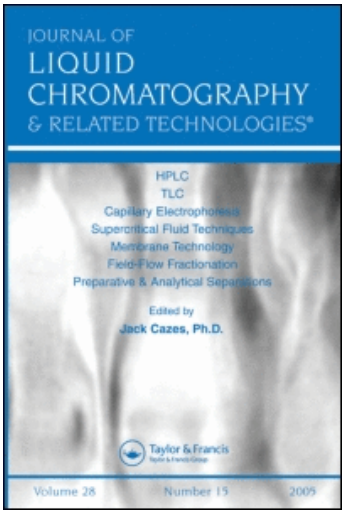

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HPLC Analysis of Cosurfactants Used in Enhanced Oil Recovery

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HPLC ANALYSIS OF COSURFACTANTS USED IN ENHANCED OIL RECOVERY

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ABSTRACT

A reverse phase ion pair HPLC method has been developed in this work for separation not only between sulfonate surfactant (Chevron CHASER XP 1000) and ethoxylated alcohol cosurfactants (Amoco 120 and 122) but also between two Amocos. Amoco 120 and 122, a homolog mixture of C_5 and C_6 alcohol ethoxylates respectively, were separated according to their alkyl group without influence of the ethylene oxide group.

The analysis was performed on a C_{18} column and acetonitrile-water containing PIC A modifier as mobile phase with a refractive index detector. The results showed that the method was able to analyze ethoxylated alcohols in complex sample matrix and gave a dynamic range from µg to mg with a standard deviation of 0.06%. Little or no effect of salt, polymer and biocide on the analytical results were demonstrated. The HPLC method is rapid, specific and therefore provides better results compared to colorimetric methods.

INTRODUCTION

The formulated sulfonate surfactant fluids used in the surfactant flooding process for enhanced oil recovery (EOR) normally contain low concentrations of ethoxylated alcohols as cosurfactants to increase their effectiveness in the oil recovery. To evaluate the flooding process and to optimize the fluids formulation, analysis of both surfactant and cosurfactant in produced fluids is necessary. Despite the fact that the sulfonate surfactant can be readily analyzed by a colorimetric method [1] in core flood effluent, analyses of ethoxylate alcohol have been hampered by the lack of reliable methods. Conventional analysis of ethoxylated alcohols using colorimetric methods presents problems because of strong interference from alcohols and other ethoxylated compounds.

The situation prompted us to develop an efficient method for analysis of Amoco 120 in core flood effluents and produced fluids. The method we describe here is a high performance liquid chromatographic (HPLC) technique which provides separation of surfactant and cosurfactant in a complex sample matrix, resulting in more reliable qualitative and quantitative analysis.

EXPERIMENTAL SECTION

Chemicals

Amoco 120 and 122 were obtained from Amoco with various degrees of ethoxylation. The Amoco's and Chevron Chaser XP 1000 were used as received. Acetonitrile was HPLC grade from J. T. Baker and the water was purified by a Millipore filtration system. PIC A (tetrabutyl ammonium phosphate) was purchased from Waters Associates.

Instrument

HPLC analyses were performed on a Waters System equipped with a model 6000 pump, a 440 UV detector and a 401 differential refractive index detector, an automatic sampler (WISP) and a 721 data module. The column was a Waters radial compression reverse phase C-18 column with a dimension 10 x 0.8 cm and 10 μ particle size.

Sample Preparation

All formulated surfactant fluids and core flood effluents contained ≅1% or less Chevron XP 1000 and Amoco 120 respectively. These samples were filtered

with a Millipore Millex-ST (0.5 μm PTFE membrane) prior to HPLC analysis.

HPLC Analysis

Sample ranged from 50 to 200 ul was injected onto the HPLC system described above. The mobile phase was 40% acetonitrile and 60% H_2O with 0.005M PIC A for routine analysis. The flow rate varied from 3 to 1 ml/min depending on the sample viscosity and hence the HPLC back pressure. The effluent was monitored using the refractive index detector. Quantitation was based on the peak height measurement.

Polymer Removal

The experiment was carried out to remove the polymer by adding equal volume of acetone to the formulated surfactant fluids resulting in the precipitation of the polymer. After filtering off the polymer and blowing down dry the aliquot, the remaining sample was brought up to the original volume by using the mobile phase and was then analyzed.

