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ANALYTICAL STUDY OF NON-IONIC SURFACTANTS USED IN ENHANCED OIL RECOVERY

OPTIMIZATION OF ANALYTICAL CONDITIONS IN REVERSED-PHASE PARTITION CHROMATOGRAPHY

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SUMMARY

The analysis of non-ionic polyoxyethylenic surfactants used in enhanced oil recovery was investigated by reversed-phase partition chromatography with UV detection. A systematic comparative survey of commercially available non-polar stationary phases (C_{18}, C_8, C_6, C_4, C_2, phenyl, cyano and diol) is presented. Various solvents miscible with water (methanol, acetonitrile, tetrahydrofuran, dioxane, acetone and 2-propanol) were tested as mobile phases. A good evaluation of the distribution *versus* the number of ethylene oxide groups in these surfactants was obtained with alkyl-bonded silica (C_{18} and C_8) by isocratic elution with tetrahydrofuran or acetonitrile as solvent additives. Peaks were identified by the simultaneous elution of pure standards.

INTRODUCTION

Various chromatographic methods have been proposed for the analysis of polyoxyethylenic surfactants similar to those used in enhanced oil recovery. Most of the studies have been performed by normal-phase high-performance liquid chromatography (HPLC). The literature[1–5] suggests that adsorption chromatography will not give a satisfactory analysis of surfactants that have a wide distribution of polyoxyethylene oxide units. The only HPLC technique that appears to offer promise for the analysis of surfactants in terms of their ethylene oxide distribution is normal-phase partition chromatography using amino-bonded silica[6–9], cyano-bonded material[10–13] and, more recently, diol-bonded packings[14–16]. In particular, we have previously reported the analysis of non-ionic surfactants (KL 6, KM 11 and KM 20) containing ethylene oxide units of various lengths condensed with long-chain (C_{16} and C_{18})

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aliphatic alcohols via normal-phase partition chromatography on diol-bonded silica[16,17]. The mean lengths of the polyoxyethylene chains in these compounds are 6.2, 11.4 and 19.8 ethylene oxide units (E.O.), respectively, according to the standard method AFNOR NFT 73403 (cloud point measure)[18]. These values are rounded off by the manufacturer to 6, 11 and 20 E.O., respectively. It is interesting that these values are in good agreement with the mean lengths of polyoxyethylene chain deduced from ^{1}H NMR measurements[19]. These complex mixtures also contain 2–3% of polyoxyethyleneglycol (PEG), determinated by the Weibull method[20,21]. They are finally characterized by the presence of various fatty alcohol chains that we have analysed by gas chromatography (GC) after cleavage in the presence of hydrobromic acid[22]. For KM 11 and KM 20, the repartition of fatty alcohol chains is saturated C_{16} chains 30% and saturated C_{18} chains 70%, and for KL 6 saturated C_{16} chains 30%, saturated C_{18} chains 35% and unsaturated C_{18} chains 35%.

We have previously analysed these surfactants in *n*-decane, as a model of a petroleum phase, and in brine[17]. In order to perform the analysis of these surfactants in crude oil phases, a specific and sensitive detection method, such as electrochemical detection, is required. As this detection method is difficult to carry out in normal-phase partition chromatography, we considered reversed-phase partition chromatography, already used in surfactant studies.

Non-ionic surfactants, such as phenyl derivatives of polyoxyethylene glycols[23,24] and ethylene oxide condensates with fatty alcohols[7,23,25–28], have been studied by reversed-phase partition chromatography. Various bonded alkyl silicas (C_2, C_8 and C_{18}) and various polar mobile phases (mainly methanol) have been used in isocratic elution[23,26,27] and gradient elution[25,29,30]. Previous work on the analysis of polyoxyethylene condensates of fatty alcohols showed that it was impossible to study the distribution of polyoxyethylene chains *versus* the ethylene oxide number with C_8 or C_{18} bonded silica and an aqueous methanol mobile phase[7,23,28]. Under these conditions, the separation obtained was a function of fatty chain length. The separation as a function of the number of ethylene oxide units was possible on C_2 bonded silica with acetonitrile as a solvent additive, provided that there was only one fatty alcohol chain[27]. We have found only one reference concerning the study of the distribution of polyoxyethylene chains in a mixture of surfactants obtained from C_{12} and C_{16} fatty alcohols[25]. A C_{18} bonded silica stationary phase was used, and the analysis was performed by gradient elution with water–methanol. Unfortunately, the overlap of the two distributions (corresponding to C_{12} and C_{16} alkyl chains) was too great and the interpretation of these distributions was difficult.

