CHROM. 18 014

CHARACTERIZATION OF NEUTRALIZED β-NAPHTHALENESULFONIC ACID AND FORMALDEHYDE CONDENSATES

T. G. MILLER

Dowell Schlumberger, P.O. Box 2710, Tulsa, OK 74101 (U.S.A.)

SUMMARY

A liquid chromatographic method has been developed to show relative molecular weight distributions for different neutralized condensation products of β-naphthalenesulfonic acid and formaldehyde. This method can be used for quality control in manufacturing and for predicting the relative performance of condensates from different sources.

The separation was achieved on a pellicular, reversed-phase column using ion pairing and solvent programming. The components of the chromatogram were monitored with continuous UV detection at 280 nm. The chromatographic data are used to detect the different components formed during the condensation reaction.

The molecular weight distribution of the condensates can be correlated with their performance as dispersing agents in oil-well cementing services. Ion chromatography and ^{13}C NMR spectrometry provide complementary characterization data.

INTRODUCTION

Sodium salts of the condensation products of β-naphthalenesulfonic acid and formaldehyde have been used extensively as dispersing agents in oil-well cementing services for many years[1]. In addition, the sodium salts of the condensation products constitute the most important class of synthetic tanning agents for hides[2], and are used as dispersants for ceramics and pigments[3].

Previously, the condensates have been studied using electrophoresis, paper chromatography and salting-out chromatography[4]. Unfortunately, these methods gave incomplete results or were very lengthy. A short analysis time is desirable to compare a large number of condensates, or to closely monitor a manufacturing process of a condensate.

This report describes the use of high-performance liquid chromatography (HPLC) to determine relative molecular weight distributions of different condensates. Ion chromatography and ^{13}C NMR spectrometry provide additional characterization of the condensates.

EXPERIMENTAL

Naphthalene, paraformaldehyde, concentrated sulfuric acid, sodium hydroxide, glacial acetic acid, sodium carbonate and sodium bicarbonate were reagent grade. Tetrabutylammonium hydroxide (TBAH), 40% aqueous solution, was obtained from Aldrich. Distilled-in-glass acetonitrile was obtained from Burdick & Jackson Labs. The anion separator resin is a type commonly used in ion chromatography. The suppressor column resin was AG™ 50W-X16, 200–400 mesh in the acid from Bio-Rad Labs. Sodium polystyrene sulfonates were obtained from Pressure Chemical Co.

Apparatus

The liquid chromatograph was a Waters Assoc. Model ALC 202/401 equipped with a second Model M-6000 pump, Model 660 solvent programmer and a U6K injector. The column was a Water Assoc. Bondapak™ Phenyl/Corasil (60 cm × 2.8 mm I.D.). The chromatographic data were obtained using a Supergrator II from Columbia Scientific. The ion chromatograph consisted of a Model 212 conductivity meter and cell from Wescan Instruments, a Model 396-89 Milton Roy miniPump™, a Model R6031SV injector equipped with a 100-μl loop, glass columns, PTFE tubing and associated fittings from Laboratory Data Control. The nuclear magnetic resonance spectrometer was a Varian CFT-20, operating at 20 MHz for [13]C.

Condensate preparation

The monomer, β-naphthalenesulfonic acid, was prepared[1] by refluxing 128 g (1 mole) of naphthalene and 118 g (1.2 moles) of concentrated sulfuric acid at 160°C for two h. The monomer solution was cooled below 100°C, then 75 g (2.5 moles) of formaldehyde (as paraformaldehyde) was added. This was refluxed for periods of 24, 28, 72 and 96 h at 100°C and for periods of 4 and 8 h at 130°C. The reaction medium was cooled to room temperature and neutralized with aqueous sodium hydroxide. The condensate products were then dried at 110°C and crushed to a fine powder.

Solvent preparation

Solvent A, for the solvent programming, consisted of 0.01 M of TBAH and 1% (v/v) of glacial acetic acid in deionized water. Solvent B consisted of 0.01 M TBAH and 1% (v/v) of glacial acetic acid in acetonitrile. The TBAH went into solution faster when dissolved in the acetic acid, then added to the solvent. All solutions were filtered through a 0.5-μm filter.

