

Determination of reaction by-products in high-molecular-weight polysulfonated scale inhibitors by ion chromatography

Sonia E. Atwood

Marathon Oil Company, Petroleum Technology Center, P.O. Box 269, Littleton, CO 80160 (USA)

ABSTRACT

In the inhibition of oilfield barium sulfate mineral scale, it is counterproductive to increase the concentration of scaling anions in the system. Sulfate and other potentially scaling ions are produced during the sulfonation of organic polymers. Upon injection into a high-barium, oil-producing formation, these ions tend to form large quantities of sparingly soluble salts. Such precipitates damage oil-producing zones and reduce oil productivity. It is therefore necessary to determine the concentrations of these anions prior to application.

An ion chromatographic technique has been developed for the simultaneous determination of hydroxyethylsulfonate, sodium vinylsulfonate, chloride and sulfate reaction by-products. This technique can be used to analyze monomer, polymer and brine solutions. Linearity ranges were determined for these ions.

INTRODUCTION

In the production of oil and gas from a porous rock matrix, deposition of mineral scales either within the rock matrix or oil well pipework can reduce oil flow to a trickle. Common mineral scales are barium sulfate, calcium carbonate and calcium sulfate. Changes in pressure or temperature or the mixing of different geologically stable, but incompatible brines generally results in some scale precipitation [1–3].

When millions of gallons of oil and natural pore water are removed from a reservoir each day, the overall reservoir pressure soon declines. Lower reservoir pressure means slower flow from oil wells and decreased production. Thus, water is often injected into the reservoir to replace oil and maintain pressure. The most abundant water source is sea water that contains close to 3000 mg l⁻¹ of sulfate. After a short period of time, the sulfate-rich sea water has migrated from the point of injection to a producing well. In the turbulent high-flow region close to the producing well, the injected water mixes

with the natural pore water, which contains calcium and/or barium ions (up to 5000 mg l⁻¹). The resultant precipitate of barium or calcium sulfate will severely damage an oil well.

Scale inhibitors are organic molecules which retard the kinetics of precipitate growth. They do not sequester or chelate very well but sterically interfere with active crystal growth sites. Scale inhibitors are injected into a producing oil well (not an injection well) to adsorb onto the porous matrix. When the oil well is allowed to flow back, scale inhibitor is produced along with oil, natural pore water and the incompatible injected water. It is thus, obviously, counterproductive to inject a scale inhibitor which contains ions incompatible with brines known to be present in the reservoir. Inhibitors containing high levels of phosphate, sulfate or carbonate are likely to form precipitates when pumped into a wellbore rich in calcium or barium ions. The damage can easily cost millions of dollars a day in lost oil production.

It is therefore critical to establish safe levels of the aggressive anion prior to using any scale inhibitor

and to reject batches which may damage an oil reservoir. Using gradient ion chromatography (IC), a procedure was developed using a three-eluent system with a two-step gradient program. This procedure simultaneously separates hydroxyethylsulfonate (HES), sodium vinylsulfonate (SVS), chloride and sulfate reaction by-products. A methanol extraction process [4] is one of the purification processes used to clean up scale inhibitor prior to field use. The IC procedure was used to evaluate the effectiveness of this process.

EXPERIMENTAL

Instrumentation

The method presented was performed on a Dionex 4500i ion chromatograph equipped with a gradient pump [plumbed with polyether ether ketone (PEEK) tubing and fittings], conductivity detector (CDM-2), eluent degas module (EDM-2), autosampler and AI-450 software. The columns used were: (1) anion trap column (24 × 9 mm, high-capacity anion-exchange resin in the hydroxide form); (2) Dionex OmniPac PAX-100 [5] column (250 mm × 4 mm, an alkanol quarternary amine anion-exchange resin); and (3) Dionex OminiPac PAX-100 guard (50 × 4 mm).

The columns were used with a Dionex Anion MicroMembrane Suppressor (AMMS-II) operating via a Dionex AutoRegen System.

