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DETERMINATION OF ANIONIC HIGH-MOLECULAR-WEIGHT WATER-SOLUBLE POLYMERS BY SIZE-EXCLUSION CHROMATOGRAPHY

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SUMMARY

A method was developed for the determination of anionic high-molecular-weight water-soluble polymers in oil field brines using size-exclusion chromatography with ultraviolet detection. The stationary phase is coated controlled pore glass and the mobile phase is 0.1 M potassium dihydrogen phosphate. Various polymers were determined by this technique. The detection limits are 1–2 ppm with typical relative standard deviations less than 2% and linear response in the range 0–200 ppm. The polymer samples in oil field brines can be analyzed without prior dialysis, shearing, or solvent extraction.

INTRODUCTION

Water-soluble polymers in general and polyacrylamides in particular have been used for enhanced oil recovery and other industrial applications. Various techniques have been reported to determine polyacrylamides in solution, so that the extent of polymer adsorption by various media can be determined.

Michaels and Morelos¹ developed a turbidimetric method based on the reaction of hydrolyzed polyacrylamide with a quaternary ammonium cation (Hyamine 1622). The method was modified by Crummet and Hummel², and recently Allison *et al.*³ applied and automated the method for the determination of polyacrylamides and other anionic polymers. While turbidimetric techniques are sensitive, they are subject to interferences from heavy metal ions. A hydrolysis method² based on the colorimetric determination of liberated ammonia suffers interferences from background nitrogen compounds.

Scoggins and Miller^{4,5} developed a method for the determination of acrylamide-based polymers in brine solution. The method was based on the bromine oxidation of the amide functional group. Excess bromine was destroyed with sodium formate and the bromoamide oxidation product was reacted with iodide to form iodine which is measured colorimetrically as the starch–triiodide complex. The method was automated at Phillips Petroleum and generally gave good results for a wide range of polyacrylamide core flooding samples, yet interferences in the redox iodide–iodine reaction were observed occasionally.

Edwin and Neuman⁶ developed a very sensitive spectrofluorometric method for the determination of polyacrylamide at levels as low as 20 ppb in aqueous solution. Polyacrylamide is converted to its amine derivative which is then reacted with a buffered fluorogenic reagent made of borate buffer, *o*-phthalaldehyde and 2-mercaptoethanol. The method is involved and could not be used with high salinity and hardness common to most oil field brines.

Size-exclusion chromatography (SEC) has been applied for the determination of molecular weights and molecular weight distribution of polyacrylamides and other water-soluble polymers⁷⁻¹². Various column packings have found applications in aqueous SEC^{13,14}. Preliminary work has been done using columns packed with controlled pore glass for the determination of nonionic polymers¹⁵. Recently, Beazley¹⁶ developed a size-exclusion method employing diol bonded phase silica columns for the quantitative determination of partially hydrolyzed polyacrylamide in dirty oil field waters.

Anionic water-soluble polymers, designated as HE[®] polymers, have been synthesized at Phillips Petroleum. These polymers are designed for enhanced oil recovery applications in the "hostile environment" of high salinity and hardness at elevated temperatures. Some of these polymers lack the primary amide functional group, as has been previously disclosed¹⁷, thus many traditional methods of analysis were not applicable. A new method applicable for the determination of a variety of water-soluble polymers in brine was needed.

In this work we have investigated aqueous SEC with UV detection for the determination of various anionic water-soluble polymers in different brines and core effluents. We have found that the high-molecular-weight polymers ($2 \cdot 10^6$ – $15 \cdot 10^6$ MW) can be separated from other interferences and detected at low ppm levels in brine, with a typical relative standard deviation of less than 2%.

EXPERIMENTAL

Instrumentation

The liquid chromatograph used in this study was a Hewlett-Packard Model 1090. This system was equipped with a ternary solvent delivery system, an autosampler, an autoinjector, and a photodiode-array detector, HP Model 1040. The UV detector was set at 200 or 205 nm. Data were collected using a Nelson Analytical Data System Model 4416. A spectrophotometer, HP Model 8450A, was used to obtain the UV spectra of the various polymers.