In order to obtain the distribution of polyoxyethylene chains in KL 6, KM 11 and KM 20 surfactants with both C_{16} and C_{18} fatty alcohol chains (and also an unsaturated C_{18} chain in KL 6), we have optimized the analysis. We tested the commercially available stationary phases used in reversed-phase partition chromatography (C_2, C_4, C_6, C_8, C_{18}, phenyl, cyano and diol) and various aqueous-organic mobile phases [methanol, tetrahydrofuran (THF), acetonitrile, dioxane, 2-propanol and acetone].

EXPERIMENTAL

Materials

The apparatus consisted of a PU 4003 dual-piston pump and associated controller (Philips Analytical, Cambridge, U.K.), a Model 7010 injector with a 10–100-μl sample loop (Rheodyne, Cotati, CA, U.S.A.) and a PU 4025 UV–VIS detector (Philips Analytical). The signal from the detector was displayed on a Kipp & Zonen (Delft, The Netherlands) recorder. A Hewlett-Packard (Palo Alto, CA, U.S.A.) terminal 1, level 4 integrator from an HP 5880A gas chromatograph was used to handle the data. A Gilson (Villiers-le-Bel, France) Model 202 fraction collector and an R 401 refractometric detector (Waters Assoc., Milford, MA, U.S.A.) were added to the system in order to prepare standards with various polyoxyethylene chain lengths.

The eight columns tested had the same inside diameter (4.6 mm) but different lengths. The 5-μm Nucleosil C_4 column (SFCC, Gagny, France) was 100 mm long, the 5-μm Nucleosil C_6 (SFCC), the 5-μm Ultraspher C_{18} (Beckman, Fullerton, CA, U.S.A.) and the 7-μm Nucleosil CN columns (the last was packed in our laboratory by the method reported by Coq *et al.*[31]) were 150 mm long and the 5-μm Nucleosil phenyl (SFCC), 7-μm LiChrospher diol (Merck, Darmstadt, F.R.G.), 5-μm Nucleosil C_8 and 5-μm LiChrosorb C_2 columns (the last two were packed in our laboratory by the Rocca method[31]) were 250 mm long.

All the organic solvents were of HPLC grade from Merck (Darmstadt, F.R.G.), BDH (Poole, U.K.), SDS (Ivry, France) and Prolabo (Paris, France). The water was made using Milli-Q and Milli-Ro systems (Millipore, Molsheim, France). The surfactant standards with six ethylene oxide units and either a C_{16} or a C_{18} moiety were purchased from Nikko Chemicals (Tokyo, Japan). The surfactants studied (KL 6, KM 11 and KM 20, from Marchon France, Saint Mihiel, France) were of technical grade; their characteristics are given in Table I. 3,5-Dinitrobenzoyl chloride (DNB) (RP grade) derivatization reagent was purchased from Prolabo.

An HP 5880A gas chromatograph (Hewlett-Packard) fitted with a 25 m × 0.25 mm I.D. CP Sil5 capillary column (Chrompack France, Les Ulis, France) was used for the determination of fatty alcohol chains in the different non-ionic surfactants.

TABLE I
CHARACTERISTICS OF THE THREE SURFACTANTS ANALYSED

Characteristic	*KL 6*	*KM 11*	*KM 20*
Mean number of E.O. units:			
According to AFNOR standard[18]	6.2	11.4	19.8
According to NMR[19]	6.4	12.1	19.0
PEG content* (%)	2.4	2.5	3.0
Repartition of fatty alcohol chains (%)**			
Saturated C_{16}	30 ± 2	30 ± 2	30 ± 2
Saturated C_{18}	35 ± 2	70 ± 2	70 ± 2
Unsaturated C_{18}	35 ± 2	–	–

* Determined by means of the Weibull method[20].

** PEG = polyethylene glycol; determined by GC analysis after treatement with hydrobromic acid–acetic acid[22].

Measures of molar absorptivity of the standards obtained by semi-preparative HPLC (after derivatization to the esters with DNB) were performed using an HP 8450A UV–VIS spectrophotometer (Hewlett-Packard).

Method

The water present in each sample was removed by Dean and Stark azeotropic distillation[32] with benzene. DNB was added in a stoichiometric amount, together with magnesium shavings to remove hydrochloric acid formed in the reaction. KL 6 and KM 11 required refluxing for 30 min; KM 20 required 1 h. After refluxing, the solution was cooled and filtered and the benzene was evaporated. The resulting ester was suitable for analysis by HPLC without further preparation.

The standards of polyethoxylated alcohols containing a fixed number of ethylene oxide units were obtained after semi-preparative separations of KM 11 components (derivatized to DNB esters) by normal-phase HPLC with diol-bonded silica using the previously described conditions[16].

