Water-Soluble Copolymers. V. Compositional Determination of Random Copolymers of Acrylamide with Sulfonated Comonomers by Infrared Spectroscopy and C13 Nuclear Magnetic Resonance

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Synopsis

Compositional analyses of random copolymers of acrylamide with sodium-2-sulfoethyl methacrylate and with sodium-2-acrylamido-2-methylpropane sulfonate have been performed utilizing elemental analysis, infrared spectroscopy, and C13 NMR. A mathematical method involving nitrogen to sulfur ratios has been developed to eliminate errors which often arise from associated water in hydrophilic copolymers. The ratios of infrared absorbances at 1043 cm^{-1} and 1664 cm^{-1} were used to determine the composition of AM—NaAMPS copolymers; likewise, absorbance ratios at 1040 cm^{-1} and 3200 cm^{-1} were utilized for determination of the AM—NaSEM copolymer composition. Carbon-13 NMR spectra of the copolymers were also obtained, and characteristic peaks were utilized to quantitate copolymer composition. The results obtained by elemental analyses, infrared spectroscopic studies, and NMR were in excellent agreement. These techniques are of great value for determining composition of hygroscopic copolymers which can crosslink or form strong intramolecular hydrogen bonds, often precluding further characterization.

INTRODUCTION

Water-soluble copolymers of acrylamide (AM) have been utilized in a number of applications.[1,2] Copolymers of AM with sulfonated comonomers, especially sodium-2-acrylamido-2-methylpropane sulfonate (NaAMPS), offer hydrogen-bonding capability and polyelectrolyte behavior in aqueous solution—characteristics of special interest in enhanced oil recovery.[3-18] The solution properties and the ultimate performance of these polymers as mobility control agents are dictated by molecular structure.

Compositional analyses of acrylamide copolymers have usually been based on nitrogen elemental analysis[19-21] or potentiometric titration.[22-24] These methods require accurate weighing of a completely dry sample. Unfortunately, acrylamide copolymers easily crosslink during the drying process at elevated temperatures.[1] These copolymers are quite hygroscopic and must be properly handled during weighing to avoid large errors in concentration of solutions prepared for light scattering, size exclusion chromatography, and viscosity measurements.

In this work, we report characterization of previously synthesized copolymers of AM with NaAMPS and with NaSEM[14,17,18] utilizing elemental analysis, infrared spectroscopy, and C13 nuclear magnetic resonance. Although Muller et al.[25] reported qualitative infrared analysis for partially hydrolyzed polyacryl-

amide and Shaglayeva et al.[26] for copolymers of acrylamide and acrylic acid, no satisfactory infrared or C^{13} procedures for compositional analysis of random copolymers of acrylamide with sulfonated comonomers appear to have been published in the literature.

EXPERIMENTAL

Materials

The homopolymers of acrylamide (AM), sodium-2-sulfoethyl methacrylate (NaSEM), and sodium-2-acrylamido-2-methylpropane sulfonate (NaAMPS), and the series of copolymers of AM with NaSEM and with NaAMPS used in this investigation were synthesized under conditions reported previously.[18] In a typical example, AMPS-1-5 (Table I) was prepared by first dissolving 13.370 g (0.188 mol) of acrylamide, 4.331 (0.021 mol) of 2-acrylamido-2-methylpropane sulfonic acid (AMPS), and 0.836 g of NaOH (0.021 mol) in 220 g of distilled water. The pH of the aqueous solution was then adjusted to a value of 9.0 ± 0.1 by dropwise addition of 0.1N NaOH. The aqueous solution was transferred to a 500 mL, three-necked, round-bottomed flask equipped with mechanical stirrer, nitrogen inlet tube and rubber septum. The solution was deareated with oxygen-free nitrogen for 15 min and warmed to 30°C in a constant temperature bath. Potassium persulfate (0.0565 g) dissolved in 10 mL of distilled water was injected into the solution through the rubber septum. After 4 h of stirring, the reaction solution was distilled with water (5:1). The polymer was precipitated from solution by addition to acetone. The copolymer was further purified by redissolution into water followed by passage through a Dowex HCRW-2 exchange resin (sodium salt form). After precipitation into acetone, the polymer was dried under vacuum at 50°C to constant weight.

TABLE I
Copolymer Composition Data Derived from Elemental Analysis of AM—NaAMPS and AM—NaSEM Copolymers

Sample[a]	Mole Fraction of sulfonated monomer in feed	Reaction time (min)	N (wt %)	S (wt %)	Sulfonated monomer units in copolymer (mol %)
AMPS-1-5	0.10	240	14.03	3.05	9.51 ± 0.76
AMPS-2-5	0.20	240	12.15	5.28	19.01 ± 1.03
AMPS-3-5	0.30	240	10.65	6.78	27.85 ± 1.34
AMPS-4-5	0.40	240	9.65	8.30	37.63 ± 1.69
AMPS-7-5	0.70	240	6.94	10.43	65.75 ± 3.16
K-16-2	0.10	60	8.84	6.75	25.04 ± 1.31
K-16-3	0.10	120	9.94	5.68	20.00 ± 1.11
K-16-5	0.10	240	11.65	4.92	15.60 ± 0.90
K-6-2	0.20	60	6.48	8.32	35.93 ± 1.87
K-6-5	0.20	240	7.99	7.65	29.52 ± 1.51
K-17-2	0.30	60	3.73	10.38	54.90 ± 4.00
K-17-5	0.30	240	4.89	9.58	46.18 ± 2.85

[a] AMPS series are copolymers of AM—NaAMPS; K series are copolymers of AM—NaSEM.

Elemental Analyses

Elemental analyses for nitrogen and sulfur for each copolymer were conducted by Galbraith Laboratories of Knoxville, Tennessee. The error in determination for each element is reported to be ±0.2%.