RESULTS AND DISCUSSION

Amoco 120 and 122 are a homologous mixture of polyoxyethylene hexanol and pentanol respectively.

The HPLC separations of polyoxyethylene alcohols reported in the literature [2, 3] were mostly influenced by the ethylene oxide unit. Conceivably a high resolution HPLC system can separate each Amoco into its individual component, differing only by the number of ethylene oxide units. This would generate a great number of peaks on the chromatogram for each Amoco. As a result, interpretation of chromatographic data and quantitation would be difficult.

The HPLC system used in this work was not only able to separate Chevron XP 1000 from Amoco's but between Amoco 120 and 122. This is illustrated in Figure 1. The feature of the technique is that the separation between two Amoco's was based on the alkyl group without the influence of the ethylene oxide unit. This results in a simplified chromatogram and yields better quantitation. Note that analysis time is relatively short.

With the addition of pair ion agent (PIC A) to the mobile phase, all of the peaks were sharpened up, as shown in Figure 2. While the peak polarization of Chevron XP 1000 changed, the two Amoco's remained unchanged. The improvement on the peak shape certainly increased the ratio of signal to noise and gave better quantitative results. Another effect of PIC A was both Amoco's eluted earlier. The reduction in retention of the two Amoco's was unexpected because

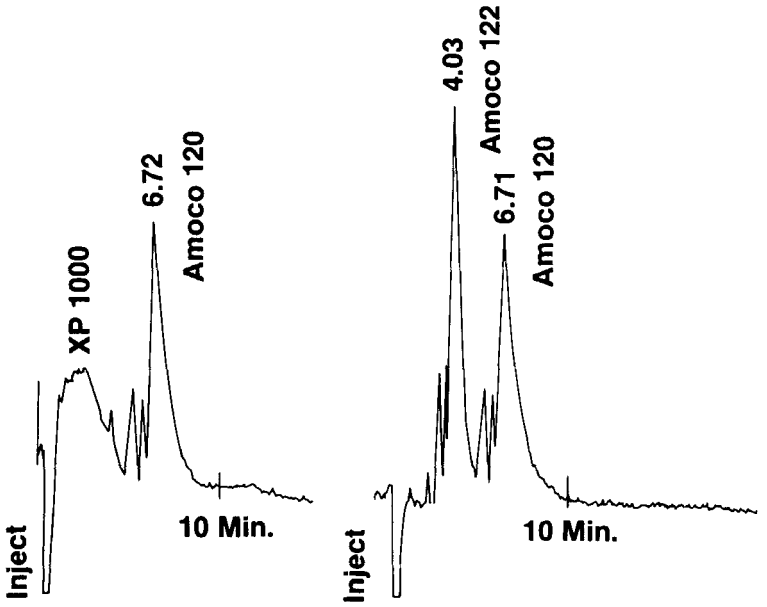

Figure 1 HPLC Reverse Phase Chromatograms of Chevron XP 1000, Amoco 120, and Amoco 122 (Mobil phase: 40/60 Acetonitrile/Water, Flow Rate: 3 ml/min)

the neutral molecules should remain unaffected by the presence of ion pair reagent (4). An investigation is underway to reveal the cause of this uncommon retention behavior.

The effect of salt, polymer and biocide on the analysis was also studied. The compositions of the formulated surfactant fluid samples analyzed are listed in Table 1. The results shown in Figure 3

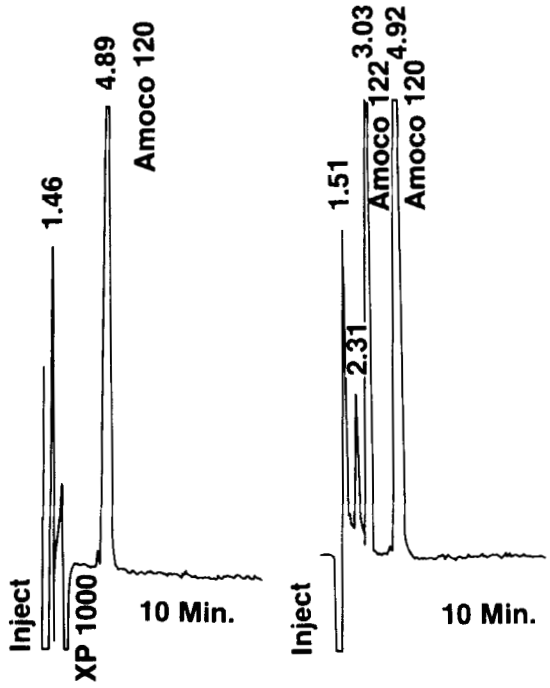

Figure 2 HPLC Reverse Phase Ion Pair Chromatograms of Chevron XP 1000, Amoco 120, And Amoco 122 (Mobile phase: 40/60 Acetonitrile/Water with 0.005 M PIC A, Flow Rate: 3 ml/min)

