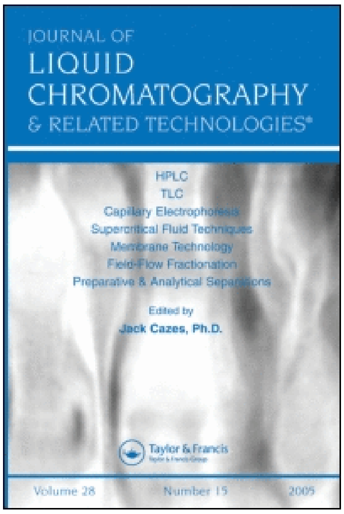

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REVERSE PHASE HPLC ANALYSIS OF ALKYL SULFONATES WITH NON-SUPPRESSION CONDUCTIVITY DETECTION

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ABSTRACT

C_{10}-C_{16} alkyl sulfonates were used as surface active reagents in a micellar flooding study for enhancing oil recovery. They were analyzed by reverse phase high performance liquid chromatography (RP-HPLC). Sodium dihydrogen phosphate of low concentration was used as eluent component and conductivity detector was used for detection. The eluted alkyl sulfonate was detected directly and no suppressor column was required. This method was characterized by its simplicity, rapidity and sensitivity.

INTRODUCTION

Surface active petroleum sulfonate has been widely used as a chemical flooding agent in the petroleum industry. This sulfonate is obtained by sulfonation of a certain petroleum fraction, and its composition is rather complex.

Depending upon the degree of sulfonation, there may be mono-, di- and poly-sulfonates. According to the parent compound used for the sulfonation, there may be alkyl sulfonates and aryl sulfonates.

Clarification of the composition of the sulfonate is very important in studying the flooding mechanism, guiding the synthesis of petroleum sulfonate, and understanding the chromatographic separation phenomena in the flooding process. In this paper, the analysis of the alkyl sulfonate with liquid chromatography is studied.

The alkyl sulfonate exhibits only a weak ability to absorb ultraviolet light; it cannot be detected with the UV detector usually used in HPLC. The differential refraction detector cannot be used either; its sensitivity is too low and cannot meet the requirement of the analysis of low sulfonate concentration. Thus, besides the search for good separation conditions in the analysis of alkyl sulfonate with HPLC, it is also important to choose the proper detection system. Eppert, et. al.[1,2] and Larson[3] used indirect photometric detection for the analysis of alkyl sulfonate with ion pair chromatography (IPC). Pan et. al.[4] used ion chromatography and Weiss[5] adopted the mobile phase ion chromatography (MPIC) with ion pair reagent added to the mobile phase for the analysis; a suppressing conductivity detector was used in their system. The whole method is rather complex and it is necessary to regenerate the suppressor column, periodically; the entire operation is tedious.

In this paper, RP-HPLC is used for the analysis of C_{10} - C_{16} alkyl sulfonate, usually encountered in enhanced oil recovery processes. The mobile phase used contains sodium dihydrogen phosphate and a conductivity detector is used directly for the detection. No suppressor column is required. The inorganic salts and alcohol mixed in the sample do not interfere with the detection, and there is no necessity to remove them in advance. Thus, the operation is simple and the sensitivity is higher.

EXPERIMENTAL

Apparatus

The liquid chromatographic system was comprised of a Gilson 302C pump, a DDJ-01 conductivity detector (Sichuan Analytical Instrument Plant, China), two Rheodyne 7125 injection valves (10 and 20 μL) and a XWT 200 recorder (Shanghai Dahua Instrument and Meter Plant, China).

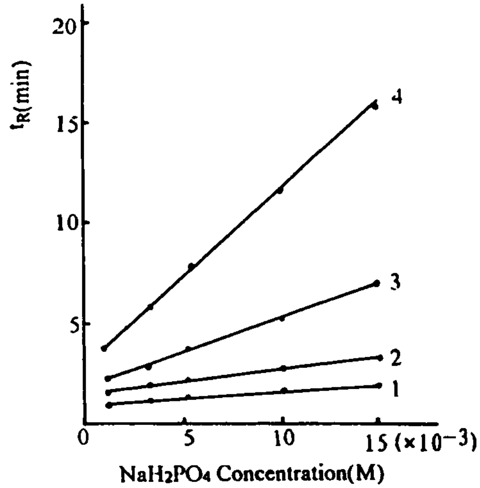

Figure 1. Relationship between alkyl sulfonate retention and phosphate concentration in the mobile phase. Mobile phase: 0.001M. NaH$_2$PO$_4$: MeOH = 35:65; Flow rate: 1mL/min; 1. C_{10} alkyl sulfonate, 2. C_{12} alkyl sulfonate, 3. C_{14} alkyl sulfonate; 4. C_{16} alkyl sulfonate.

