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APPLICATION OF HIGH-SPEED LIQUID CHROMATOGRAPHY TO THE ANALYSIS OF POLYOXYETHYLENE SURFACTANTS AND THEIR DECOMPOSITION PRODUCTS IN INDUSTRIAL PROCESS WATERS

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SUMMARY

Complementary high-speed liquid chromatographic techniques have been combined with infrared spectroscopy for the characterization and analysis of polyoxyethylene fatty acid surfactants and their decomposition products in industrial process waters. The combination of molecular sieve chromatography and infrared spectroscopy offers a selective and simple method for the analysis of trace concentrations (detection limit approx. 0.05–0.1 ppm) of these surfactants. Liquid–solid and reversed-phase chromatography have proven useful for the characterization and analysis of free fatty acids. Some of the parameters that affect the reversed-phase separation of fatty acids are discussed.

INTRODUCTION

Fatty acid esters of polyoxyethylenes (POE), a common class of non-ionic surfactants, are used extensively in industry. In GS heavy water-plants, based on a dual temperature process for the exchange of deuterium between water and hydrogen sulfide, *i.e.* the so-called Girdler-Sulfide process, these surfactants are used in formulations, such as antifoams, that are used to help control processes that affect the hydrogen–deuterium isotopic exchange. Large concentrations of these surfactants and/or their decomposition products (mainly fatty acids) can cause excessive foaming and also decrease oil coalescer efficiency. Consequently, it has been important to have analytical methods for the surfactants and their decomposition products that can be applied to process waters (hydrogen sulfide-saturated water containing large amounts of oil, organosulfur compounds, and other organics), effluent water, and bulk oil.

A wide variety of analytical methods for POE non-ionic surfactants is available and these have been reviewed recently[1]. The analysis of non-ionic surfactants is very difficult[1] and most of the methods developed have been applied only to the analysis of commercial formulations and are not selective enough for the determination of small concentrations in complex matrices. Recent applications of high-speed liquid chromatography (HSLC)[2–7] have illustrated its potential for the characterization of POE surfactants. Both liquid–solid and liquid–liquid systems have been used. For

liquid–solid systems we found irreversible absorption occurred on silica gel and eventually the column changed to a liquid–liquid system. Strong absorption of POE surfactants on silica gel has also been observed elsewhere[4]. For both liquid–solid and liquid–liquid systems a portion of the POE surfactants studied in this work was sterically excluded from the pores of the support causing rapid elution of the large molecules followed by broad tailing peaks. Consequently, these HSLC techniques are not suitable for the analysis of these surfactants. Molecular sieve chromatography (MSC) should not have these problems of steric exclusion and adsorption. However, a problem of sensitive and selective detection still exists since these compounds exhibit no apprecialbe UV adsorption. We felt that a combination of MSC and infrared (IR) spectroscopy might prove suitable for the analysis of these surfactants.

In the presence of heat and acids, fatty acid esters hydrolyze to give free POE and fatty acids. Fatty acids are foaming agents and it is important to be able to follow their concentration with time. Methods for fatty acid analysis can also be used to characterize the fatty acids used for the manufacture of these surfactants, important information which is often not available. The separation of fatty acids by HSLC has been reviewed recently[8]. Most studies have used derivatization to improve UV detection, but direct analysis does offer some advantages[9]. Since our initial studies had indicated that the concentrations of fatty acids were sufficient for refractive index (RI) detection, it was felt that a reversed-phase system could be used for the separation and analysis of fatty acids.