indicated that these samples with complex matrix had little effect on the separation of Amoco 122 and 120 even though their concentration ratios were 10:1. The Figure 4 showed that the detector had a good linear response for Amoco 120 ranging from low µg to 1000 µg with a standard deviation of 0.06% at 0.5% concentration.

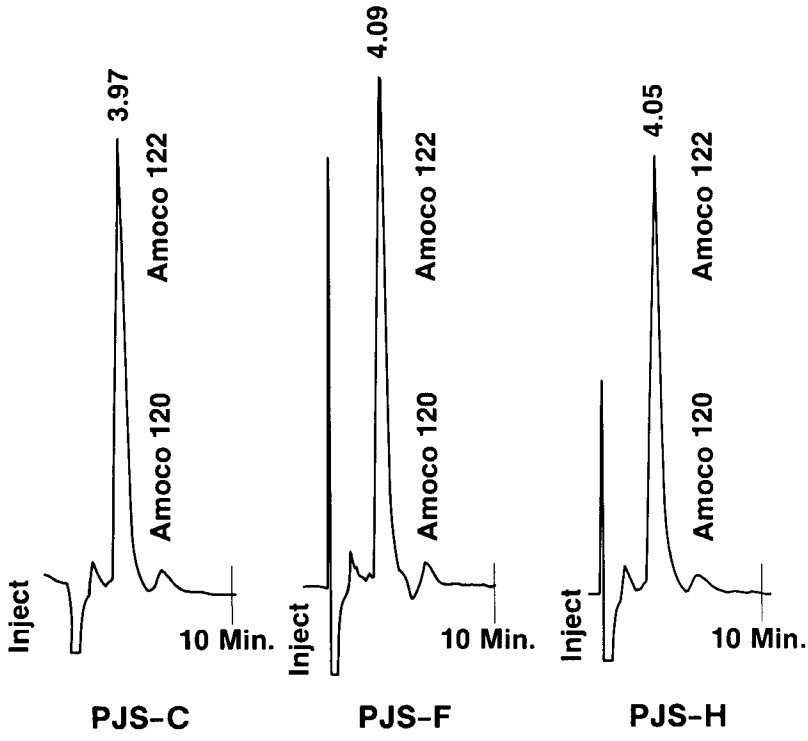

Figure 3 HPLC Chromatograms to Demonstrate Little Effect of Salinity, Polymer and Formaldehyde on the Separation

Moreover, the effect of oil on the analysis was also checked. The West Coyote produced oil was thoroughly shaken with the formulated surfactant fluid and the mixture was then injected on the HPLC system. Fortunately, oil eluted very early and gave no interference on the analysis of Amoco 120. This is shown in Figure 5.

TABLE 1

Compositions Of Formulated Surfactant Fluids

Sample	% Chevron XP 1000	% Amoco 120	% Amoco 122	Salinity	PPM Polymer	PPM Formaldehyde
PJS-A	0.5	0.5		DIW		
PJS-B	0.5	0.5		DIW		500
PJS-C	0.5	0.5	5	DIW		500
PJS-D	0.5	0.5		0.5% NaCl		500
PJS-E	0.5	0.5		50% SWCIW		500
PJS-F	0.5	0.5	5	50% SWCIW		500
PJS-G	0.5	0.5		50% SWCIW	2000	500
PJS-H	0.5	0.5	5	50% SWCIW	2000	500

Note - DIW - Deionized Water
50% SWCIW - Synthetic Field Brine; 6000 ppm TDS 100 ppm Hardness as Ca^{++}
Polymer is Cyanatrol 950 Polyacrylamide