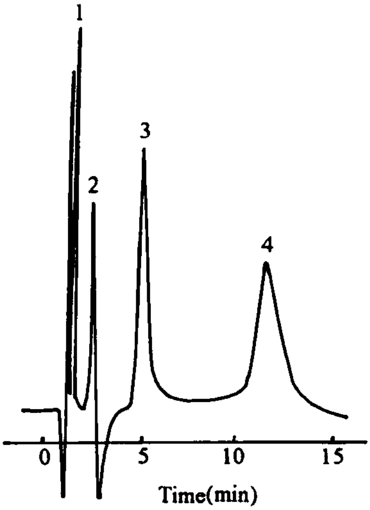

Figure 2. Chromatogram of alkyl sulfonates. Mobile phase: 0.001M. NaH$_2$PO$_4$: MeOH = 65:35; Flow rate: 1mL/min; 1. C_{10} alkyl sulfonate, 2. C_{12} alkyl sulfonate, 3. C_{14} 10^7 Pa. alkyl sulfonate; 4. C_{16} alkyl sulfonate.

The chromatographic column was a 4.6mm x 150mm stainless steel tube, slurry packed with ODS (3-5μm, Shanghai First Reagent Plant, China) under 3.5 x 10^7 Pa.

Reagents

C_{10}-, C_{14}-, and C_{16}- alkyl sulfonates were supplied by Xinjiang Institute of Chemistry, Chinese Academy of Sciences.

C_{12}- alkyl sulfonate was a chemically pure reagent (Bei He Chemical Plant, China), and was recrystallized before use.

Sodium dihydrogen phosphate, analytically pure (Xian Chemical Reagent Plant , China).

Methanol, analytical pure reagent. Both methanol and freshly distilled and deionized water were filtered through a sintered glass filter before use.

The mobile phases were composed of methanol and aqueous sodium dihydrogen phosphate of various concentrations.

RESULTS AND DISCUSSION

Effect of Sodium Dihydrogen Phosphate Concentration on Retention

The retention of alkyl sulfonate is affected by the concentration of sodium dihydrogen phosphate in the mobile phase. When the concentration is very low, the alkyl sulfonate is not retained at all. By contrast, when the concentration is higher, the alkyl sulfonate is difficult to elute. This is caused by the salting out effect.

When the amount of phosphate in the mobile phase is increased, the distribution of alkyl sulfonate in water-containing mobile phase will decrease and its distribution in the hydrophobic stationary phase will enhance accordingly, so that its retention will increase.

The experimental results showed that the mobile phase containing a proper concentration of sodium dihydrogen phosphate can elute and separate C_{10} - C_{16} alkyl sulfonates; the retention increased with the increasing of phosphate concentration.

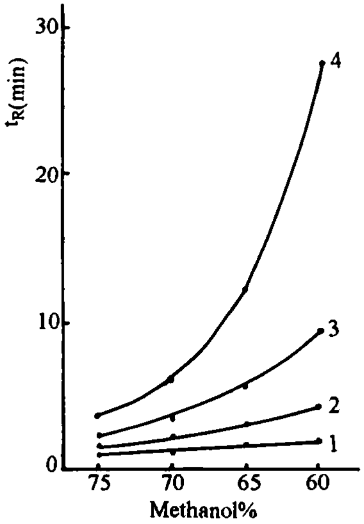

Figure 3. Relationship between alkyl sulfonate retention and methanol content in the mobile phase. Mobile phase: 0.001M NaH_2PO_4/MeOH; Flow rate: 1 mL/min; 1. C_{10} alkyl sulfonate, 2. C_{12} alkyl sulfonate, 3. C_{14} alkyl sulfonate; 4. C_{16} alkyl sulfonate.

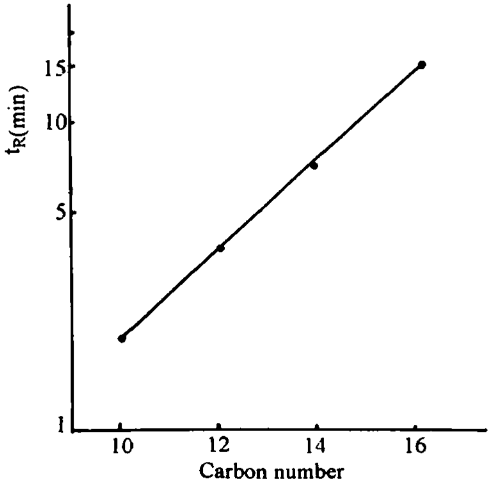

Figure 4. Relationship between alkyl sulfonate retention and number of carbon atoms. Mobile phase: 0.001M. NaH_2PO_4 : MeOH = 65:35; Flow rate: 1mL/min.