Reagents

Inorganic standards were prepared from Johnson Matthey/Aesar ultra dry, 99.99% sodium chloride and Puratonic grade of sodium sulfate (99.999%). HES was prepared from Aldrich isethionic acid, sodium salt, 98% that had been freeze dried. SVS was prepared from vinylsulfonate monomer, sodium salt (30% in water) manufactured by Hoechst, Frankfurt, Germany. Eluents were prepared from Baker 50% sodium hydroxide, Burdick & Jackson methanol (HPLC grade), Burdick & Jackson acetonitrile (HPLC grade) and distilled water passed through a Millipore Milli-Q system. All eluents were degassed with helium and kept under a blanket of helium at all times.

Stock solutions of approximately 1000 µg/g were prepared for each of the four components. A set of mixed standards of chloride and sulfate was pre-

pared. Individual standards for HES were prepared fresh as they may contain small amounts of impurities and the composition changes with time. The individual standard for SVS must also be prepared fresh as it may polymerize over time.

Sample preparation

The twelve samples analyzed in this study were high-molecular-weight polysulfonated scale inhibitors (polymeric sulfonates, PSs). These were obtained from three separate sources. Additionally, the procedure can be utilized for the analyses of monomer and brine samples. By-products/contaminants of interest were sulfate, chloride, HES and SVS. Carbonate and phosphate ions were not involved in this chemistry. The samples were diluted on a weight/weight basis using water, to allow each component to be within the calibrated range. Where possible, an appropriate dilution was chosen to obtain data for all four components in a single run.

Procedure

The gradient IC conditions are listed in Table I.

RESULTS AND DISCUSSION

Calibration graphs for the four components of interest were performed using five standards, ranging from about 1 to 500 µg/g. The graph was ex-

TABLE I
GRADIENT IC CONDITIONS

Columns: anion trap column, OmniPac PAX-100 and PAX-100 guard; suppressor: anion micromembrane suppressor-II (AMMS-II); autoregen: 50 mM sulfuric acid, flow-rate: 11.0–11.5 ml/min; injection: 5 µl; detection: conductivity, range: 0–1000 µS.

Eluent 1: 0.7 M sodium hydroxide in water–methanol (92.5:7.5).
Eluent 2: 150 mM sodium hydroxide in water–methanol (95:5).
Eluent 3: acetonitrile–water (90:10).

Gradient program			
Time (min)	Flow-rate (ml/min)	Eluent 1–eluent 2–eluent 3	Comment
0.0	1.0	100:0:0	Equilibrate
5.1	1.0	100:0:0	Load
6.0	1.0	100:0:0	Inject
23.0	1.0	50:20:30	Ramp 1
30.0	1.0	20:40:40	Ramp 2

TABLE II
CALIBRATION DATA

No.	HES		SVS		Cl ⁻		SO ₄ ²⁻	
	μg/g	Peak Area	μg/g	Peak Area	μg/g	Peak Area	μg/g	Peak Area
1	0.000	0.00000	0.000	0.00000	0.000	0.00000	0.000	0.00000
2	0.970	1.03400 · 10 ⁶	1.057	1.08700 · 10 ⁶	0.947	6.13480 · 10 ⁶	0.992	4.15500 · 10 ⁶
3	9.972	1.43064 · 10 ⁷	10.613	1.68784 · 10 ⁷	10.056	7.60814 · 10 ⁷	10.047	4.41524 · 10 ⁷
4	50.129	7.80384 · 10 ⁷	75.806	1.37095 · 10 ⁸	48.603	4.17717 · 10 ⁸	48.245	2.38115 · 10 ⁸
5	96.794	1.61984 · 10 ⁸	128.480	2.38665 · 10 ⁸	100.210	8.81126 · 10 ⁸	100.070	5.20342 · 10 ⁸
6	479.360	8.95821 · 10 ⁸	570.240	1.16871 · 10 ⁹	500.570	4.66363 · 10 ⁹	502.430	2.80486 · 10 ⁹

Correlation coefficients: HES $R^2 = 0.999$, SVS $R^2 = 0.999$, chloride $R^2 = 1.000$, sulfate $R^2 = 1.000$

tended through the origin although the chromatogram was not run. The calibration data in Table II illustrate good linearity for all four components of interest (correlation coefficients of 0.999 to 1.000).