The limit of the error for determining mole fractions of NaAMPS and NaSEM in the respective copolymers with acrylamide are given below:

$$\left(\begin{array}{c} \text{limit of error in analysis} \\ \text{of AM—NaAMPS copolymer} \end{array}\right) = \frac{14.0\ (S)}{32.1\ (N)}\left[\frac{dS}{S} + \frac{dN}{N}\right]$$

$$\left(\begin{array}{c} \text{limit of error in analysis} \\ \text{of AM—NaSEM copolymer} \end{array}\right) = \frac{14.0\ (S)}{32.1\ (N) + 14.0\ (S)}\left[\frac{dS}{S} + \frac{dN}{N}\right]$$

The absolute errors are dS and dN; S and N represent sulfur and nitrogen contents, respectively.

Infrared Measurements

The purified homopolymers of AM, NaSEM, and NaAMPS were redried at 60°C for 24 h before preparing films. Series of mixtures of poly(AM) with poly(NaSEM) and with poly(NaAMPS) were dissolved in distilled water; clear polymer films were obtained for all blended ratios by casting onto silver chloride minicell windows. The polymer films were dried under vacuum at room temperature for 1 h. Infrared spectra were recorded with a Perkin-Elmer 567 Grating Infrared Spectrophotometer. Errors reported from infrared studies are estimated at 5% of the absorbance ratio measured.
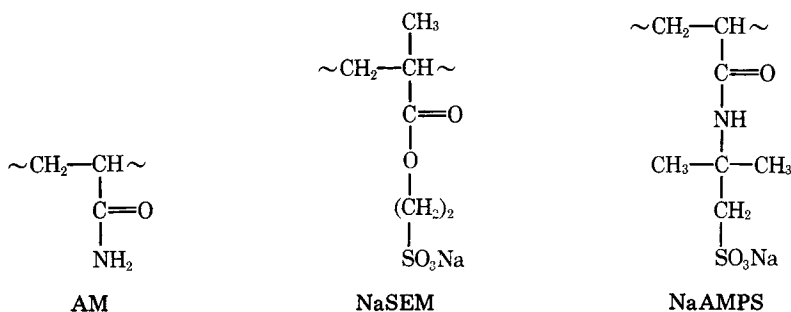
C^{13} Nuclear Magnetic Resonance Spectrometry

Solutions of the AM—NaSEM and AM—NaAMPS copolymers were prepared by dissolving 0.1 g of copolymer in 2 mL of a 50/50 D_2O/H_2O mixture. Carbon-13 NMR spectra were accumulated at 22.5 MHz on a JEOL FX-90Q Spectrometer using 10 mm tubes. Quadrature detection was employed with a 5000 Hz window and 8K data points. The sodium salt of 3-(trimethylsilyl)-1-propanesulfonic acid was used as an internal standard and D_2O as the internal lock. Due to high viscosities of the polymer solutions, vortex plugs were utilized. Errors were estimated as 5% of the relative intensity ratios measured for the resonances.

RESULTS AND DISCUSSION

In order to assess the structure/solution property relationships for the copolymers listed in Table I, it was necessary to accurately measure composition of the copolymers. The ratios of the comonomers in the feed for the NaAMPS/AM system were varied from 1:9 to 7:3 for samples AMPS-1-5 through AMPS-7-5. For the NaSEM/AM system, the ratios were varied from 1:9 to 3:7

for samples K-16-2 through K-17-5. Additionally, for the latter series, the reaction times were varied. Repeating units in the copolymers are shown below:

$$
\begin{array}{ccc}
& \overset{\displaystyle CH_3}{\underset{\displaystyle |}{\sim CH_2-CH\sim}} & \sim CH_2-CH\sim \\
\end{array}
$$

<div style="text-align:center">

~CH₂—CH~   ~CH₂—CH~   ~CH₂—CH~

| | |

C=O   C=O   C=O

| | NH

NH₂   O   CH₃—C—CH₃

(CH₂)₂   CH₂

SO₃Na   SO₃Na

AM   NaSEM   NaAMPS

</div>

Elemental Analyses

In order to eliminate errors which may arise from incomplete water removal (or different extents of water removal) from the copolymer samples, molar ratios of two elements, sulfur and nitrogen, may be calculated from elemental analysis data. The weight percentages of sulfur and of nitrogen present in a selected AM—NaAMPS copolymer are represented by eqs. (1) and (2), respectively. The concentrations (mol) of AM and NaAMPS comonomer units in 1 g of sample are

$$\% \, S = \frac{32.1 \, c_2}{w_1} \tag{1}$$

$$\% \, N = \frac{14.0 \, (c_1 + c_2)}{w_1} \tag{2}$$

represented by c_1 and c_2, respectively. Since a single sample is used for both analyses, the mole fraction of NaAMPS units may be determined by eq. (3). Any errors associated with values of w_1 (the weight of the copolymer) are thus cancelled in this expression:

$$\frac{c_2}{c_1 + c_2} = \frac{w_1}{w_1} \frac{14.0 \, (\% \, S)}{32.1 \, (\% \, N)} \tag{3}$$

Likewise, the mol % of NaSEM in 1 g of a selected sample of AM—NaSEM copolymer is given by eq. (4), where c_3 represents the molar concentration of NaSEM in 1 g of the copolymer.

$$\frac{c_3}{c_1 + c_2} = \frac{14.0 \, (\% \, S)}{32.1 \, (\% \, N) + 14.0 \, (\% \, S)} \tag{4}$$

The elemental analysis data for each synthetic copolymer is given in Table I along with the calculated mol % of the sulfonated comonomer in the copolymer. The error reported for each determination is calculated as described in the experimental section.

Infrared Spectroscopy

Infrared spectra for homopolymers of AM, NaAMPS, and NaSEM are shown in Figures 1, 2, and 3, respectively. The absorbance at 1664 cm^{-1}, attributed to C=O stretching, is present in both AM and NaAMPS units. The absorbance bands were used for quantitative analysis of the AM—NaAMPS copolymers. Similarly, the absorbances at 3200 cm^{-1} (NH) and 1040 cm^{-1} (S=O) were used as characteristic peaks for compositional analysis of the AM—NaSEM copolymers.