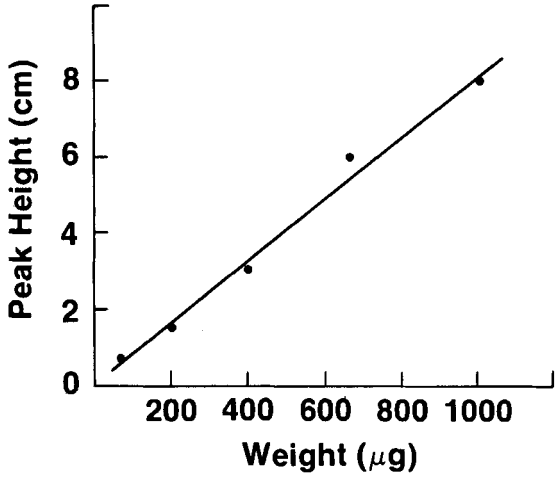

Figure 4 Calibration Curve of Amoco 120

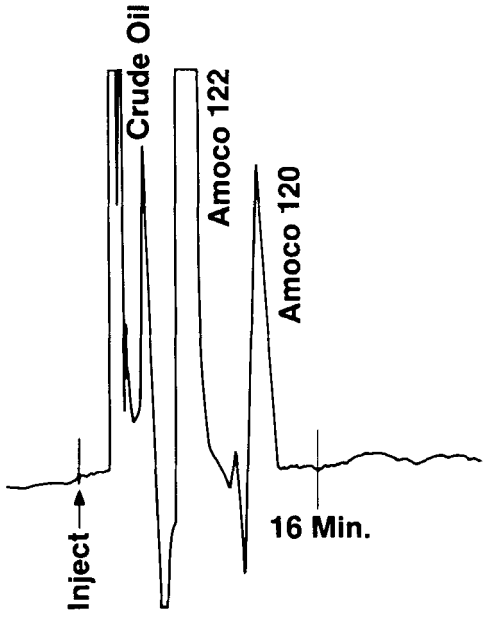

Figure 5 HPLC Chromatogram to show Little Effect of Crude Oil on the Separation

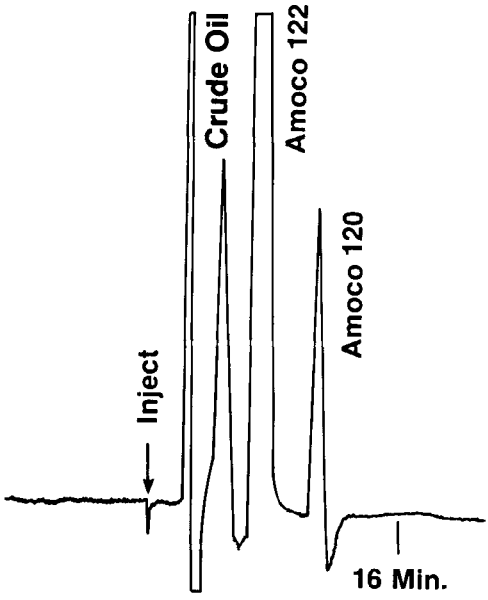

Figure 6 HPLC Chromatogram of Coreflood Effluent

The removal of polymer from the formulated surfactant fluids prior to the HPLC analysis was highly desirable because it often caused a high HPLC back pressure and shut down the operation. The analysis of the polymer removed sample yielded the same result as shown in Figure 5 in which the polymer wasn't removed. This demonstrates that the polymer removal procedure didn't change the result and can be included in the procedure as needed.

Finally, effluents of micellar (surfactant) core flood were analyzed after polymer removal and their

results were comparable with those of the test samples described earlier. Figure 6 shows a representative chromatogram of effluent analyses, demonstrating effectiveness of the method for analysis of the real world samples.

Thus a HPLC method has been developed for analysis of the cosurfactant, Amoco 120, in the formulated sulfonate surfactant fluids. The method is rapid and specific, providing better analytical results.

ACKNOWLEGEMENT

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REFERENCES

1. ASTM, D2330 (1974)

2. McClure, J. D., J. Amer. Oil Chem. Soc., 59, 364 (1982)

3. Garti, N., Kaufman, V. R., and Aserin, A., Separation and Purification Methods, 12, 49 (1983)

4. Bidlingmeyer, B. A., Deming, S. N., Price, W. P., Sachok, B., and Petrusek, M., J. Chromatogr, 186, 419 (1979)

5. Footnote: This paper was presented at the 1986 Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy. Atlantic City, New Jersey, March 10-14, 1986.