Procedure for condensate ion-pair chromatogram

The condensates were dissolved in solvent A, at a concentration of 5.0 mg/ml. The solutions were filtered through a 0.5-μm filter. Initial conditions for the solvent program were 60% solvent A and 40% solvent B. After a 3-μl injection of the condensate solution, the solvent programmer and electronic integrator were started. The integrator was operated in the area normalization mode. The chromatograms were obtained using a 10-min linear gradient with a flow-rate of 1 ml/min and continuous UV monitoring at 280 nm. The final condition was held for 2 min. A 5-min reversed linear program was used to return to the initial conditions. The column was equilibrated for 5 min before another injection. Seven successive injections of a condensate

gave reproducible retention times with a 0.4% relative deviation and reproducible peak areas with a 0.7% relative deviation for the larger and longer retained peak.

Procedure for sulfate ionogram

After dissolving a condensate in the eluant of 0.003 M sodium bicarbonte and 0.002 M sodium carbonate, 100 μl was injected onto a 150 $\times$ 3 mm anion separator column. The suppressor column was 500 $\times$ 3 mm I.D. A flow-rate of 1 ml/min was used to obtain a retention time of 5.4 min.

RESULTS AND DISCUSSION

Anion-exchange chromatography

The initial study of the condensates was done within the Dow Chemical Company using anion-exchange chromatography[5]. With this methodology, the retention times of the components of a condensate increase as the number of sulfonate groups per molecule increases. The components of the condensates appear to be well resolved in Fig. 1, but failure to return to the baseline suggests that additional components are present, which elute very slowly. This was found to be the case.

By collecting injections with the column in-line and not in-line, it was found for one condensate that only 35%, based upon UV absorbance at 280 nm, had eluted within the 12-min solvent program. It is believed that the peaks are due to the monomer, dimer, trimer and higher oligomers of polynaphthalenesulfonates. The first peak had the same retention time as the monomer (β-naphthalenesulfonate). Since the condensate did not elute in an acceptable manner, this procedure was abandoned and a different approach was taken.
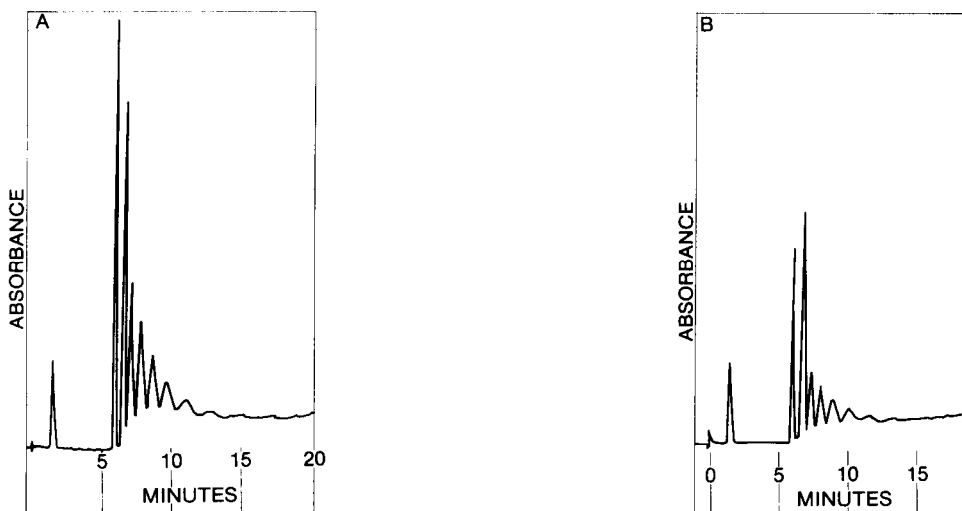

Fig. 1. Anion-exchange chromatograms of 100°C condensation reaction products of neutralized β-naphthalenesulfonic acid and formaldehyde: A, 48-h reaction; B, 96-h reaction.

Ion-pair chromatography

Probably the most powerful technique to separate highly ionic organic compounds is ion-pair chromatography[6]. Therefore, this methodology was investigated for a separation of the condensate components. Since a difference in the condensate components would be varying numbers of naphthyl rings per molecule, a phenyl-silica stationary phase was chosen over the more popular octadecyl column. Tetrabutylammonium cation was the pairing ion for the sulfonate anion. With the phenyl-base column, ion pairing and solvent programming, a chromatogram for the total condensate was obtained. Without the pairing ion in the mobile phase, the condensates eluted unretained.

Fig. 2 shows the chromatograms from several condensation products. At first glance, the two-peak chromatograms may not appear to show good separation, since the anion-exchange chromatograms of Fig. 1 contain several distinct peaks. However, a closer study of the chromatograms yields a vast amount of information about the reaction and the condensation product. The first peak in Fig. 2 is strongly believed to be the peak shown in Fig. 1. This is supported by the fact that the monomer has the same retention time as the front of the first peak of the chromatograms in Fig. 2 and the first peak in Fig. 1. In addition, the area of the first peak in Fig. 2 decreases with increasing reaction time at constant temperature, as does the area of the group of peaks in Fig. 1. Chromatographic data for Fig. 2 are shown in Table I.