Upon analyses, PSs from two of the three sources were nearly identical in by-product contamination. Typical chromatograms for PS samples are found in Fig. 1. The PS from one source contained HES,

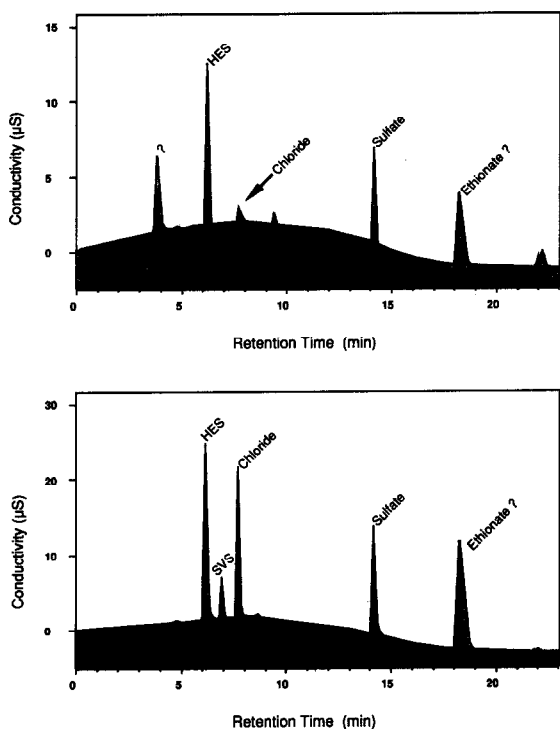


Fig. 1. Typical chromatograms. Top: source one; bottom: source two.

chloride and sulfate but not SVS. It also contained several unidentified peaks, possibly other by-products. The peak at 4.8 min is removed by the addition of barium chloride. The PSs from the two other sources contained all four contaminants and also some unidentified peaks. These samples also contained a peak at 18.9–19.2 min. This peak is suspected to be ethionic acid, which is formed from the hydrolysis of carbyl sulfate, a monomer precursor [6–10]. Both structures are shown in Fig. 2. In common with sulfate, the compound is precipitated with barium and is retained in the non-polymer phase during various organic liquid–liquid extrac-

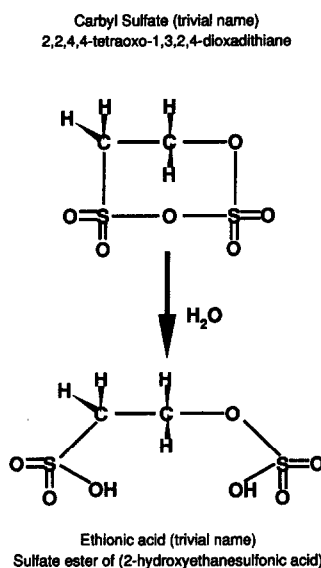


Fig. 2. Structure of carbyl sulfate and its hydrolysis product.

TABLE III
COMPARISON OF SULFATE BY SEC AND IC

Sample	Sulfate (%)	
	SEC	IC
1	3.31	0.60
2	0.65	0.28
3	0.48	0.29
4	2.45	0.55
5	1.95	0.66
6	1.35	0.31
7	1.59	0.47
8	1.77	0.29
9	1.87	1.48
10	1.71	0.35
11	2.97	0.56
12	3.00	0.67

tions. This compound was co-eluted with sulfate by size-exclusion chromatography (SEC). Comparison of the sulfate determination by SEC *versus* IC is shown in Table III. Because of the coelution problem during SEC separation, there is no correlation between sulfate by SEC and sulfate by IC.

The effectiveness of the methanol liquid-liquid extraction [4] was evaluated by using IC to analyze the products of a 25% and a 40% methanol extraction in addition to the untreated product. Comparison chromatograms are shown in Fig. 3. Both of the extractions partially remove sulfate, chloride, HES and SVS. The 25% and 40% extractions removed

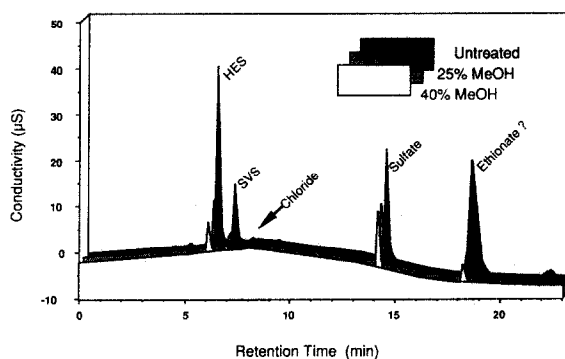


Fig. 3. Effectiveness of methanol extraction procedure.

similar amounts of sulfate. However, the 40% methanol extraction removed larger proportions of all remaining contaminants. Both extractions removed some of the suspected ethionic acid, again confirming its chemical similarity to sulfate.

