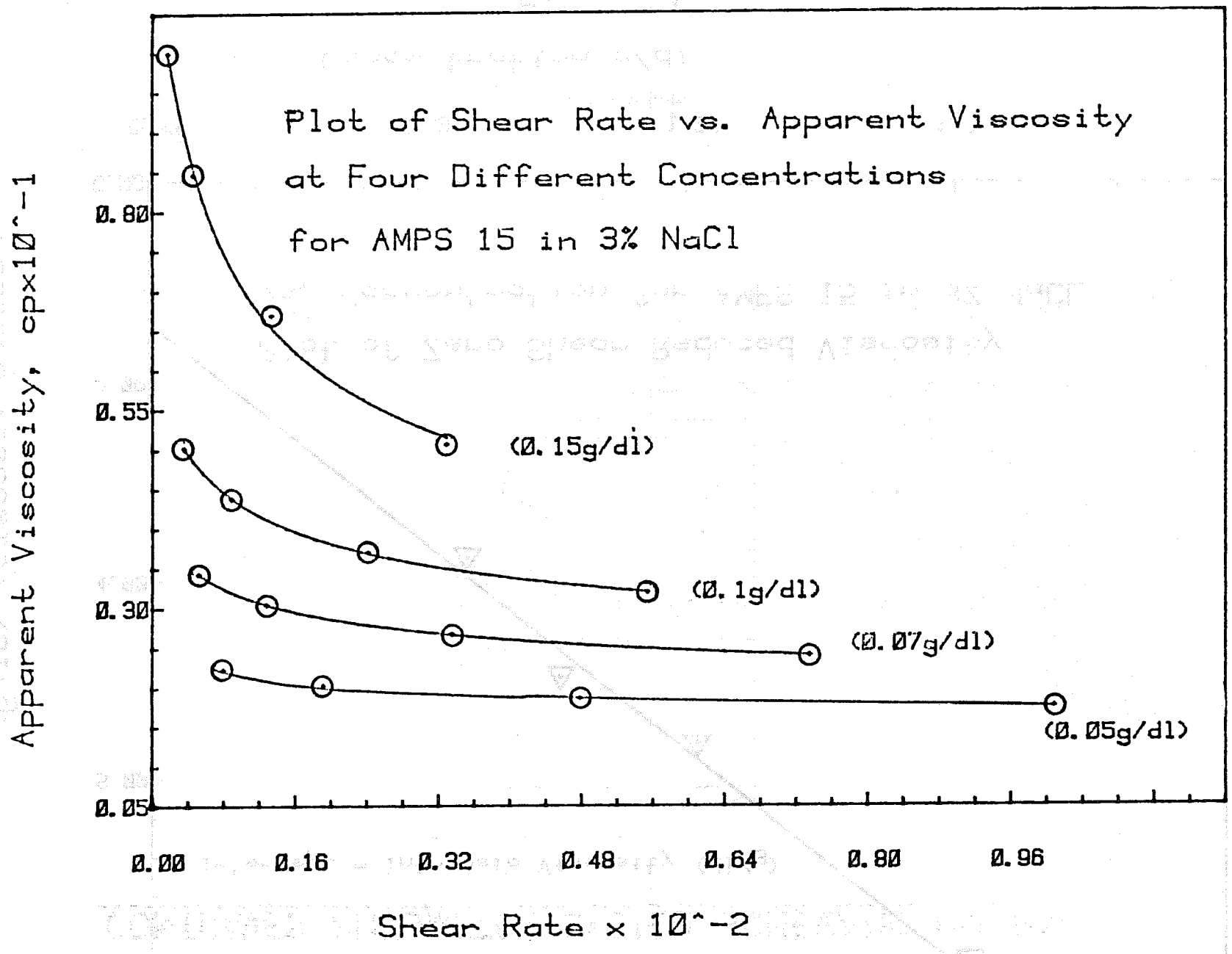

Plot of Shear Rate vs. Apparent Viscosity
at Four Different Concentrations
for AMPS 15 in 3% NaCl
Apparent Viscosity, cpx10^-1
0.80
0.55
0.30
0.05
(0.15g/dl)
(0.1g/dl)
(0.07g/dl)
(0.05g/dl)
0.00
0.16
0.32
0.48
0.64
0.80
0.96
Shear Rate x 10^-2

