Analytical Methods

PAPER

Determination of alkylamine carbonate nonionic–anion oil displacement agent in oil-field water using HPLC after derivatization with 4-methoxybenzenesulfonyl fluoride

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In this study, a method for the determination of alkylamine carbonate (AAC) nonionic–anion oil displacement agent in oil-field water was developed for the first time, involving pre-column derivatization using a novel labeling agent and HPLC with diode-array detection. The derivatization and chromatographic separation conditions were investigated thoroughly. The analyte was labeled with 4-methoxybenzenesulfonyl fluoride at 50 °C for 20 min. When the method was applied in the determination of C18A5C (an AAC oil displacement agent containing eighteen alkyl and five amino groups) a linear calibration curve was obtained from 1.0 to 100.0 $\mu g\ mL^{-1}$ with a correlation coefficient of more than 0.999 and a detection limit of 0.05 $\mu g\ mL^{-1}$. In the determination of real oil-field water samples, the recovery range of C18A5C was 91.8% to 96.2%, and the intra-day and inter-day relative standard deviations were 2.9–3.5% and 3.8–4.3%, respectively. The experimental results demonstrate that this method, with its merits of simplicity in pretreatment, rapidity in derivatization, and stability of the derivatives, can be employed in the analysis of C18A5C and has potential application in the detection of other oil displacement surfactants containing amino groups. It is of great significance to develop a fast, easy-to-operate, sensitive and reliable method for environmental impact assessment.

1 Introduction

In oil field operations, surfactants can be applied in oil drilling, oil gathering and transportation links. Polymer flooding is a way of injecting the aqueous solution of polymeric surfactant into the oil layer.[1] In order to meet the requirements of enhancing oil recovery and to reduce the costs of the flooding system, a number of nonionic–anionic polymeric surfactants have been developed. Containing two different hydrophilic groups and possessing the advantages of anionic and nonionic surfactants, these nonionic–anionic polymeric surfactants are applied more extensively in flooding systems. For example, in China, an alkylamine carbonate (AAC) oil displacement agent as a novel nonionic–anionic polymeric surfactant has been used widely. Its molecular structure is shown in Fig. 1.

However, this process of polymer flooding produces a complex and stable emulsion system. Compared with water flooding, its treatment is more difficult.[2] Side effects caused by the surfactants have long been a focus of concern and the application of the surfactants may lead to a series of environmental problems such as water pollution.[3] Therefore, it is particularly necessary to analyze the content of one kind of surfactants for the purpose of the quality assurance of commercial products and for environmental pollution control. Although many methods have been described for the determination of various surfactants in the daily use, there are few methods reported on the detection of surfactants in flooding systems. And no method has been reported for the determination of AAC in oil-field water. Thus, it is of great significance to develop a fast, easy-to-operate, sensitive and reliable method for the quality control and hazard evaluation of oil-field water.

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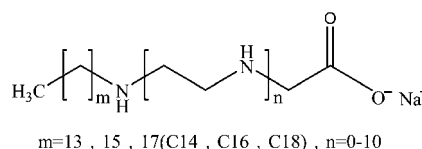

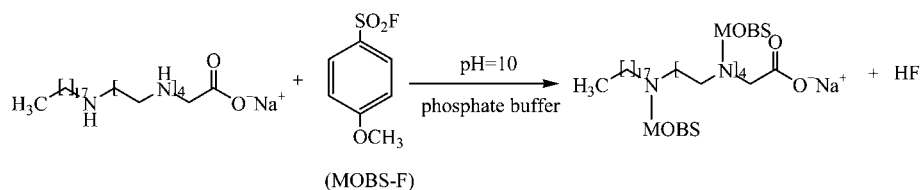Fig. 1 Structure of alkylamine carbonate (AAC) oil displacement agent.