The chromatograms in Fig. 2 strongly indicate that the products formed early in the reaction undergo significant changes as the reaction time increases. Since this is a polymerization reaction, components with varying molecular weights are expected. It is apparent from the trend of the ion-pair chromatograms that the second peak is produced, to some extent, from the components in the first peak. The condensation reaction is analogous to an acid-catalyzed phenol–formaldehyde conden-
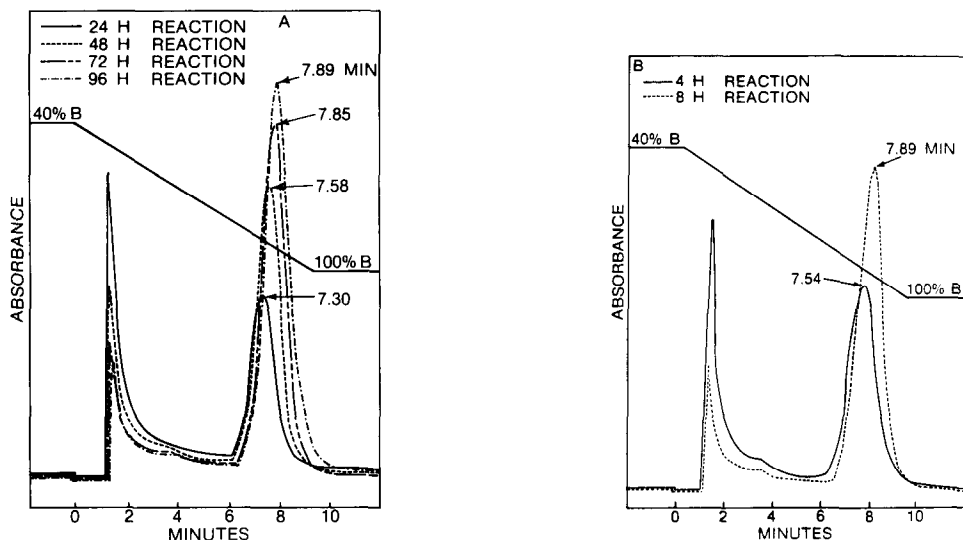

Fig. 2. Ion-pair chromatograms of neutralized β-naphthalenesulfonic acid and formaldehyde condensation products: A, 24-, 48-, 72- and 96-h reaction at 100°C; B, 4- and 8-h reaction at 130°C.

TABLE I

DATA FOR ION-PAIR CHROMATOGRAMS

Sample	Retention time (min)		Area (%)	
	Peak No. 1	Peak No. 2	Peak No. 1	Peak No. 2
Monomer	1.35			
24–100	1.38	7.30	43.9	56.1
48–100	1.35	7.58	22.8	77.2
72–100	1.36	7.85	14.5	85.5
96–100	1.33	7.89	10.9	89.1
4–130	1.37	7.51	35.3	64.7
8–130	1.33	7.89	13.0	87.0

sation reaction[7]. Initially, the reaction products would be expected to consist of linear, low-molecular-weight molecules, producing chromatograms as observed in Fig. 1. These small molecules could react with more monomer, or each other. When most of the monomer has been depleted and additional formaldehyde is present, the small molecules can react with each other to produce larger molecules. In turn, the larger molecules can react with each other to form the largest molecules. This stepping of molecular size would account for the absence of a continuum of oligomers in the condensation reactions, as observed in Fig. 2. If the larger molecules did not condense with each other, the second peak in Fig. 2 would not increase in retention time but only grow in percent area. As observed in Fig. 2, the retention time and percent area of the second peak increase with longer reaction times. The argument that the increased retention time of the second peak represents a higher molecular weight is supported by the increasing retention time and molecular weight for a set of polystyrene sulfonate standards using the ion-pair procedure. Table II listst these data.

   As with phenol–formaldehyde condensates[7], the branching of the products is controlled by the amount of the formaldehyde. Since the formaldehyde is in excess of the naphthyl rings, branching of the condensate molecules would be expected. Thus, the second peak in Fig. 2 is likely not only higher molecular weight molecules, but also molecules having branched structures. Fig. 3 illustrates possible molecular structures for the condensate products.