RESULTS AND DISCUSSION

Two of the surfactants (KM 11 and KM 20) have no chromophoric group and cannot be detected by UV methods. We therefore derivatized the surfactants with DNB by the method of Nozawa and Ohnuma[27] to obtain absorption at 254 nm. Although KL 6 has a chromophoric group (unsaturation), it was also derivatized. We have verified with standards obtained from KM 11 by semi-preparative HPLC that, regardless of the polyoxyethylene chain length, and within experimental error, the molar absorptivity is constant ($\varepsilon_{254} = 8100$). This result is in agreement with those obtained by Ahel and Giger[9] for polyoxyethylated alkylphenols.

In order to optimize the separation of the polyoxyethylene chains of the surfactants, we undertook a comparative study of various available reversed-phase columns.

Whatever the bonded silica considered (diol, cyano or phenyl) and regardless of the nature of the added solvents (methanol, THF, acetonitrile, acetone, 2-propanol), these systems were not sufficiently selective and did not allow an acceptable resolution. This was particularly true with the diol and cyano phases, where no separation was observed as a function of number of ethylene oxide units. The phenyl phase was the most selective of the three moderately polar phases tested, but its resolution was still insufficient and did not allow the analysis of the surfactants as a function of number of ethylene oxide units.

From the literature data, the C_2 stationary phase appeared, among the commercial alkyl phases, to be the most promising[27]. Therefore, we first tested the efficiency of this phase. With different solvent additives (THF, mixtures of THF and 2-propanol and, mainly, acetonitrile), the chromatograms showed a better resolution of the most polar compounds in the complex mixtures analysed than the chromatograms obtained with the preceding phases of intermediate polarity. However, regardless of the nature of the mobile phase, their resolution was still insufficient.

For all non-ionic surfactants analyzed (KL 6, KM 11 and KM 20), the C_4 bonded silica, which is, in theory, more apolar than the preceding one, did not give improved resolution. Among the solvent additives, acetonitrile gave the best selectivity.

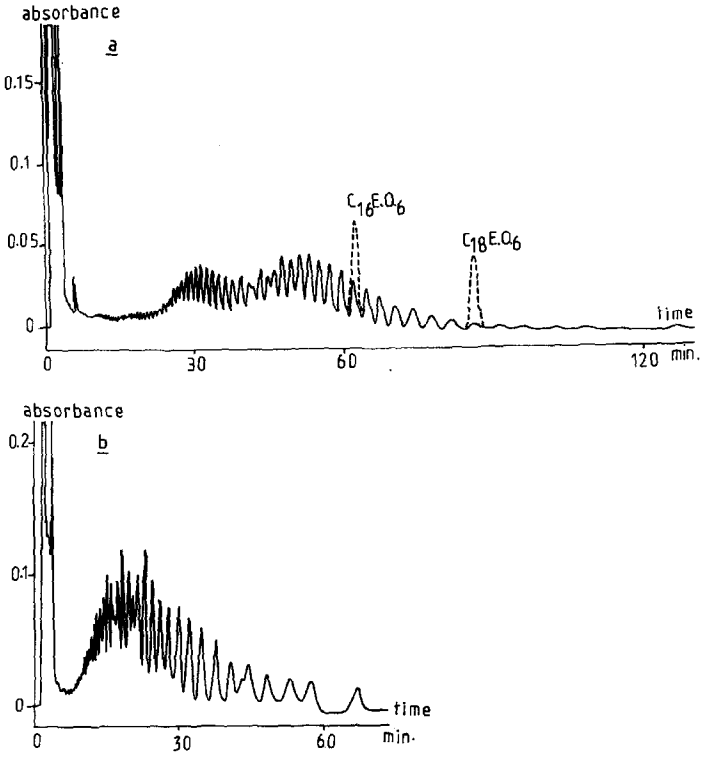

Fig 1. Chromatograms of non-ionic surfactants, derivatized with DNB, obtained with a C_6 stationary phase (Nucleosil C_6, d_p = 5 μm). Column, 15 × 0.46 cm I.D.; mobile phase, acetonitrile–water (60:40) or acetone–water (65:35); flow-rate, 1 ml/min; detection wavelength, 254 nm with acetonitrile and 340 nm with acetone as solvent additive. (a) KM 20 ester; (b) KM 11 ester.