EXPERIMENTAL

Reagents and materials

High-purity solvents were used where possible (Burdick and Jackson, Muskegon, Mich., U.S.A.). All other chemicals were reagent grade except for fatty acid standards, which were high-purity reagents (Chromatographic Specialties, Brockville, Ont., Canada). Two main formulations of fatty acid POE esters were studied in this work, *viz.* MYRJ (mono fatty acid ester), and a mixture of disubstituted fatty acid esters (linoleic, linolelaidic, oleic, and elaidic acids). The molecular sieve columns were standardized with C_5–C_{40} *n*-hydrocarbons (Chromatographic Specialties) and polystyrene and polypropylene standards (Waters Assoc., Milford, Mass., U.S.A.). The molecular sieve packings (15–37 μm) were styrene-divinylbenzene copolymers (Styragel; Waters Assoc.). This small-particle packing (15–37 μm) was slurry packed into 90 cm × 4.8 mm I.D. stainless-steel columns as described previously[10]. The 10 cm × 4.8 mm clean-up column was slurry packed with 20 μm silica gel (LiChrosorb SI-60; Brinkmann, Rexdale, Ont., Canada). A C_{18} μBondapak column (Waters Assoc.) was used for reversed-phase separations.

The liquid chromatographs were custom-built from commercial components and have been described elsewhere[10]. Samples were introduced by syringe injection into a modified sample loop[10]. IR spectra were recorded in microcells (2.5 or 4.5 μl, Perkin-Elmer, Montreal, Quebec, Canada) with a Perkin-Elmer Model 467 spectrophotometer.

Surfactant standardization

Known amounts of the surfactant were added to a mixture of 0.5 ml pump-seal

oil (a C_{25} hydrocarbon oil and the major organic component present in the process water) and 100 ml water. The final concentrations of the surfactant were normally 2, 5, 8, and 10 μg/ml. These mixtures were extracted with 10 ml of chloroform and 3-ml aliquots of the extracts were evaporated to dryness under nitrogen. These residues were separated by MSC and the high-molecular-weight fraction that contained the emulsifier was collected and evaporated to dryness. This fraction was dissolved in carbon tetrachloride (10–50 μl) and the absorption at 1740 cm^{-1} was measured using a IR micro cell.

Fatty acid clean-up

Oil samples and dried extracts from chloroform or methylene chloride extractions from water samples were dissolved in the mobile phase (20% chloroform in hexane, sample volume approx. 2.5 ml) and injected into a 10-ml sample loop. The sample was then washed onto the column at a flow-rate of 7–8 ml/min and the oil and other non-polar components were eluted (10–15 ml wash). Then the sample loop was filled with 10% methanol in chloroform and this was used to elute the fatty acids. The first 5–8 ml of eluate, which contained the acids, were collected and saved for the reversed-phase separation. The column was then reconditioned with approx. 30 ml of the original mobile phase.

RESULTS AND DISCUSSION

Surfactant characterization

Before the analysis results for POE surfactants or their decomposition products can be interpreted sensibly, the chemical composition of the surfactant must be known. Our experience has shown that MSC is valuable for rapid, routine monitoring of surfactant formulations. Total sample analysis is one of its main advantages and since the surfactants are relatively large molecules, any imputiries (normally free POE or fatty acids) present are usually well separated. If desired, fractions are easily obtained for IR spectra to tell if the surfactants are mono- or disubstituted POE (presence or absence of characteristic R–OH frequency for terminal OH group) or if the impurities are mainly POE (OH stretch) and/or fatty acids (C=O stretch and hydrogen bonded OH). Fig. 1 illustrates the usefulness of MSC. The surfactant was autoclaved with hydrogen sulfide to study its decomposition under plant conditions but other acids, such as hydrochloric, could be used if only surfactant characterization is of interest. From this chromatogram the extent of decomposition could be easily determined and IR spectra of peaks A and B showed these components were POE and carboxylic acids, respectively. The acids were further separated by reversed-phase chromatography (see below) and found to be a mixture of linoleic, linolelaidic, oleic, and elaidic acids. All C_{18} acids gave molecular sizes equivalent to C_{23} *n*-hydrocarbons, possibly due to solvation effects. From this information it was possible to reasonably estimate the chemical composition of the surfactant.