Figure 3

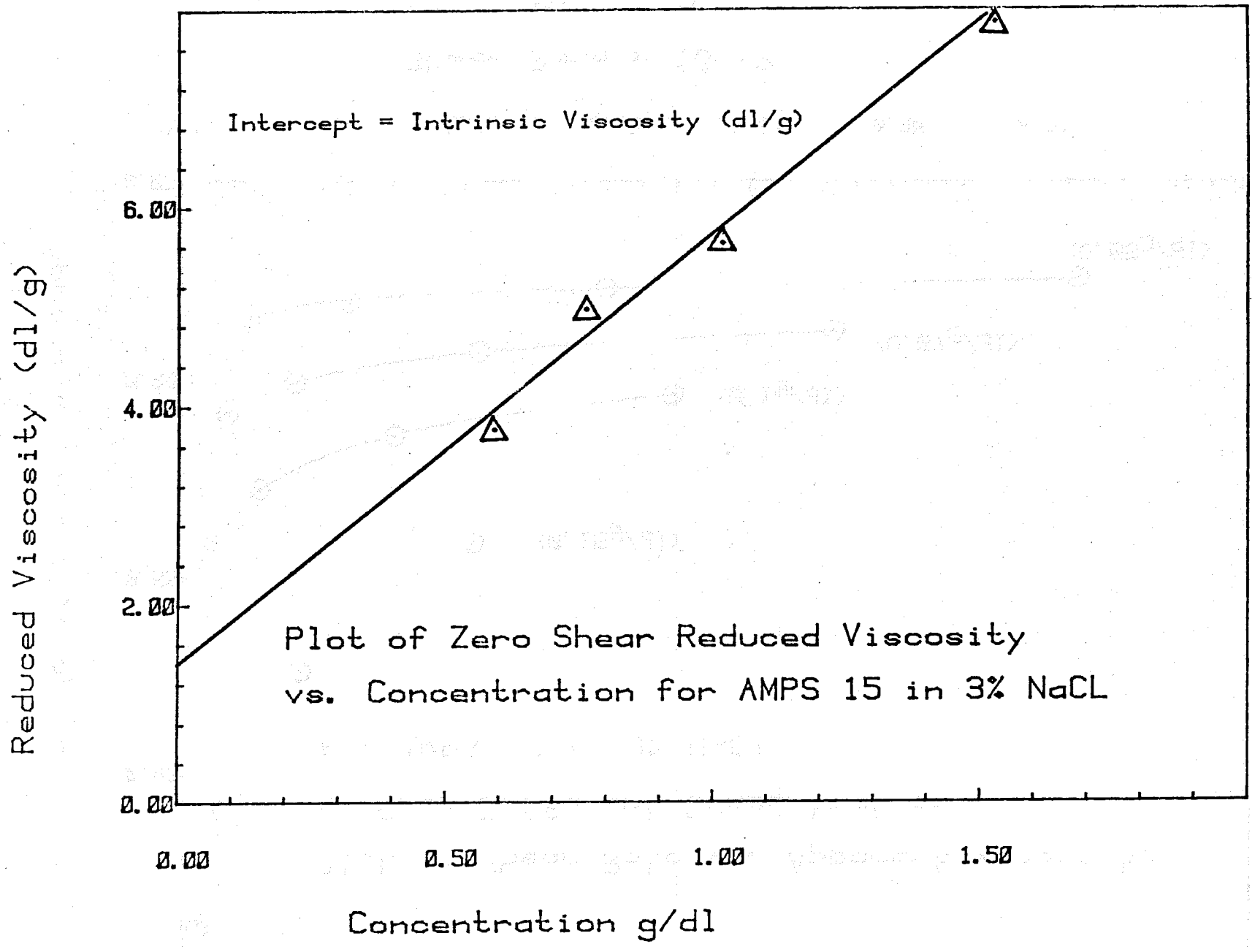

Intercept = Intrinsic Viscosity (dl/g)
Plot of Zero Shear Reduced Viscosity
vs. Concentration for AMPS 15 in 3% NaCL
Reduced Viscosity (dl/g)
6.00
4.00
2.00
0.00
0.00
0.50
1.00
1.50
Concentration g/dl