Fig. 2 Probable reaction scheme for the derivatization of C18A5C with MOBS-F as labeling agent.
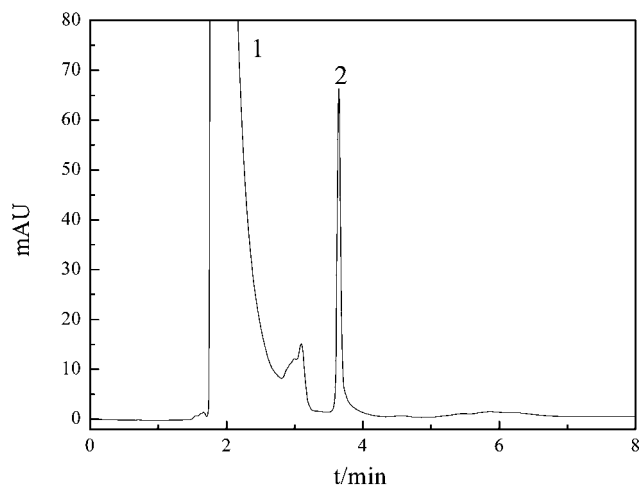
Fig. 3 Chromatogram obtained for a standard solution of C18A5C labeled with MOBS-F (peaks: 1 = MOBS–OH; 2 = MOBS–C18A5C). Chromatographic conditions: the separation of the derivatives was achieved using an isocratic elution of 60% A and 40% B (A: ultra-pure water; B: methanol) with DAD detection at 240 nm.

Table 1 Repeatability of the determination of C18A5C by RP-HPLC ($n = 5$)[a]

	RSD[b] (%)											
	Retention time						Integrated area					
	Run-to-run			Day-to-day			Run-to-run			Day-to-day		
Compound	A	B	C	A	B	C	A	B	C	A	B	C
C18A5C	0.13	0.09	0.08	1.3	1.1	1.2	2.5	2.6	2.3	3.3	3.7	3.6

[a] The result was obtained from 5.0 μg mL^{-1} (A), 20.0 μg mL^{-1} (B), to 50.0 μg mL (C) of C18A5C. [b] RSD, relative standard deviation.

Morelli and Szajer[4,5] provided a critical review on the analysis of various surfactants. These methods mainly include electrochemical analysis,[6,7] flow injection analysis,[8,9] spectrophotometry,[10,11] attenuated total reflection Fourier transform infrared spectroscopy,[12] capillary electrophorsis,[13] supercritical fluid chromatography,[14,15] ion chromatography,[16,17] gas chromatography[18,19] and high performance liquid chromatography.[20–22] The above methods are more applicable to the determination of real samples with simple components, whereas the components in oil-field samples are complex. In flooding systems, the chemical reagents contain other chemicals such as alkali, salt, polymer and trace oil, resulting in great difficulties in the determination of the oil displacement agent in oil-field water.

In the related reports on the quantitative analysis of surfactants in the complex system, gas chromatography (GC) and high performance liquid chromatography (HPLC) techniques have been the most popular because of their superiority in precision and accuracy. Alkylamine carbonate nonionic–anionic surfactant is of low volatility and thermal instability (due to the presence of multi-amino groups), so it cannot be determined by means of GC. HPLC has advantages in the detection of non-volatile molecules[4,5] and can be used to determine the alkylamine carbonate nonionic–anionic surfactant by conventional ultraviolet (UV) detection, or without derivatization by using specific detectors, such as evaporative light scattering and mass spectrometry (MS). However, the evaporative light scattering detector lacks specificity and sensitivity, so it is not an easy task to assay the complex components in oil-field samples. Though HPLC–MS has emerged as a powerful technique for the determination of alkylamine surfactant,[23,24] it is not likely to be adopted as a routine industrial monitoring technique due to its high cost and complexity. HPLC with UV detection is more widely applied in the routine monitoring of oil field operations. Due to the lack of ultraviolet and fluorescent chromophores, the AAC requires derivatization prior to assay. Therefore, HPLC combined with pre-column derivatization[25–28] is an ideal method for the assay AAC.

In our previous reports, a novel ultraviolet labeling agent 4-methoxybenzenesulfonyl fluoride (MOBS-F) with facile reaction conditions and simple operation procedures was employed in the detection of primary and secondary amines with satisfactory results.[29,30] Our aim was to develop a quantitative method for the determination of AAC in order to provide reliable data for environmental impact assessment (EIA).