A technique for determining absorbance ratios was utilized to eliminate the effects of film thickness. Beer's law relates the absorbance A to concentration c as follows:

$$A = atc \qquad (5)$$

in which a is the molar absorptivity for a characteristic frequency and t is the film thickness. At 1664 cm^{-1} the total contribution to the absorbance from both carbonyl functionality in poly(AM) and poly(NaAMPS) is given in eq. (6), where a_1 and a_2 represent the absorptivities and c_1 and c_2 the concentrations of each unit, respectively. At 1043 cm^{-1}, the contribution

$$A_{1664} = a_1 t c_1 + a_2 t c_2 \qquad (6)$$

to absorbance [eq. (7)] comes from the functionality of poly(NaAMPS); a_3 represents the absorptivity:

$$A_{1043} = a_3 t c_2 \qquad (7)$$

The ratio of the absorbances at 1664 cm^{-1} and 1043 cm^{-1} is then given by

$$A_{1664}/A_{1043} = (a_1 t c_1 + a_2 t c_2)/a_3 t c_2 \qquad (8)$$

Substituting $k_1 = a_1/a_3$ and $k_2 = a_2/a_3$, the following is obtained:

$$A_{1664}/A_{1043} = k_1 c_1/c_2 + k_2 \qquad (9)$$

Absorbance ratios A_{1664}/A_{1043} were determined for a series of mixtures of homopolymers of AM and NaAMPS (Fig. 4) and plotted as a function of c_1/c_2. The resulting calibration curve (Fig. 5) may be represented mathematically by eq. (10) with a correlation coefficient of 0.99:

$$A_{1664}/A_{1043} = 0.80 \, c_1/c_2 + 0.87 \qquad (10)$$

Mole fractions of each unit in the copolymer are thus easily determined.

For the AM—NaSEM copolymers, composition was measured monitoring the ratio of the absorbance at 1040 cm^{-1} (S=O of NaSEM) to that at 3200 cm^{-1} (C=O in AM) for each sample according to

$$A_{1040}/A_{3200} = a_4 c_3/a_5 c_4 - k_3 \, c_3/c_4 \qquad (11)$$

Concentrations of the NaSEM and AM units are represented by c_3 and c_4, respectively. Spectra of thin films obtained from compatible mixtures of NaSEM and AM homopolymers (Fig. 6) were used to construct a linear calibration curve (Fig. 7) obeying eq. (11) and having a correlation coefficient of 0.98.

The spectra for the AM—NaAMPS copolymers (Fig. 8) and for the AM—NaSEM (Fig. 9) were analyzed utilizing the appropriate calibration curve (Figs. 5 and 7, respectively). Mol % of the sulfonated comonomer in each respective random copolymer is shown in Table II.
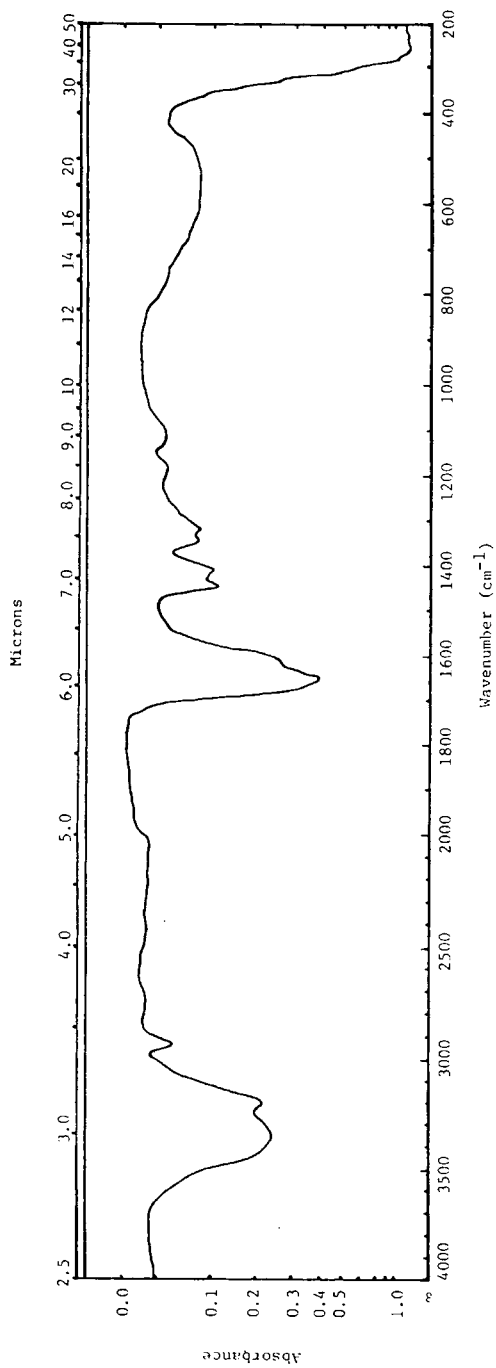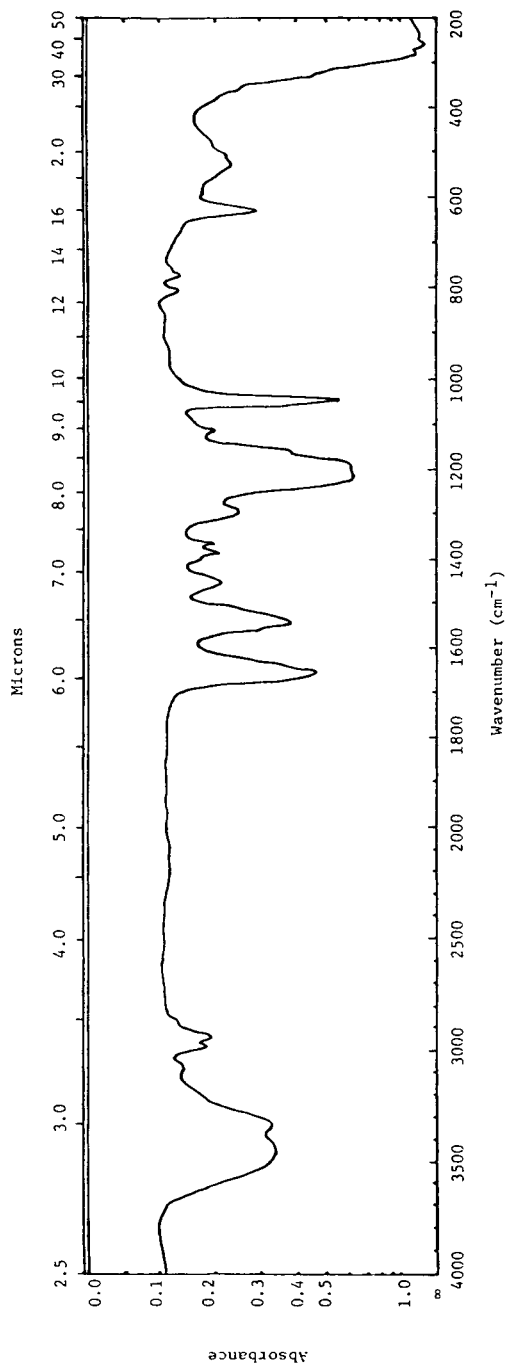
Fig. 1. Infrared spectrum of polyacrylamide.