Surfactant analysis

The analysis of POE surfactants is complicated by the fact that they contain large numbers of telomers and the distribution of these can vary. Consequently, the

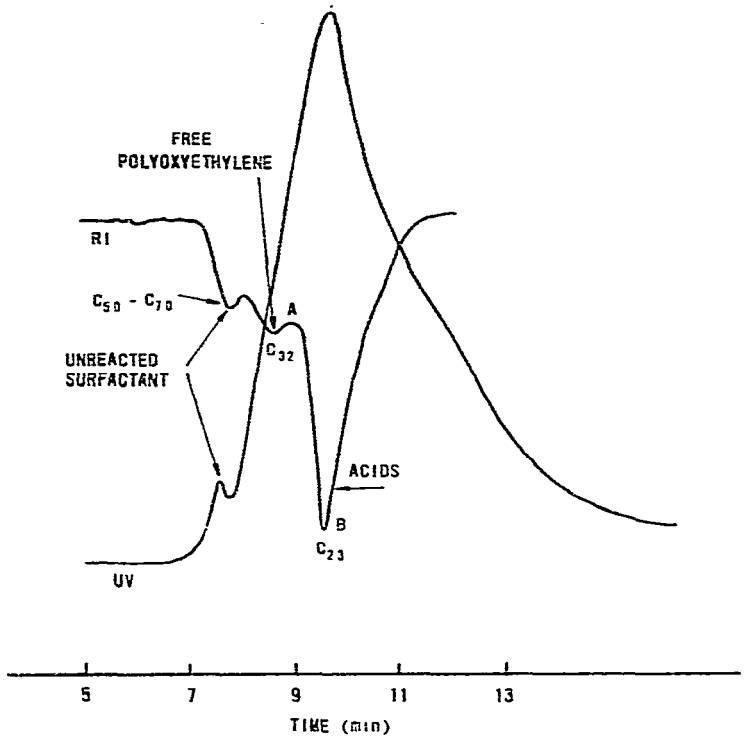

Fig. 1. Molecular sieve separation of surfactant after contact with hydrogen sulfide and water at 150° for 110 h. Experimental conditions: column, 1 m × 4.5 mm I.D. Styragel 100; mobile phase, chloroform; flow-rate, 1 ml/min; sample, 100 μl of approx. 2 mg/ml solution; refractive index and UV detection. Equivalent molecular sizes in terms of *n*-hydrocarbons are indicated on the curves.

choice of a standard is difficult. For this work samples of commercial products were used and their purity was checked by MSC.

MSC has two main attractive features for the preliminary separation of POE surfactants. Firstly, it is not too selective and the majority of the telomers can be collected quickly and in a small volume. Secondly, it quickly separates the high-molecular-weight surfactant molecules from the bulk of the other organics (C_{25} oil in this case). For some samples the ratio of organic to POE surfactant was approx. 3000:1. These features are illustrated in Fig. 2, which is representative of most of the process water samples analyzed. The dotted line shows the position at which the surfactant is eluted.

Due to the poor sensitivity of LC detectors for these fatty acid esters, detection is not possible on the shoulder of the peak due to the other organics, but this fraction can be collected for further analysis. The peak at 15 min is elemental sulfur[10]. For simple and rapid analysis of the surfactant in this fraction it was felt that IR offered the best choice of selectivity and sensitivity. The detection limits were found to be approx. 10 μg for a 100-ml water sample (0.1 ppm) and this could be reduced if larger water samples were extracted. Standard curves were linear and the relative standard deviation for 100-ml, 2-ppm standards, containing 0.5 ml oil, was 10%.