TABLE II

RETENTION TIME OF SODIUM POLYSTYRENE SULFONATE MOLECULAR WEIGHT STANDARDS

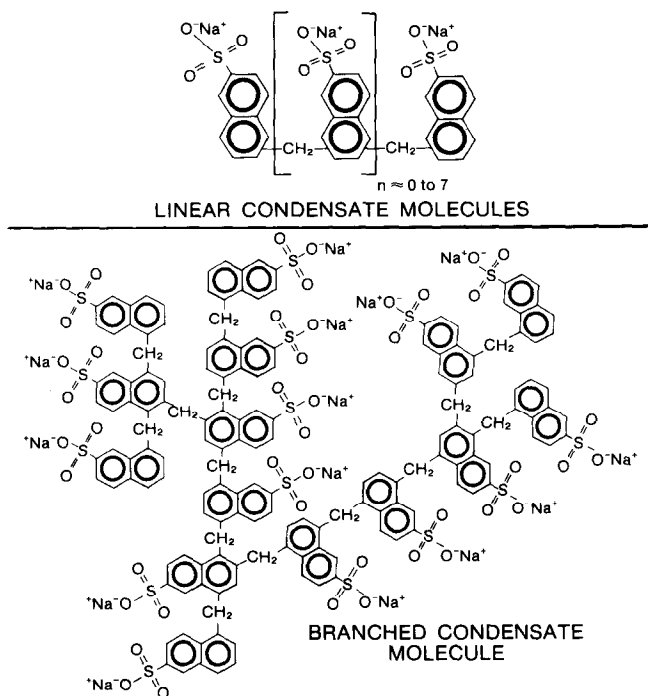| Molecular weight	Retention time (min)
1 800	1.57
4 600	6.15
8 000	6.72
18 000	7.30

Fig. 3. Models of linear and branched condensate molecules.

^{13}C NMR

^{13}C NMR spectra support the argument that the first peak consists essentially of linear molecules and the second peak consists of branched molecules. ^{13}C NMR spectra show a broadening of peaks as the reaction time increases. This is expected for a branching polymer. If both peaks represented linear molecules, the spectra should have reasonably well-resolved peaks, as observed for the monomer[8]. Viscosity of the samples should not be the cause of the broadness, since the NMR solutions did not show any appreciable increase of viscosity. The spectra show the aromatic carbons (ca. 142 to 120 ppm) and the bridging methylene carbons (ca. 35 ppm). The peaks at ca 140 ppm and higher represent the sulfonated naphthyl carbons.

Sulfate and moisture

After the condensation reaction, neutralization forms a significant amount of sodium sulfate. This may affect the performance of the polymer by decreasing its purity. Thus, a large excess of sulfuric acid in the initial reaction may be undesirable. The sulfate content can be determined by ion chromatography, as illustrated in Fig. 4. The large condensate molecules elute in front of the sulfate in the chromatogram and do not interfere with the determination. The condensates were dissolved and diluted in the eluent to eliminate the "water dip" commonly occurring in ion chromatography. Also, the hygroscopic nature of the condensates causes a significant quantity of water to be present, which further reduces the purity of the polynmer. The water content can be determined by drying 1 g of the condensate product at
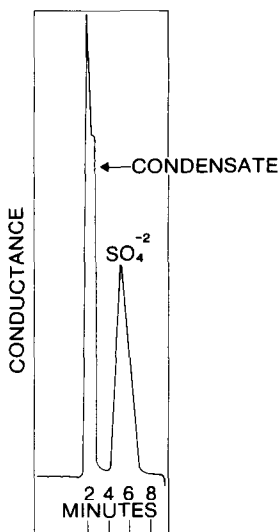
Fig. 4. Chromatogram showing sulfate in condensate product.

110°C for 1 h. The sulfate and water contents of the condensates in this report were not taken into consideration. The contents would remain nearly constant with the same reactant ratios in all reactions. The water and sulfate content in condensation products from different sources should be determined to predict their relative performances with a greater degree of confidence.

CONCLUSIONS

The utility of ion-pairing and solvent programming provides an informative and fast method for the chromatographic analysis of β-naphthalenesulfonic acid–formaldehyde condensation products. The chromatograms show the various components formed during the reaction and yield a relative molecular weight distribution. This method could easily be used to determine when a condensation reaction has reached a desired point by comparing chromatograms to that of a selected standard. In addition, different sources of condensates can be compared based upon the percent area and the retention time of the second peak. A condensation product can be further characterized by determining the moisture and sulfate content. The use of anionic pairing reagents and solvent programming should allow chromatographic analysis of cationic polymers.

ACKNOWLEDGEMENTS

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