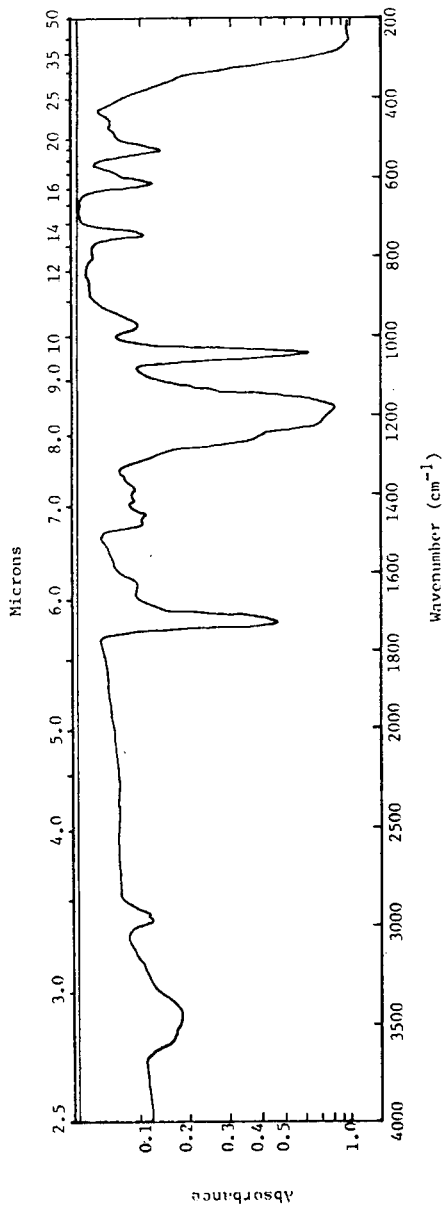Fig. 2. Infrared spectrum of NaAMPS homopolymer.

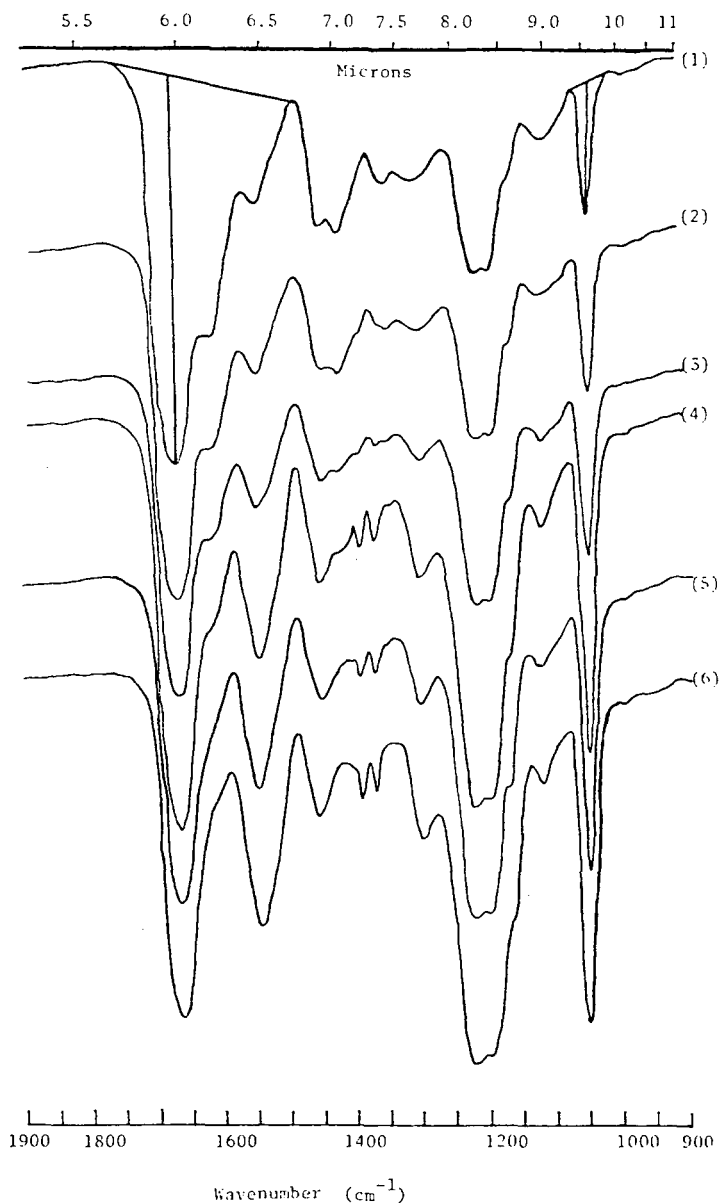Fig. 3. Infrared spectrum of NaSEM homopolymer.

Fig. 4. Infrared spectra for polymer mixtures of poly(acrylamide) and poly(sodium-2-acrylamido-2-methylpropane sulfonate). Mol % of NaAMPS units: (1) 15.7; (2) 21.4; (3) 33.8; (4) 53.3; (5) 65.5; (6) 83.8.