With the more apolar C_6 bonded silica it was impossible to obtain a separation of the polyoxyethylene chains when methanol was used as the solvent additive, but the other additives (THF, acetone and acetonitrile) allowed a more or less satisfactory resolution, depending on the nature of the surfactant being analysed. Using acetonitrile or acetone as solvent additives, this stationary phase allowed an acceptable resolution of KM 20 (Fig. 1a). In fact, we observed under these conditions two distinct series of peaks. The first series, having the smallest capacity factor, corresponded to the polyoxyethylene chains condensed on a C_{16} fatty alcohol. The second series, which was observed at a higher elution volume, corresponded to the ethylene oxide condensates with a C_{18} fatty alcohol. The simultaneous elution of two standards, each with a polyoxyethylene chain of 6 units and with a C_{16} and a C_{18} fatty chain, showed that there was a shift of 7 ethylene oxide units between the two series. Unfortunately, the C_6 phase, which gave an acceptable analysis for surfactants with high ethylene oxide numbers (such as KM 20), was less suitable for the analysis of surfactants with shorter polyoxyethylene chains, such as KM 11 (Fig. 1b). These encouraging results led us to study more lipophilic stationary phases.

We also studied the influence of the solvent additives on selectivity and resolution with C_8 bonded silica. In agreement with literature data[7,23], methanol did

not allow a separation with respect to number of ethylene oxide units, but fatty alcohol chains were separated. Using dioxane, resolution as a function of the number of ethylene oxide units was not achieved. The other solvent additives (THF, THF–2-propanol, acetone, acetonitrile) gave a satisfactory resolution of KM 20 and KM 11. The addition of 2-propanol to THF did not modify the selectivity. Acetonitrile gave the best selectivity, as with C_2 and C_6 stationary phases, and allowed separation. As with the C_6 bonded silica, the presence of two series of peaks indicated of a further separation of the aliphatic chains. In order to obtain a correct determination of the number of ethylene oxide units for each peak, we performed the simultaneous elution of standard samples. The distance between the two alkyl chains, for the same number of ethylene oxide units, was 8 E.O. This shift was sufficient to allow the study of the distribution of KM 11 and KM 20 *versus* the number of ethylene oxide units. The relative abundances of the C_{16} and C_{18} fatty chains was known (30% and 70%, respectively; see Experimental), so it was possible to quantify the distributions by correcting for the partial overlap. The mean value of the number of ethylene oxide units ($\bar{n}$) could therefore be calculated for each surfactant. In fact, the plots of log k' *versus* n E.O for each fatty chain (C_{16} or C_{18}) are linear and parallel. Because of the peak broadening when the elution time increased and the partial overlapping of the two series of peaks, the chromatograms such as those given in Fig. 1 (KM 11 and KM 20) gave a distorted representation of the distribution of these surfactants as a function of their number of ethylene oxide units. To avoid these distorsions, we give the histograms of the distribution of KM 11 and KM 20 in Figs. 2 and 3. These histograms are easily obtained from the integration of chromatographic peaks, the molar absorptivity being constant, as mentioned above, regardless of the polyoxyethylene chain length. Therefore, all further chromatograms of the surfactants are presented in the form of histograms. The mean length of the polyoxyethylene chains was easily deduced from the histograms or was calculated. The following values were found: $\bar{n}_{exp.} = 12.9$ E.O. for KM 11 and $\bar{n}_{exp.} = 18.3$ E.O. for KM 20.

For KL 6, the selectivity obtained with this phase was not sufficient with THF or acetonitrile to allow the study of its distribution *versus* the number of ethylene oxide units. This important difference in chromatographic behaviour resulted from the greater complexity of the KL 6. This surfactant was obtained by condensing ethylene oxide on fatty alcohols with C_{16}, C_{18} and unsaturated C_{18} chains (see Experimental). The three series of distributions were not sufficiently separated to allow meaningful

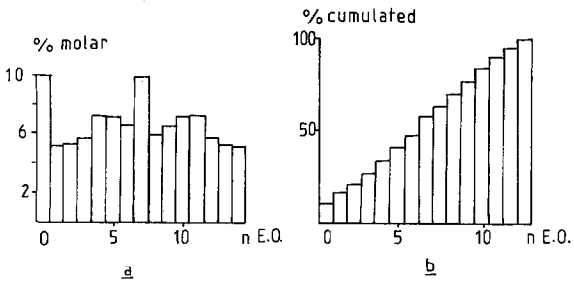

Fig. 2. Distribution histograms of KM 11 determined from the chromatographic data obtained with a C_8 stationary phase (Nucleosil C_8). Mobile phase, acetonitrile–water (60:40); flow-rate, 1 ml/min; detection wavelength, 254 nm. (a) Retention as a function of E.O.; (b) cumulated retention as a function of E.O.