Columns

A bank of five stainless-steel columns (140 cm × 4.6 mm I.D.) was used. The columns were dry packed with controlled pore glass beads coated with glycerol, CPG/200 Glycophase G, pore diameter 200 Å, particle size 37–74 μm (Pierce, Rockford, IL, U.S.A.). A flow-rate of 2 ml/min was used.

Reagents

Potassium dihydrogen phosphate (KH₂PO₄) was Mallinckrodt AR grade. Water was distilled and then deionized using a pressure cartridge system (Sybron/Barnstead, Boston, MA). Sodium lauryl sulfate was obtained from Sargent-Welch

(Skokie, IL, U.S.A.). Polyacrylamide standards were commercial products supplied by various manufacturers. Other polymers were synthesized at Phillips Petroleum, Bartlesville, OK, U.S.A. All chemicals were used as received without further purification.

Mobile phase

The 0.1 M KH_2PO_4 in water was filtered through 0.45 μm Nylon-66 membrane (Rainin Instrument, Woburn, MA, U.S.A.).

Procedure

New, dry packed columns were conditioned by flushing with water for 15 min at a flow-rate of 2 ml/min. The columns were checked and any voids were repacked with additional stationary phase. The columns were washed with 1% sodium lauryl sulfate in water for 30 min at a flow-rate of 1 ml/min and flushed again with water for another 30 min. Finally, the columns were equilibrated with the mobile phase at a flow-rate of 2 ml/min until a steady baseline was observed. Working standards (0–200 ppm) for each polymer were prepared by proper dilution with the mobile phase. An injection volume of 200 μl for standards and samples was used. No sample dilution was required since the polymer feed solutions used for the core studies had a concentration of 200 ppm. Concentrations of each polymer were determined from peak areas using linear calibration curves.

RESULTS AND DISCUSSION

The UV spectra of each of the polymers listed in Table I were obtained. Each polymer absorbed in the low UV region. However, direct spectrophotometric determination of the polymers in oil field brines and emulsions is not practical due to interferences from inorganics, surfactants, and other UV-absorbing materials. To illustrate the point, the UV spectra of two aqueous polymer solutions, a commercial polyacrylamide and HE Polymer C, and also the spectrum of synthetic seawater (see

TABLE I
ABSORPTIVITY OF POLYMERS

Polymer type	a (200 nm)*	a (205 nm)*	Group
HE Polymer B	25.4	17.9	A
HE Polymer X1	18.6	9.9	A
HE Polymer E	17.5	8.6	A
HE Polymer C	16.9	10.0	A
Commercial polyacrylamide I**	10.8	5.7	B
Commercial polyacrylamide II***	8.5	3.5	B
Commercial polyacrylamide III***	7.7	3.9	B
HE Polymer X2	5.9	3.5	B

* Absorptivity expressed as ml/mg cm.

** 15% hydrolyzed.

*** 30% hydrolyzed.

TABLE II
SYNTHETIC SEAWATER COMPOSITION (BRINE)

Compound	g/l
NaHCO ₃	0.2051
Na ₂ CO ₃	4.2881
NaCl	23.833
CaCl ₂ · 2H ₂ O	1.6433
MgCl ₂ · 6H ₂ O	10.7735

Table II for composition) are presented in Fig. 1. Thus, SEC was investigated to separate the high-molecular-weight polymer from the UV-absorbing interferences.

Our attempts to separate the polymers using aqueous high-performance size-exclusion columns packed with bonded silica failed. Different buffers were tried, but the silica-based packing seemed to adsorb the polymers and erratic results were obtained. Due to the vast differences in the molecular size between the polymers and the interfering species, highly efficient columns were not a requirement and we decided to try packing our own columns using the coated controlled pore glass Glycophase G, with a 200 Å pore diameter. This packing has hydrophilic surface groups, is quite insensitive to high salt concentration, and has an exclusion limit of *ca.* $1.0 \cdot 10^5$ MW¹³. The polymers were expected to be totally excluded in a single peak while the interfering small molecules would elute at the total permeation volume.