A large number of water and oil samples have been analyzed for POE surfactants and the results are considered satisfactory. Further improvements in reprodu-

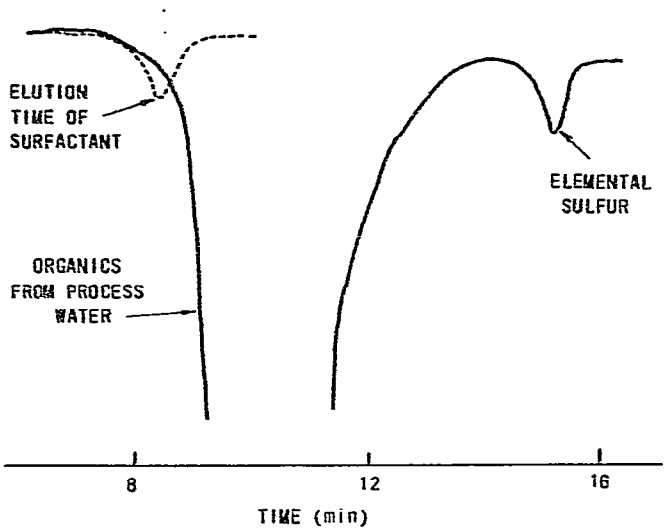

Fig. 2. Molecular sieve separation of surfactant from process water extract. Experimental conditions: column, 1 m × 4.8 mm I.D. Styragel 100; mobile phase, chloroform; flow-rate, 1 ml/min; samples 250 μl (1/4 of total) of extract from 100 ml water; refractive index detection.

ibility are not considered warranted due to the problem of choice of standard. Selectivity is good and the large concentrations of fatty acids (up to 4 mg/ml oil) and free POE do not interfere. Plastic bottles are not recommended for sample storage. Not only can plastic adsorb and/or absorb trace organics but it will also contaminate samples with phthalate plasticizers which can interfere with the analysis of lower-molecular-weight POE surfactants.

If more than one type of POE surfactant is present, then this method will give only semi-quantitative results, unless the molecular weights of the two surfactants are significantly different so as to permit their separation by MSC. Since the fatty acid content of POE surfactants is often different for different formulations, it appears that the best method for the analysis of mixtures might be a combination of MSC clean-up with gas chromatographic analysis of the fatty acids via transesterification.

Fatty acid analysis

Free POE and fatty acids were the two main decomposition products found for POE surfactants under GS process conditions. The concentration of free POE was not of direct interest and the analysis of this component was not studied.

For fatty acid analysis, clean-up on silica gel gave good recoveries (>98%) and reproducibility (relative standard deviation, approx. 1% for 0.7–4 mg/ml oil). Most of the samples studied were bulk oil and for these it is important to wash all the oil off the column prior to elution of the acids. Small volumes of oil in the eluate will extract the acids and cause low results. The effectiveness of the clean-up procedure was reflected by the steady baselines and reproducible retention times for the reversed-phase separation of the acids discussed below.

For the reversed-phase separation of fatty acids (only C_{12}–C_{18} acids were of

interest in this work) the choice of mobile phase was an important factor. With solvents less polar than water, such as acetonitrile or methanol, long retention times and very broad peaks and unreproducible results were observed (Fig. 3a). The addition of small amounts of water gave better results (Fig. 3b) but small concentrations of acetic acid were much more effective (Fig. 3c). Increases in the acetic acid concentration (0.1–0.8%) caused only a slight reduction in capacity factors (k')*. When the series C_3, C_4, C_7, C_9, and C_{10} *n*-carboxylic acids was used in place of acetic acid there was a small increase in k' up to C_9 and then a decrease with C_{10}. When C_9 and C_{10} acids were used as modifiers, they were desorbed on sample injection and observed as peaks in the chromatogram.