The precision of the method was investigated from the sample preparation to the final calculation. The polymer studied contained all four contaminants plus the suspected ethionic acid. A 200-fold dilution was chosen in order to obtain data for five contaminants in a single run. These higher dilutions significantly extend the life of the columns. These data are presented in Table IV. This method shows remarkably good precision for such large dilutions of a high-molecular-weight sulfonate. Ethionic acid

TABLE IV

PRECISION STUDY RESULTS

All replicates were diluted 1:200 by weight.

Replicate	[HES] ($\mu\text{g/g}$)	[SVS] ($\mu\text{g/g}$)	[Cl ⁻] ($\mu\text{g/g}$)	[SO ₄ ²⁻] ($\mu\text{g/g}$)	Ethionate? (area)
1	27 845	2590	5289	6323	42 534
2	28 109	2545	5328	6381	42 974
3	28 180	2567	5362	6364	42 852
4	28 259	2577	5383	6399	43 313
5	28 182	2543	5324	6372	43 231
6	28 219	2528	5309	6338	43 053
7	28 315	2636	5377	6382	43 475
8	28 455	2669	5363	6402	43 356
9	28 292	2651	5355	6407	43 266
10	28 061	2659	5388	6406	43 265
Mean + S.D.	28 192 ± 156	2596 ± 50	5348 ± 32	6377 ± 27	43 132 ± 267
Relative S.D. (%)	0.6	1.9	0.6	0.4	0.6

is not readily available; therefore, the precision was determined by comparative peak area.

CONCLUSIONS

Gradient IC simultaneously detected HES, SVS, chloride and sulfate in PS samples, monomer and brine samples. Because of excellent linearity to about 500 $\mu\text{g/g}$, concentrations of all four components were determined with good precision. This procedure demonstrates the effectiveness of methanol extraction in removing unwanted contaminants.

Currently, sulfate contamination cannot be determined by any of the traditional methods usually employed. Sulfate by SEC cannot be correlated with the IC data and, thus, cannot be used in the evaluation of products. IC remains the only viable method in this matrix. PS is currently being squeezed without formation damage in the world's most severe scaling system in the North Sea. The polymer may be appropriate for use on three similar fields.

ACKNOWLEDGEMENTS

The author wishes to thank Marathon Oil Company's Management and the Chemical Technology Department's Scale Group for their support of this project.

REFERENCES

- 1 J. C. Cowan and D. J. Weintritt, *Water Formed Scale Deposit*, Gulf Publishing Co., Houston, TX, 1988.
- 2 A. G. Ostroff, *Introduction to Oilfield Water Technology*, NACE, Houston, TX, 1979.
- 3 C. C. Patton, *Applied Water Technology*, Cambell Petroleum Series, Norman, OK, 1986, p. 84.
- 4 R. T. Barthorpe, Marathon Oil Company, US Pat., 4 995 982 (1991).
- 5 *Dionex Installation and Troubleshooting Guide for the Omni-Pac PAX-100 Analytical Column*, Dionex, Sunnyvale, CA, 1991.
- 6 D. S. Breslou, R. T. Hough and J. T. Fairclough, *J. Am. Chem. Soc.*, 76 (1954) 5361.
- 7 D. S. Breslou and A. Kutner, *J. Polymer Sci.*, 27 (1957) 295.
- 8 D. S. Breslou and R. R. Hough, *J. Am. Chem.*, 79 (1957) 5000.
- 9 D. L. Wooton and W. G. Lloyd, *J. Org. Chem.*, 39 (1974) 2112.
- 10 BASF Aktiengesellschaft, *Eur. Pat.*, 0 054 142 A1 (1982)