The addition of an electrolyte to the aqueous mobile phase helps to minimize the ionic interactions between the analyte and the stationary phase and controls the hydrodynamic volume of the polymer^{13,14}. Potassium dihydrogen phosphate was used to adjust the ionic strength of the mobile phase because it is practically transparent in the UV region (see Fig. 1a).

We have observed that the conditioning of the columns with a 1% solution of sodium lauryl sulfate improved the separation by reducing the tailing of the polymer peak. A similar observation was reported by Beazley¹⁶, who used pentanesulfonic acid in the mobile phase. The mechanism for the improvement is unclear, but it can

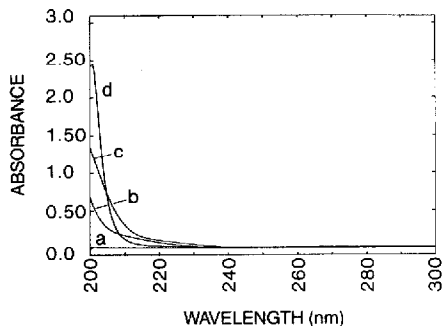


Fig. 1. UV spectra: (a) 0.1 M KH₂PO₄; (b) a commercial polyacrylamide (80 ppm); (c) HE Polymer C (80 ppm); (d) synthetic seawater (brine).

be stated that the stationary phase is modified by adsorption of the organic sulfate.

In developing this method, the first group of polymers was measured at 205 nm. Later, a second group of polymers, which exhibited lower absorbance, was measured at 200 nm. Based on the absorptivity values, these polymers are classified as group A and group B in Table I.

Attempts to filter 3–5 ml of the samples and of the standards (20–200 ppm) through a 0.45- μm Nylon-66 syringe filter unit (Rainin No. 38-150) revealed that some of the polymer was retained on the membrane and recoveries ranged from 5–100% depending on the concentration and polymer type. Thus, we placed an inline 2- μm stainless-steel filter between the injection valve and the columns and have not experienced excessive pressure build-up or column plugging problems. The stainless-steel filter was cleaned occasionally by sonification in 50% nitric acid.

Typical chromatograms for two different polymers in synthetic seawater (3.46% salinity) are presented in Figs. 2 and 3. The polymer is totally excluded and elutes at 9.5 ml while the brine is totally permeated and elutes at 18.6 ml. The separation is illustrated further in in Fig. 4, which is the determination of HE Polymer E in a core effluent at a concentration of 37 ppm in 16.5% salinity (15% sodium chloride and 1.5% calcium chloride).

This SEC method was also applied to the determination of percent monomer conversion in a polymerization reaction. The separation of the polymer from the monomers and other UV absorbing species is illustrated in Fig. 5. Chromatogram a represents near 100% conversion while chromatogram b represents 37% conversion. Both samples were in inverse emulsion form and were diluted with the mobile phase. It is possible to determine the polymer content, using this procedure, without prior shearing¹⁶, extraction, or dialysis.

To check the accuracy and precision of this method, standards (0–200 ppm) for each polymer, prepared in the mobile phase (0.1 M KH_2PO_4) and in synthetic seawater, were analyzed. Table III shows the accuracy and precision for each of the