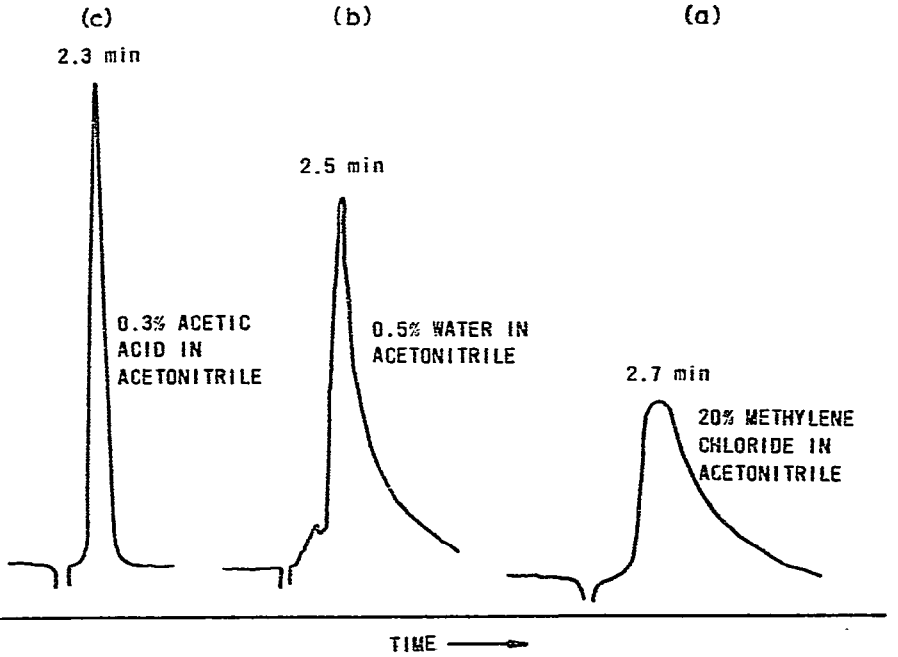

Fig. 3. Effect of polar modifiers on peak symmetry. Experimental conditions: column, 30 cm C_{18} μBondapak; flow-rate, 2.0 ml/min; sample, 100 μl of an approx. 1 mg/ml solution of dodecanoic acid in the mobile phase; refractive index detection.

The mechanism by which these acids improve reproducibility and peak symmetry is not completely understood. Deactivation of free silanol groups on the reversed-phase packing is not likely important since with the solvent used, fatty acids are eluted at the solvent front on silica gel columns and peak symmetry is good. Deactivation of impurities introduced during the preparation of the packing[11] could play a role but the importance of this is uncertain. Carboxylic acids form dimers and this type of interaction between the acid modifier and sample could be important. This interaction would cause a reduction in k' and explain the increase in k' with

* k' = (peak retention time − inert peak retention time)/ (inert peak retention time).

chain length of the acid modifier. The maximum in k' at C_9 is likely a result of overloading of the support with modifiers larger than C_9.

The effect of basic modifiers was examined briefly. Pyridine, a weak base, gave only slight improvements. Diethylamine, a much stronger base, gave symmetrical peaks but reduced k' to approx. 0 for all components of interest.

Various mixtures of acetonitrile or methanol with methylene chloride and/or water were examined as mobile phases. The best solvent system was a mixture of methanol (major component) with methylene chloride and water plus 0.1–0.3% acetic acid. This was a better solvent for the fatty acids than acetonitrile-based solvents. The k' of the acids was easily controlled through variations in the water and methanol content. Fig. 4 shows the separation of four acids with one of the solvent systems used. With this mixed solvent system evaporation in the solvent reservoir caused small changes in solvent composition and baseline shift was severe unless a long narrow reservoir was used.