Carbon-13 Nuclear Magnetic Resonance Studies

Carbon-13 nuclear magnetic resonance studies on high molecular weight, water-soluble copolymers were conducted on the AM—NaAMPS and AM—NaSEM copolymers in order to obtain copolymer composition.[27] However, for quantitative evaluation, the relaxation time (T_1) of each carbon[28] and its respective nuclear Overhauser enhancement (NOE) must be considered.[29]

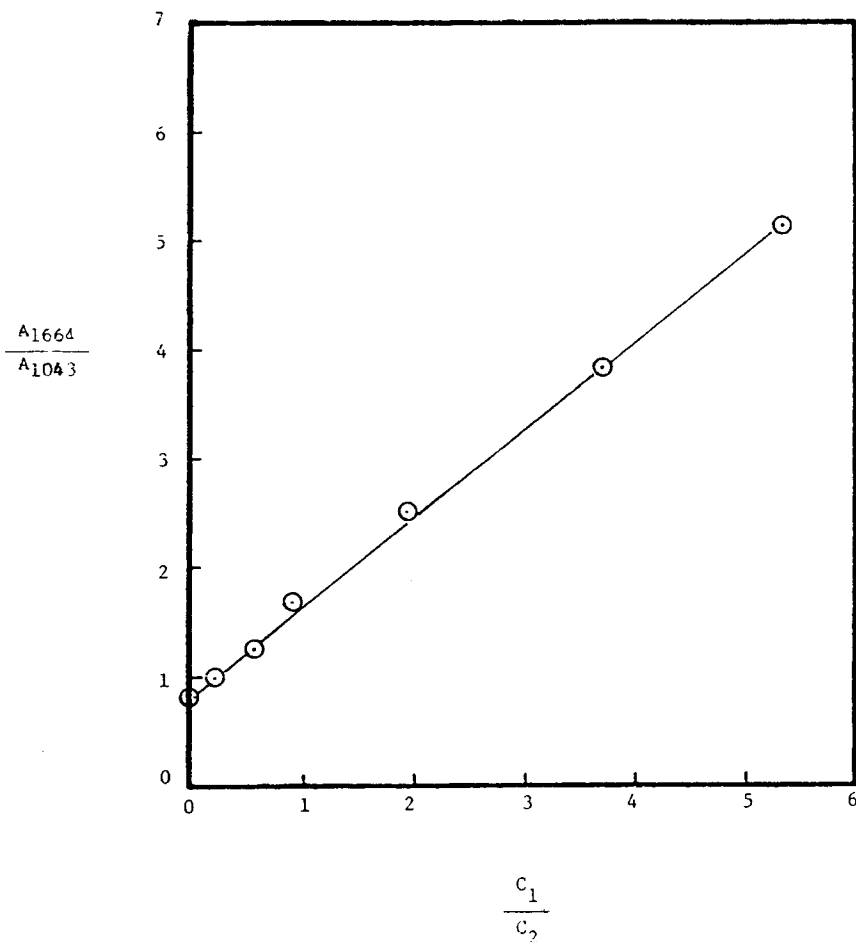For our measurements, T_1 was determined for each carbon under consider-

Fig. 5. Calibration curve for AM—NaAMPS copolymers. A_{1664}/A_{1043} represent values of absorbance ratios from infrared spectroscopy. Concentrations of AM and NaAMPS Units are C_1 and C_2, respectively.

ation. A pulse repetition rate of 25 s was used in order to exceed the longest T_1 by at least five times.[30] The NOE was eliminated by gated decoupling.[31]

Figure 10 shows the Fourier Transformed C^{13} spectrum of AMPS-3-5. Peak assignments (Table III) were made by comparing the respective homopolymers of AM and NaAMPS and by utilizing off-resonance decoupling. The mole fraction of NaAMPS in the copolymer can be obtained from eq. (12) in which A_1 represents the integrated area associated with the C=O from AM and A_2 the integrated area of one of the five resonances associated with NaAMPS (all five were used and an average obtained for each sample):

$$A_2/(A_1 + A_2) = \text{mole fraction of NaAMPS} \qquad (12)$$

The mole fraction of NaSEM in the AM—NaSEM copolymers were similarly determined from integration of the resonances at 180–182 ppm and at 63 ppm as assigned in Table IV. A typical spectrum is shown in Figure 11 for K-17-5.
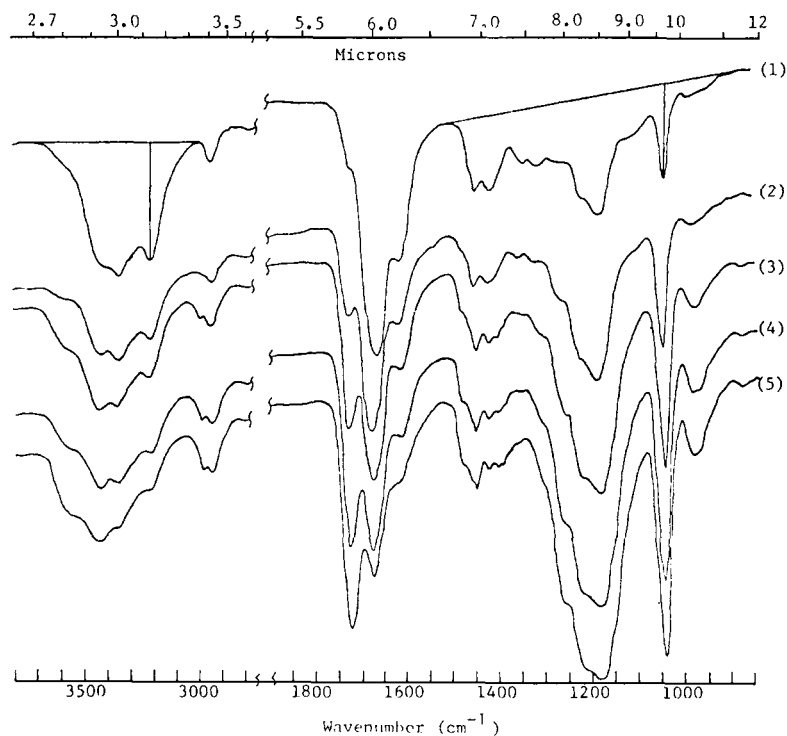
Fig. 6. Infrared spectra for polymer mixtures of poly(acrylamide) and poly(sodium-2-sulfoethyl methacrylate). Mol % NaSEM units: (1) 10.5; (2) 34.2; (3) 53.2; (4) 69.3; (5) 78.3.