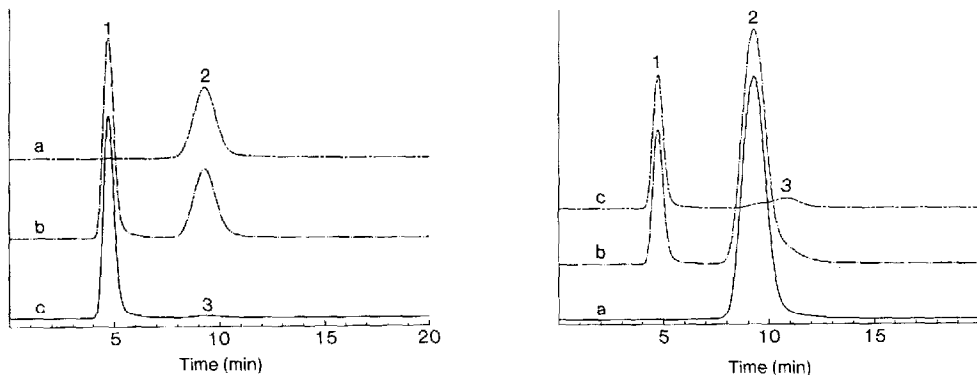


Fig. 2. Size-exclusion chromatograms monitored at 205 nm; sensitivity, 0.05 a.u.f.s.: (a) brine; (b) HE Polymer C, 200 ppm in brine; (c) HE Polymer C, 200 ppm in 0.1 M KH_2PO_4 . Peaks: 1 = polymer; 2 = brine; 3 = residual monomer. Conditions as in Experimental.

Fig. 3. Size-exclusion chromatograms monitored at 200 nm; sensitivity, 0.1 a.u.f.s.: (a) brine; (b) commercial polyacrylamide II, 200 ppm in brine; (c) commercial polyacrylamide II, 200 ppm in 0.1 M KH_2PO_4 . Peaks: 1 = polymer; 2 = brine; 3 = residual monomer. Conditions as in Experimental.

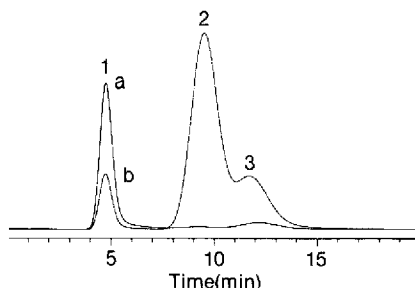
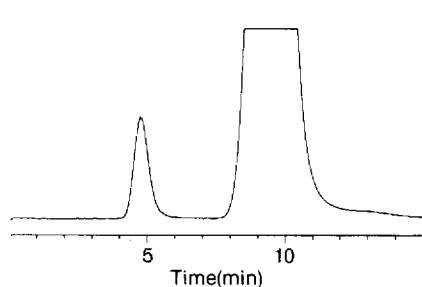


Fig. 4. Size-exclusion chromatogram of a 37 ppm HE Polymer E in a core effluent (16.5% salinity). Detector set at 205 nm; sensitivity, 0.01 a.u.f.s. Other conditions as in Experimental.

Fig. 5. Size-exclusion chromatograms for evaluating the extent of monomer conversion: (a) near 100% conversion; (b) 37% conversion. Peaks: 1 - HE Polymer B; 2 and 3 - monomers. Detector set at 205 nm; sensitivity, 0.05 a.u.f.s.; other conditions as in Experimental.

polymers listed. Generally, the accuracy was within 2 ppm at the 200 ppm level and within 0.5 ppm at the 20 ppm level. The precision was within 2% relative standard deviation (R.S.D) for seven of the polymers listed and 2.3% for HE Polymer X2. Similar results were obtained analyzing actual samples. Calibration curves for each of the eight polymers were linear, with a correlation coefficient greater than 0.999. The detection limit, using a signal-to-noise ratio of 5, was 1 ppm for the group A