Table 2 Linear range for the determination of C18A5C by RP-HPLC

Compound	Linear range/μg mL^{-1}	Linear regression equation[a]	Related coefficient	LOD[b]/μg mL^{-1}
C18A5C	1.0–100.0	$Y = 50.36282 + 2.55256X$	0.9992	0.05

[a] X, concentration of C18A5C (μg mL^{-1}); Y, peak area of C18A5C (arbitrary unit). [b] LOD, concentration detection limit.

Table 3　Determination results for C18A5C oil displacement agent in oil-field water ($n = 6$)

		Original concentration found[a]/$\mu g\ L^{-1}$	Concentration found after pre-treatment[b]/$\mu g\ L^{-1}$	Amount added/ $\mu g\ mL^{-1}$	Average recovery (%)
C18A5C	Water 1	7.26	7.26	5.00	93.6
				20.0	94.7
				50.0	95.3
	Water 2	8.64	8.64	5.00	91.8
				20.0	94.3
				50.0	92.6
	Water 3	9.58	9.58	5.00	92.8
				20.0	93.8
				50.0	95.6

[a] Original concentration found: the concentration of C18A5C in oil-field water without pre-concentration. [b] Concentration found after pre-treatment: the concentration of C18A5C in oil-field water after pre-concentration.
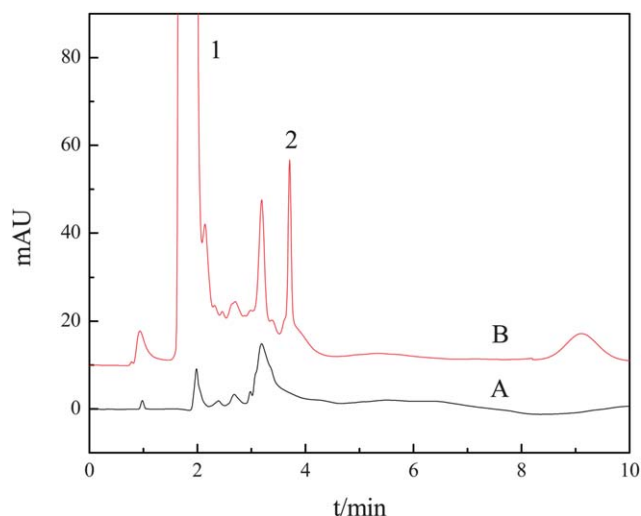

Fig. 4　Chromatograms obtained from blank oil-field water (A) and C18A5C oil displacement agent in oil-field water labeled with MOBS-F (B) (peaks: 1 = MOBS–OH; 2 = MOBS–C18A5C). Chromatographic conditions were the same as those in Fig. 3.

2　Experimental

2.1　Apparatus

The Agilent 1200 series HPLC system (Agilent Technologies Inc.) was used in the experiments. It was equipped with the following modules: a G1322A online vacuum degasser, a G1311A high-pressure gradient quaternary pump, a G1329A light-tight auto-sampler unit, a G1316A thermostated column compartment and a G1315D photodiode array detection (DAD) system. A reversed-phase ODS column (150 mm × 4.6 mm I.D., 5 μm, Shimadzu) was used as an analytical column. A Mettler-Toledo FE20 pH meter (Shanghai, China) was used to measure the pH value of the solutions. A UV-2550 spectrophotometer (SHIMADZU, Japan) was employed to detect MOBS-F and its derivatives.

2.2　Chemicals and reagents

All chemical reagents were of analytical grade except those specified. Sodium phosphate dodecahydrate, disodium hydrogen phosphate dodecahydrate, sodium dihydrogen phosphate dehydrate, n-butyl alcohol, acetonitrile (HPLC-grade) and