The resonances at 52 ppm and at 18 ppm were not used in compositional analysis due to overlap with the main chain carbon resonance in the former and decreased intensity due to sequence splitting in the latter. The mole fraction of NaSEM in the copolymer is given by eq. (13) in which A_3 represents the integrated area of the resonance at 63 ppm due to the NaSEM and A_4 the resonances due to the

TABLE II
Composition of AM—NaSEM Copolymers Determined by Infrared Spectroscopy

Sample[2]	A_{1664}/A_{1043}	A_{1040}/A_{3200}	Sulfonated comonomer units in copolymer (mol %)
AMPS-1-5	8.33	—	9.69 ± 0.48
AMPS-2-5	4.17	—	19.51 ± 0.98
AMPS-3-5	2.94	—	27.87 ± 1.39
AMPS-4-5	2.08	—	39.80 ± 1.99
AMPS-7-5	1.27	—	66.67 ± 3.33
K-16-2	—	1.28	25.12 ± 1.26
K-16-3	—	1.15	22.62 ± 1.13
K-16-5	—	0.92	17.76 ± 0.89
K-17-2	—	3.53	52.00 ± 2.60
K-17-5	—	2.84	46.06 ± 2.30

[a] AMPS series are copolymers of AM—NaAMPS; K series are copolymers of AM—NaSEM.

$C{=}O$ functional groups in both NaSEM and AM:

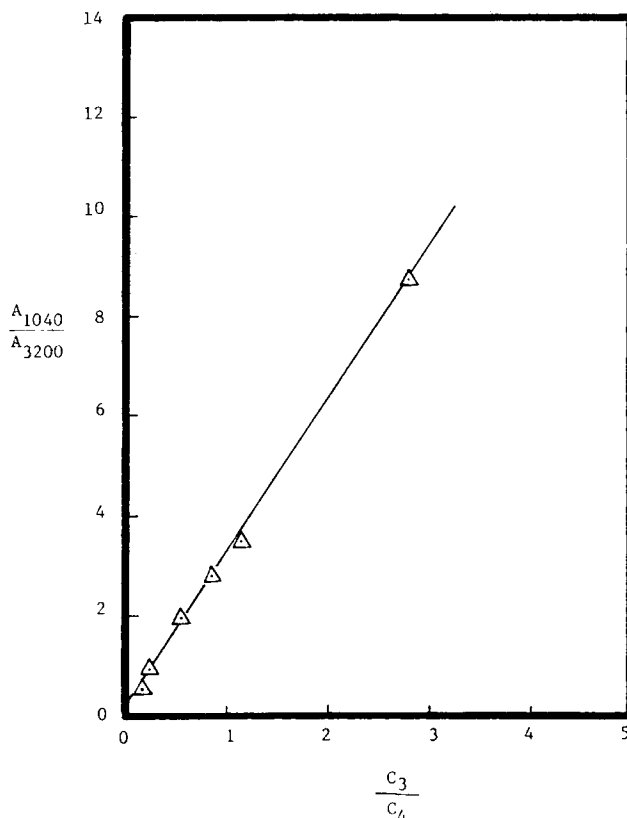$$A_3/A_4 = \text{mole fraction of NaSEM units} \qquad (13)$$

Fig. 7. Calibration curve for AM—NaSEM copolymers derived from infrared absorbance and 1040 cm^{-1} (S=O) and 3200 cm^{-1} (—NH$_2$).

TABLE III
Chemical Shift Values and Peak Assignments for AM—NaAMPS Copolymers

Peak		Chemical shift[a] (ppm ± 1)	Parent monomer in copolymer
1	$\overset{O}{\underset{\diagup C \diagdown}{\|\|}}$	182	AM
2	$\overset{O}{\underset{\diagup C \diagdown}{\|\|}}$	178	NaAMPS
3	—CH$_2$—SO$_3$Na	60	NaAMPS
4	$-\overset{\|}{\underset{\|}{C}}-$	55	NaAMPS
5	—CH$_3$	29	NaAMPS

[a] Relative to 3-(trimethylsilyl)-1-propane sulfonic acid, sodium salt.

5.5 6.0 7.0 8.0 9.0 10 11

Microns

(1)

(2)

(3)

(4)

(5)