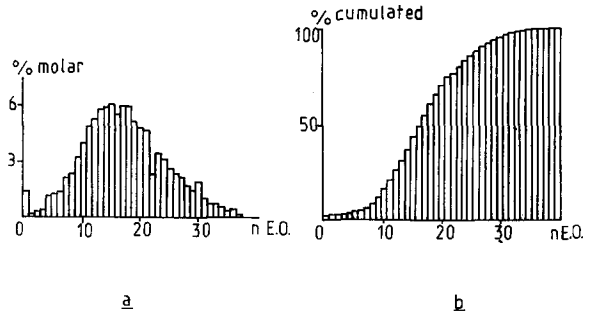

Fig. 3. Distribution histograms of KM 20 determined from the chromatographic data obtained with a C_8 stationary phase. Conditions as in Fig. 2.

corrections for overlapping peaks. In order to obtain the evaluation of the mean length of the polyoxyethylene chain of KL6, we used a more lipophilic phase.

C_{18} bonded silica allowed a good separation with KM 11 and KM 20 using acetonitrile, THF or acetone as solvent additive. No resolution was obtained using dioxane. In good agreement with literature data[25–28], methanol gave only a separation of the fatty chains. The study of the distributions of KM 11 and KM 20, as a function of their number of ethylene oxide units, with this stationary phase was performed using an acetonitrile–water mobile phase. The distance between the two alkyl chains, for the same number of ethylene oxide units, was 12 E.O. This greater selectivity allowed a better precision in the determination of ethylene oxide distributions because peak overlapping was less of a problem. The mean values of the number of ethylene oxide units are $\bar{n}_{exp}$ = 12.3 E.O. for KM 11 and $\bar{n}_{exp}$ = 18.5 E.O. for KM 20. Of course, this greater selectivity was obtained with a longer time of analysis. For KL 6, the association of acetonitrile as solvent additive with a C_{18} stationary phase allowed for the first time an almost acceptable resolution. The overlapping of the three series of peaks, corresponding to the three different fatty alcohol chain, was still complex but it was possible to obtain an evaluation of the distribution. We assumed that the ethylene oxide repartition was symmetrical. From the integration of the ten first peaks, a relatively satisfactory value was obtained (Fig 4.): $\bar{n}_{exp}$ = 6.6 E.O. for KL 6.

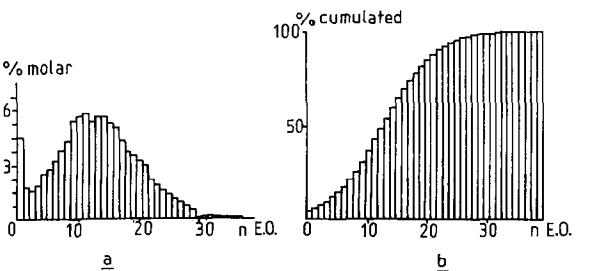

Fig. 4. Distribution histograms of KL 6 determined from the chromatographic data obtained with a C_{18} stationary phase (Ultraspher C_{18}). Mobile phase, acetonitrile–water (75:25); flow-rate, 1 ml/min; detection wavelength, 254 nm. (a) Retention as a function of E.O.; (b) cumulated retention as a function of E.O.

CONCLUSION

From this comparative survey of the various bonded phases available in reversed-phase partition chromatography, it appeared that only alkyl-bonded phases allowed the analysis of the distributions of ethylene oxide condensates of fatty alcohol mixtures as a function of the number of ethylene oxide units and alkyl chain lengths.

Methanol did not give a separation with respect to the number of ethylene oxide units. With this solvent additive, only fatty chains were separated. Dioxane did not allow a separation as a function of the number of ethylene oxide units, regardless of the nature of the alkyl-bonded silica (C_8 or C_{18}). Only three solvents, acetonitrile, THF and, to a lesser extent, acetone, gave the possibility of adapting the selectivity in order to obtain a satisfactory resolution of the non-ionic surfactants used in enhanced oil recovery as a function of their number of ethylene oxide units.

The C_{18} stationary phase gave the best performances, allowing a correct analysis regardless of the mean length of the polyoxyethylene chain. Unfortunately, this stationary phase, which gave the best selectivity, was characterized by long times of analysis.

The C_8 bonded phase afforded slightly shorter times of analysis and a satisfactory analysis of the two surfactants with longer polyoxyethylene chains (KM 11 and KM 20). For KL 6, the overlap of the three distributions did not allow the precise determination of the mean number of ethylene oxide units, but a global quantification was possible.

The selected systems, *i.e.*, C_8 or C_{18} bonded silica and THF–water or acetonitrile–water mobile phases, have been examined according to their compatibility with electrochemical detection in a further study which will be reported later[33].

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