TABLE III
PRECISION AND ACCURACY DATA

Polymer type	Actual conc. (ppm)	Exp. conc. (ppm)*	S.D. (ppm)	R.S.D. (%)
HE Polymer B	200	198.4	1.1	0.56
	20	19.5	0.29	1.5
HE Polymer C	200	201.9	0.97	0.48
	20	20.5	0.35	1.7
HE Polymer E	200	198.9	0.41	0.21
	20	19.6	0.32	1.7
HE Polymer X1**	200	201.4	0.83	0.44
	20	20.6	0.29	1.4
HE Polymer X2**	200	202.0	2.5	1.3
	20	21.3	0.50	2.3
Commercial polyacrylamide I***	200	201.4	1.5	0.74
	20	20.1	0.23	1.4
Commercial polyacrylamide II§	200	201.7	0.23	0.11
	20	19.7	0.18	0.89
Commercial polyacrylamide III§	200	198.4	1.2	0.59
	20	19.8	0.24	1.2

* The reported concentrations were the average of ten injections.

** Experimental polymer.

*** 15% hydrolyzed.

§ 30% hydrolyzed.

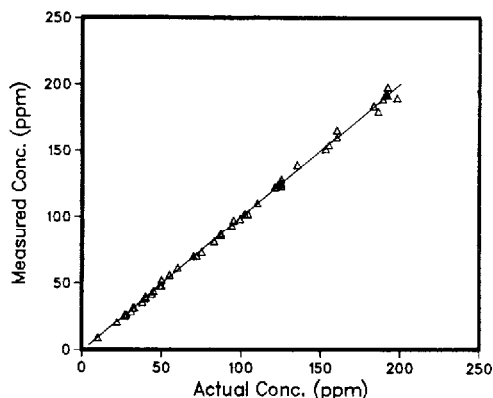


Fig. 6. Correlation plot for the determination of HE Polymer B in various brines by size-exclusion chromatography.

polymers and 2 ppm for the group B polymers. Hundreds of effluent samples obtained by flooding sandstone cores, that contained residual oil, with various anionic polymers in brines with salinities ranging from 3.46% (seawater) to 16.5% (15% sodium chloride and 1.5% calcium chloride), were analyzed for polymer content using this technique. As a quality control, three or four blind standards were submitted with each set of core effluents. Fig. 6 represents a typical plot of measured *versus* actual concentrations for the blind standards. The data presented were obtained for various samples of the same polymer in different brines during a one-year period. The correlation coefficients, based on linear regression between the measured and actual concentrations for seven polymer types are listed in Table IV.

For acrylamide-based polymers, an independent colorimetric measurement⁵ was made on some core effluents and blind standards. The results were in good agreement with SEC values. These results are listed in Table V.

This work shows that aqueous SEC is a sensitive and accurate technique for the determination of high-molecular-weight anionic polymers. The method is general and can be applied to the determination of polymers which do not contain the primary amide functional group. Also, minimal sample preparation is required. Samples can be analyzed without prior dialysis, shearing, or solvent extraction.

TABLE IV

LINEAR REGRESSION OF MEASURED AND ACTUAL CONCENTRATIONS FOR VARIOUS POLYMERS IN DIFFERENT BRINES BY SEC

<i>Polymer</i>	<i>No. of samples analyzed</i>	<i>Intercept "a"</i>	<i>Slope "b"</i>	<i>Correlation coefficient</i>
HE Polymer B	47	-0.9	1.0056	0.9983
HE Polymer C	54	-0.3	0.9980	0.9992
HE Polymer E	12	-1.9	1.0196	0.9987
HE Polymer X1	24	-0.9	1.0017	0.9987
HE Polymer X2	9	-3.4	1.0136	0.9981
HE Polymer X3	3	-2.0	0.9932	1.0000
Commercial polyacrylamide	6	1.1	0.9861	0.9997

TABLE V

COMPARISON BETWEEN COLORIMETRIC AND SEC DETERMINATION OF POLYACRYLAMIDE I

	<i>Polymer concentration (ppm)</i>		
	<i>Actual</i>	<i>Colorimetric method</i>	<i>SEC method</i>
Core effluents	—	46	44
	—	93	90
	—	189	185
	—	190	189
Blind standards	22	18	22
	97	98	99
	189	187	188

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