Figure 4

Shear Dependence of DAAM25 as Compared by Contraves and Four Bulb

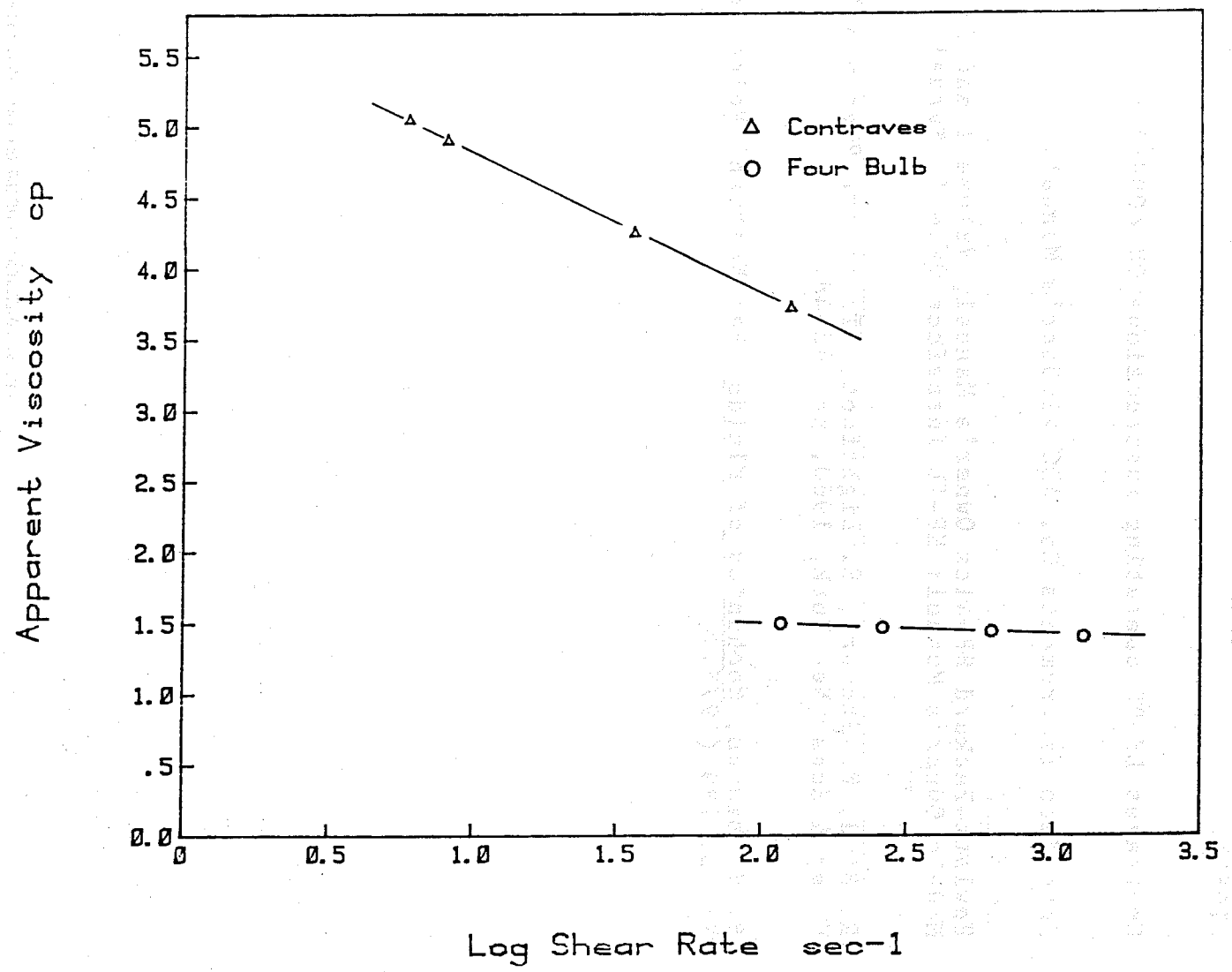


Figure 5

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