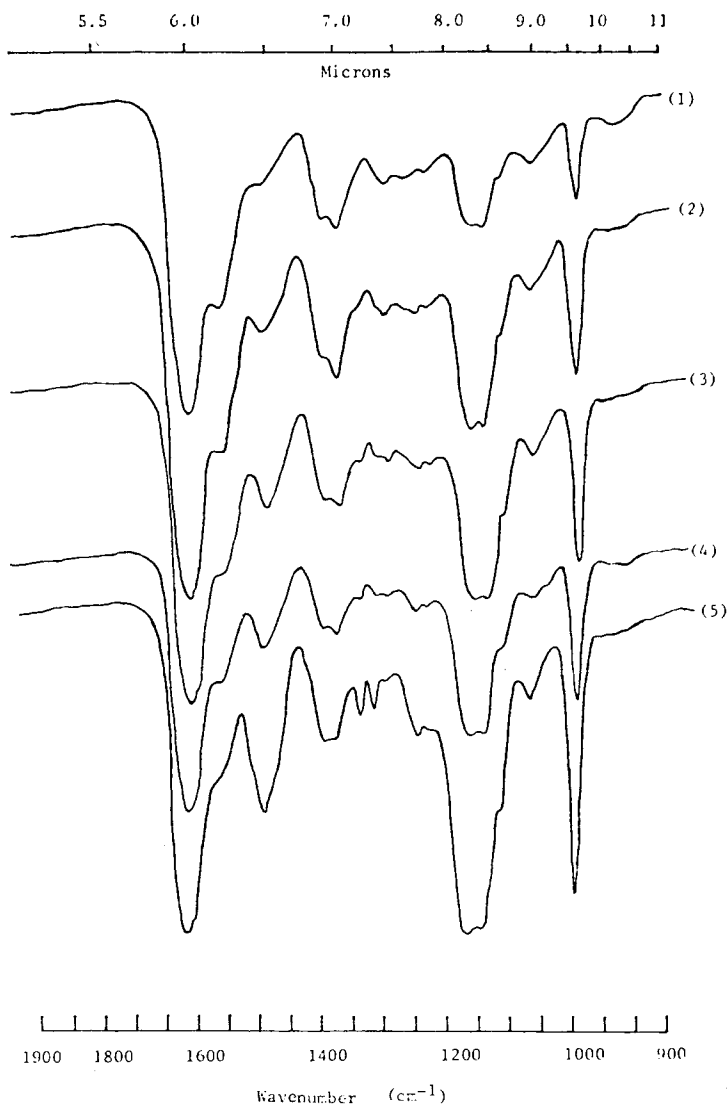1900 1800 1600 1400 1200 1000 900

Wavenumber (cm^{-1})

Fig. 8. Infrared spectra for poly(acrylamide-co-sodium-2-acrylamido-2-methylpropane sulfonates); (1) AMPS-1-5; (2) AMPS-2-5; (3) AMPS-3-5; (4) AMPS-4-5; and (5) AMPS-7-5.

TABLE IV

C^{13} Chemical Shift Values and Peak Assignments for AM—NaSEM Copolymers

Peak		Chemical shift[a] (ppm ± 1)	Parent monomer in copolymer
1	$\overset{\displaystyle O}{\overset{\displaystyle \parallel}{C}}$	180–182	AM and NaSEM
2	—CH$_2$—O—	63	NaSEM

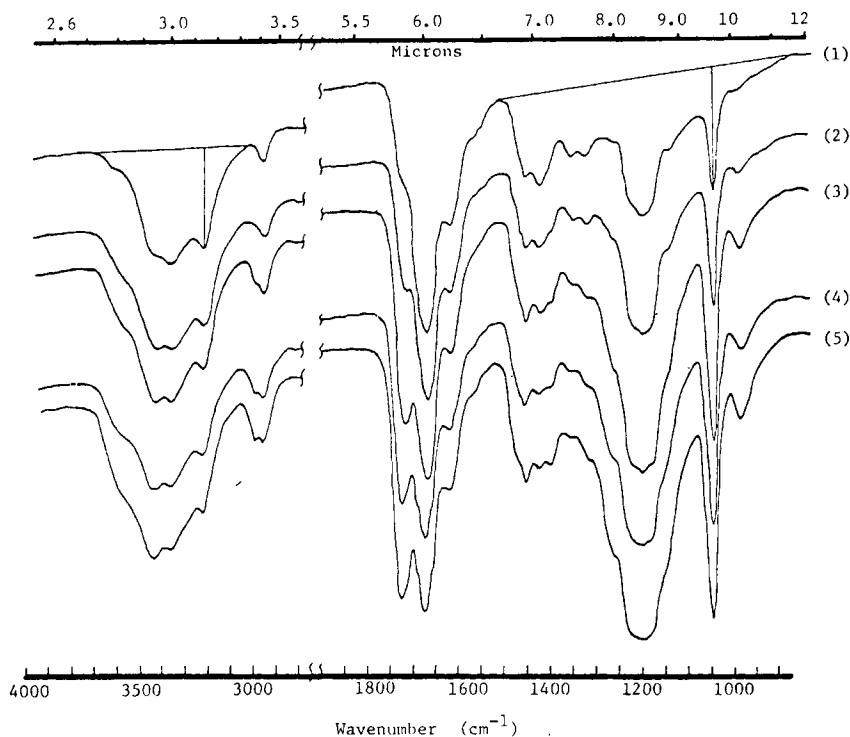[a] Relative to 3-(trimethylsilyl)-1-propane sulfonic acid, sodium salt.

Fig. 9. Infrared spectra for poly(acrylamide-co-sodium-2-sulfoethyl methacrylate): (1) K-16-5; (2) K-16-2; (3) K-6-2; (4) K-17-5; (5) K-17-2.

Experimentally determined mole percentages of NaSEM in the synthesized copolymers are reported in Table V.

Examination of Table V reveals the excellent correlation among elemental analysis, infrared, and C^{13} methods utilized in this work for AM—NaAMPS and AM—NaSEM copolymers. At high sulfonate compositions slightly higher values are predicted by the C^{13} nmr method. However, these values are well within experimental error at those concentrations. The measured copolymer compositions reinforce previous predictions[18] of compositions determined from reactivity ratios [$r_1 = 0.98 \pm 0.09$, $r_2 = 0.49 \pm 0.02$ for the AM (m_1)—NaAMPS (m_2) monomer pair and $r_1 = 0.38 \pm 0.05$ and $r_2 = 3.63 \pm 0.55$ for the AM (m_1)—NaSEM (m_2) monomer pair].