methanol (HPLC-grade) were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). C18A5C oil displacement agent (AAC, $m = 17$, $n = 4$) was provided by Jiangsu Oilfield (Yangzhou, China, 30% as the active ingredient). MOBS-F was supplied by the Institute of Chemistry, Nanjing Zhongyi. Ultra-pure water was obtained with a Milli-Q system (Millipore, Milford, MA, USA). 2.0 g C18A5C oil displacement agent was dissolved in ultra-pure water. The resultant solution was extracted twice with n-butanol and the organic phase was collected. The solution was made up to a volume of 100 mL with n-butanol to give a standard stock solution containing 6.0 mg mL^{-1} oil displacement agent C18A5C. The stock solution of C18A5C was stored in a refrigerator at +4 °C, and was further diluted before use. A phosphate buffer solution was obtained by mixing 0.05 M disodium hydrogen phosphate and 0.05 M sodium dihydrogen phosphate in ultra-pure water, adjusted to pH 10.0 with 0.05 M sodium phosphate. The buffer solution was stored in a refrigerator at +4 °C. The labeling reagent was prepared by dissolving 0.1 g MOBS-F in 10.0 mL acetonitrile (10.0 mg mL^{-1}) and was further diluted before use. The stock solution of MOBS-F was stored in a refrigerator at +4 °C.

2.3　Sample preparation and derivatization procedure

Sediments of 25 L oil-field water sample were filtered. A 10 L water sample was obtained. The water sample was concentrated to about 5 mL by thermal volatilization under ambient pressure, and extracted twice with 4 mL n-butanol. The organic phase was collected and diluted to 10 mL with n-butanol.

0.2 mL standard solution of C18A5C oil displacement agent, 0.8 mL 0.05 M phosphate buffer and 0.2 mL 10.0 mg mL^{-1} MOBS-F were successively added into a screw capped glass vial. The resultant solution was mixed well, and the mixture was maintained reacting at 50 °C for 20 min. After cooling to room temperature, the mixture was filtered through a 0.22 μm membrane.[29,30]

2.4　Mobile phase preparation and chromatographic conditions

Chromatographic separation was performed at 25 °C by iso-cratic elution. The mobile phase for HPLC analyses consisted of

(A) 60% ultra-pure water and (B) 40% methanol with a total flow rate of 1.0 mL min^{-1}. The detection wavelength was 240 nm.

3 Results and discussion

3.1 Optimization of chromatographic separation conditions

The determination of secondary amines, performed by pre-column derivatization with MOBS-F as the labeling agent, is well documented in our previous work. MOBS-F can label the C18A5C oil displacement agent under alkaline conditions. The derivative can be determined by UV spectrophotometry. A probable derivatization reaction process is shown in Fig. 2. The hydrophilic groups of the C18A5C oil displacement agent have a polyamine structure, thus the labeling reagent can react with multi-amino groups. In this experiment, the results indicated that the derivatization reaction could be completely finished by appropriately increasing the concentration of labeling reagent, and that only the derivative was obtained (there was only one peak, corresponding to the derivative, in the chromatogram). When the chromatographic conditions, including the proportion of mobile phase, the concentration of labeling reagent, reaction temperature and reaction time, were optimized, only one peak, corresponding to the derivative, was observed under each chromatographic condition, and these peaks all had the same retention time, indicating that the labeling reagent could react with all the amino groups of the C18A5C molecule.

The separation of the derivative is affected by the mobile phase polarity, thus adjusting the appropriate mobile phase proportion is essential for the separation. In this work, the effect of mobile phase ratio was investigated, and the experimental results showed that the retention time of the analyte became shorter when the proportion of methanol increased. When the proportion of methanol was too high, the derivative peak of appeared much earlier, and the derivative was affected by the hydrolytic product. When the proportion of ultra-pure water was too high, the analyte peak appeared much later, and the separation time also increased. Therefore, the optimum proportion of the mobile phase was 60% ultra-pure water and 40% methanol. A chromatogram of a standard solution of C18A5C oil displacement agent derivatized with MOBS-F is displayed in Fig. 3.

3.2 Optimization of the derivatization reaction conditions

The 20 μg mL^{-1} standard solution of C18A5C oil displacement agent was used to optimize the test concentration for derivatization. In order to obtain the optimum conditions, the reaction temperature, reaction time and MOBS-F concentration of the derivatization reaction were investigated.