Figure 1 shows the relationship between retention and phosphate concentration at a certain aqueous phosphate-methanol proportion. The complete separation of C_{10}, C_{12}, C_{14}, and C_{16} alkyl sulfonates, under proper elution condition, is given in Figure 2.

Effect of Methanol Content

The distribution of alkyl sulfonate in mobil phase is enhanced with the increase of methanol percentage in mobile phase; the retention is also decreased (Figure 3).

Effect of Carbon Number on Alkyl Sulfonate Retention

From the above experimental results, it can be seen that, under same operating condition, the retention of alkyl sulfonate which contains a greater number of carbon atoms is longer. This is due to the strengthening of lipophilic behaviour. By plotting the logarithm of the studied alkyl sulfonate retentions versus the number of carbon atoms contained in their carbon chains, a good linear relationship is obtained (Figure 4). Thus, qualitative ascertainment of the alkyl sulfonate can be obtained by determining the carbon atoms contained in the carbon chain from the retention of the sample.

Determination of Dodecyl Sulfonate in Micellar Fluid

In enhanced oil recovery studies, a micellar fluid composed of alkanes, fatty alcohols, inorganic salts, and dodecyl sulfonate was used for oil flooding. In order to take concerted study, the authors carried out the quantitative work with HPLC. Because of the fact that the reverse phase system was used for the separation and the conductivity detector was used for the detection, both alkanes and alcohols gave no signal, so they did not interfere with the detection. Besides, the retention of the inorganic salts was very short; these salts eluted before the alkyl sulfonate and did not interfere with the detection either.

For the determination in this work, a mixture composed of low concentration of aqueous sodium dihydrogen phosphate and certain amount of methanol (0.001M NaH_2PO_4:CH_3OH = 50:50) was used as the mobile phase. Also, no suppressor was used; the background conductivity was very low, so that the detection could be conducted at rather higher sensitivity.

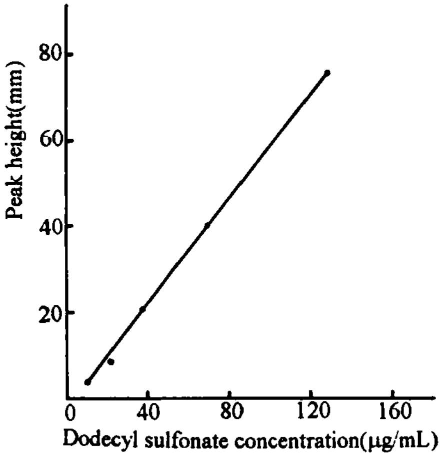

Figure 5. Calibration curve of dodecyl sulfonate. Mobile phase:MeOH : 0.001M NaH_2PO_4 = 50:50; Flow rate:1mL/min

When the sample volume was 20μL, the plot of peak height with sodium dihydrogen phosphate concentration maintained good linearity when sample concentration went up to 120ppm (Figure 5). So, this chromatographic condition was used for the determination of dodecyl sulfonate.

During the preparation of micellar fluids for enchanced oil recovery study, three phases, the upper oil phase, the middle micellar phase, and the lower aqueous phase were obtained. The contents of dodecyl sulfonate in these phases were analyzed. The result is shown in Table 1.

As shown in the table, some errors are rather high. This is caused, mainly, by the larger reading error of volume, especially the reading of the micellar phase of smaller volume. In general, the results obtained can meet the requirement of enhanced oil revovery studies.

CONCLUSION

1. RP-HPLC with conductivity detection was successfully used for the detection of alkyl sulfonate. The mobile phase contained low concentration of dihydrogen sodium phosphate; no suppressor column was necessary.

Table 1

Dodecyl Sulfonate in Micellar Fluid

	Sample Number 1	 2	 3
Upper Phase			
Volume, mL	4.4	3.3	3.7
Conc., μg/mL	---	1.05×10^3	1.79×10^3
Content, mg	---	3.47	6.62
Middle Phase			
Volume, mL	2.9	1.9	2.1
Conc., μg/mL	6.68×10^4	1.10×10^5	8.81×10^4
Content, mg	194	209	185
Lower Phase			
Volume, mL	2.7	4.6	4.0
Conc., μg/mL	2.05×10^3	1.10×10^3	---
Content, mg	**5.5**	**5.06**	---
Total Amount, mg	199	218	192
Recovery, %	99.5	109	96.6

2. Although no suppressor column was used, the results of quantitative analysis of dodecyl sulfonate show the rather higher sensitivity of the described method.

3. The separation of C_{10} - C_{16} alkyl sulfonates used in enhanced oil recovery studies can be accomplished by varying the sodium dihydrogen phosphate concentration in water and the amount of methanol in the mobile phase.

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