CONCLUSIONS

Three methods of analysis—elemental, infrared, and C^{13}—were utilized in this work to determine copolymer composition independent of water content. Copolymer compositions determined by the methods are in good agreement for model synthetic poly(acrylamide-co-sodium-2-acrylamido-2-methylpropane sulfonates) and poly(acrylamide-co-sodium-2-sulfoethyl methacrylates). These methods can be extremely useful when working with hygroscopic copolymers such as those used in enhanced oil recovery since assessment of rheological behavior is dependent on accurate concentration measurement.
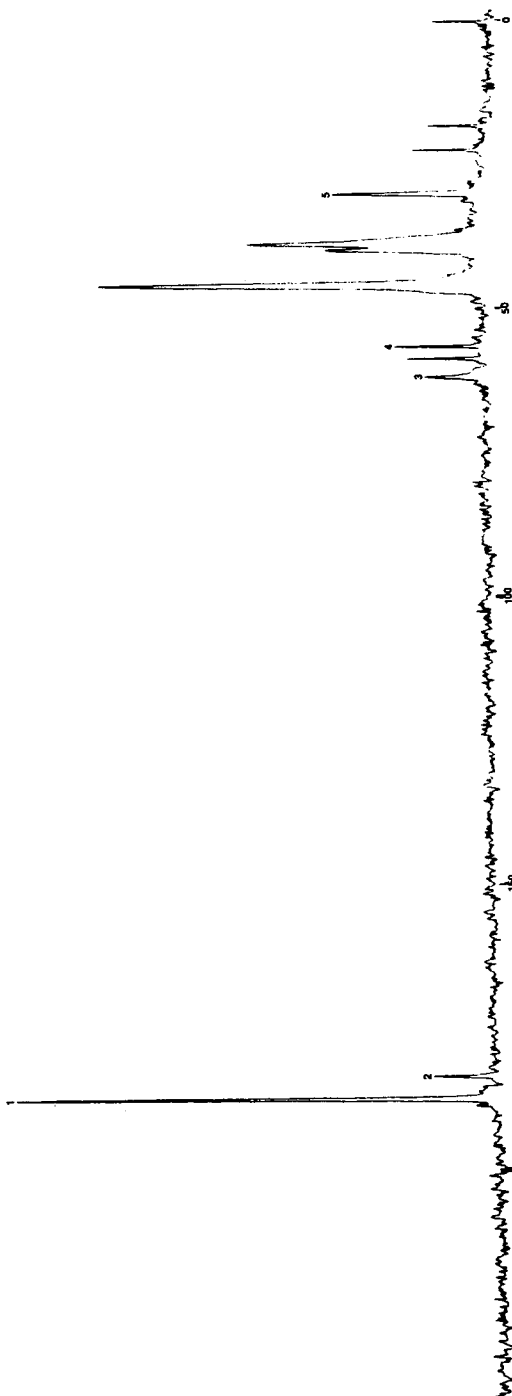
Fig. 10. Proton noise decoupled C-13 NMR spectrum of AMPS-3-5 (14,700 scans, pulse repetition, 1 s).

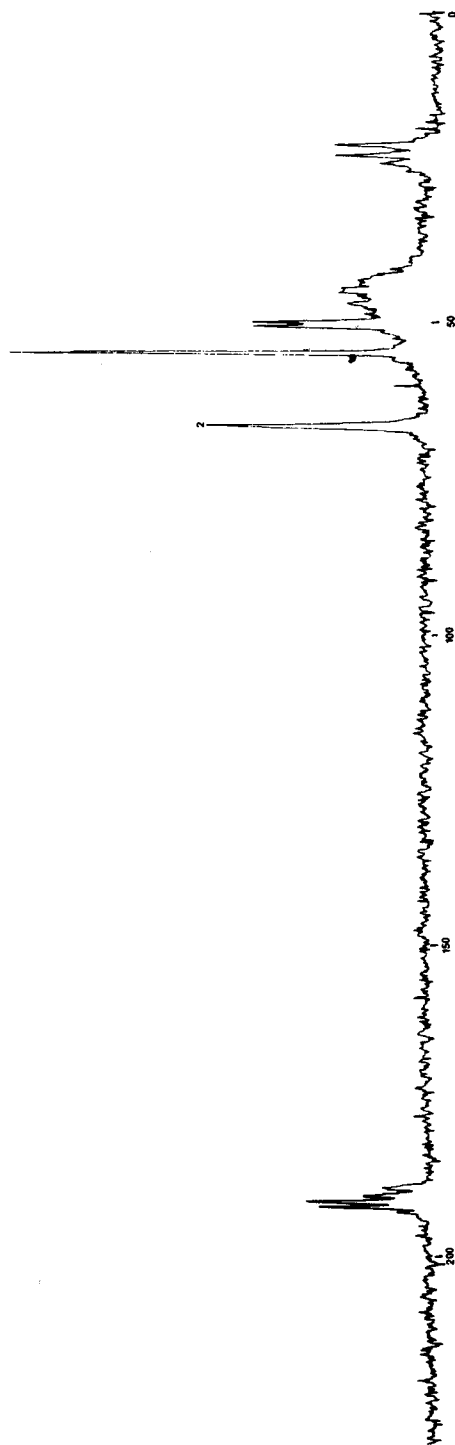Fig. 11. Proton noise decoupled C-13 NMR spectrum of K-17-5 (10,350 scans, pulse repetition, 1 s).

TABLE V
Comparison of Copolymer Composition from Elemental Analysis, IR, and C^{13} NMR
Determinations of AM—NaAMPS and AM—NaSEM Copolymers

Sample no.[a]	Sulfonated comonomer units in copolymer (mol %)		
	Elemental analysis[b]	IR[c]	C-13 NMR[d]
AMPS-1-5	9.51 ± 0.76	9.69 ± 0.48	10.66 ± 0.53
AMPS-2-5	19.01 ± 1.03	19.51 ± 0.98	17.27 ± 0.86
AMPS-3-5	27.85 ± 1.34	27.87 ± 1.39	27.21 ± 1.36
AMPS-4-5	37.63 ± 1.68	39.80 ± 1.99	—
AMPS-7-5	65.75 ± 3.16	66.67 ± 3.33	69.52 ± 3.48
K-16-2	25.04 ± 1.31	25.12 ± 1.26	—
K-16-3	20.00 ± 1.11	22.62 ± 1.13	—
K-16-5	15.60 ± 0.90	17.76 ± 0.89	17.60 ± 0.88
K-6-5	29.52 ± 1.51	—	29.45 ± 1.47
K-17-2	54.90 ± 4.00	52.00 ± 2.60	—
K-17-5	46.18 ± 2.85	46.06 ± 2.30	49.56 ± 2.48

[a] AMPS series are copolymers of AM—NaAMPS; K series are copolymers of AM—NaSEM.
[b] Errors are limit of error.
[c] Errors are estimated by 5% of the absorbance ratio measured.
[d] Errors are estimated by 5% of the intensity ratio measured.

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