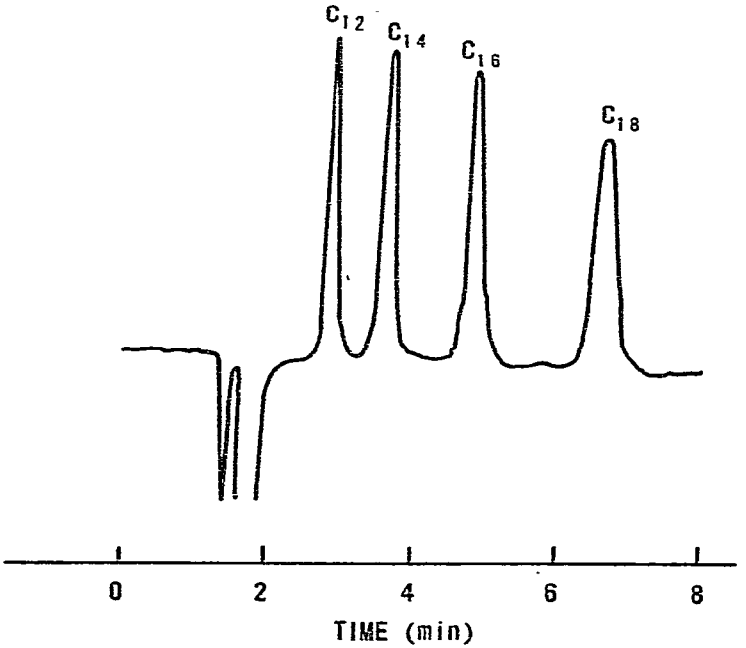

Fig. 4. Reversed-phase separation of straight-chain saturated fatty acids. Experimental conditions: column, 30 cm C_{18} μBondapak; flow-rate, 2.0 ml/min; mobile phase, 68% methanol, 16% methylene chloride, 16% water, 0.2% acetic acid; sample, 100 μl of approx. 1 mg/ml solution of fatty acids; refractive index detection.

The combination of liquid–solid clean-up and reversed-phase analysis of fatty acids has proven valuable for monitoring fatty acid concentration changes which are related to changes in POE surfactant formulations and for the identification of the fatty acids obtained when the surfactants are hydrolyzed. Fig. 5 shows the separation of the decomposition products from one of the surfactants studied. For this surfactant the HSLC identification of linolelaidic and elaidic acids, the *trans* isomers of linoleic and oleic acids, respectively, was more definitive than were mass spectrometric results.

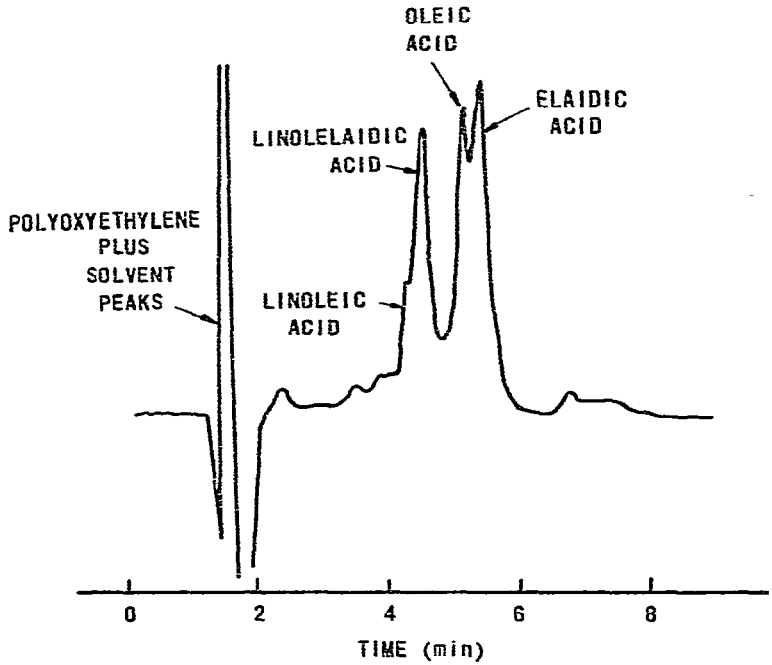

Fig. 5. Reversed-phase separation of surfactant after contact with hydrogen sulfide and water at 150° for 110 h. Experimental conditions, as for Fig. 4.

CONCLUSIONS

A combination of HSLC techniques and IR spectroscopy offers rapid and selective methods for the routine monitoring of POE fatty acid surfactants and free fatty acids in industrial process waters. These techniques can also be used to characterize unknown POE surfactants.

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