An experiment investigated the effect of derivatization temperature within the range of 20 °C to 80 °C with a 10 °C increment as below. The C18A5C oil displacement agent and MOBS-F were mixed and reacted in a water bath for 20 min at different temperatures. After cooling to room temperature, the mixture was analysed by HPLC. The results show that the chromatographic peak area of the derivative somewhat decreases when the derivatization reaction temperature is

higher than 50 °C. When the temperature is lower than 50 °C, the chromatographic peak area of the derivative significantly decreases. Namely, the derivatization reaction rate is greater than the hydrolysis rate of MOBS-F at 50 °C. Therefore, a derivatization reaction temperature of 50 °C was selected.

The effect of derivatization reaction time was examined at a reaction temperature of 50 °C. The results show that the chromatographic peak area gradually decreased when heating time was more than 20 min. This may be attributed to the decomposition of the derivative as a result of prolonged heating time. Thus, the optimum derivatization reaction time was determined to be 20 min.

The effect of the amount of derivatization reagent MOBS-F was investigated by varying the concentrations of MOBS-F to react with 20.00 μg mL^{-1} C18A5C. The results indicate that when the concentration of MOBS-F was more than 150 μg mL^{-1}, no increase of peak area shows. Therefore, a MOBS-F concentration of 150 μg mL^{-1} was found to be the optimum concentration for the derivatization.

3.3 Repeatability of chromatographic analysis

The repeatability of the chromatographic analysis can be assessed by measuring the retention time and the peak area. In this experiment, replicate injections ($n = 5$) of different concentrations of derivatization solutions were applied in intra-day and inter-day determinations. The relative standard deviations (RSDs) were calculated, and the results are shown in Table 1. The RSDs data of the intra-day and inter-day retention time precisions were 0.08–0.13% and 1.1–1.3%, respectively. RSDs of the intra-day and inter-day integrated area precisions were 2.3–2.6% and 3.3–3.7%, respectively.

3.4 Linearity and detection limit

To obtain the calibration curve, standard solutions containing different concentrations of C18A5C oil displacement agent were labeled with MOBS-F under the above optimum conditions. The experimental data of the standard solutions are shown in Table 2. The calibration curve was linear from 1.0 to 100.0 μg mL^{-1} with a correlation coefficient of than 0.999, and a detection limit of 0.05 μg mL^{-1}.

3.5 Determination of C18A5C oil displacement agent in real water samples

The concentrations of C18A5C oil displacement agent in real oil-field water samples were measured. Following the steps of each water sample processing described in Section 2.3, the derivatization reactions were carried out. And then, the derivative was determined in accordance with the chromatographic conditions described in Section 2.4. The experimental data of the detections are shown in Table 3. The blank chromatogram of C18A5C oil displacement agent in oil-field water and the derivative chromatogram are shown in Fig. 4. It can be seen from Table 3, that the detected concentration range of C18A5C oil displacement agent in oil-field water samples was 7.26 to 9.58 μg L^{-1}.

Recoveries of this proposed method were investigated by adding standard solutions containing three different concentrations C18A5C oil displacement agent to blank oil-field water. The results are shown in Table 3. The recovery range of C18A5C was 91.8% to 95.6%, indicating that the method has a better accuracy for the determination of C18A5C oil displacement agent in real oil-field water samples. The intra-day precision was examined by measuring samples seven times on one day, and the inter-day precision was examined by the daily measurement of samples over five days. The intra-day and inter-day RSDs were 2.9–3.5% and 3.8–4.3%, respectively. Thus the method was applied to the determination of C18A5C oil displacement agent in real oil-field water samples with satisfactory results.

4 Conclusions

In this paper, a method for the determination of C18A5C oil displacement agent in oil-field water was developed for the first time, involving pre-column derivatization using a novel labeling agent and HPLC with diode-array detection. We demonstrated the validity of our method by using a general HPLC instrument rather than other expensive ones. This method has potential application in the detection of other oil displacement surfactants containing amino groups with its merits of simplicity in pretreatment, rapidity in derivatization, stability of the derivatives and high sensitivity.

Acknowledgements

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