

CHROMSYMP. 1551

## POLAROGRAPHIC DETECTION OF NON-IONIC SURFACTANTS ANALYZED BY REVERSED-PHASE PARTITION CHROMATOGRAPHY

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### SUMMARY

The analysis of non-ionic polyoxyethylene surfactants used in enhanced oil recovery was performed by reversed-phase partition chromatography with polarographic detection after derivatization using 3,5-dinitrobenzoyl chloride. The optimization of the electrochemical detection was studied by varying the different parameters (organic solvent, supporting salt and reduction potential). Determinations were performed by chromatography on a Nucleosil C<sub>8</sub> column with acetonitrile–water (3:2) as the eluent containing 0.01 M (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NClO<sub>4</sub> as the supporting salt, at –1 V<sub>vs.</sub> Ag/AgCl in the direct current mode or at –0.8 V<sub>vs.</sub> Ag/AgCl in the differential pulse mode which improved the sensitivity. With polarographic detection, which is 50 times more sensitive than ultraviolet detection, surfactants can be reliably measured in the range of 10 to 1000 ppm.

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### INTRODUCTION

We have previously analyzed non-ionic polyoxyethylene surfactants used in enhanced oil recovery by reversed-phase partition chromatography and UV detection<sup>1</sup>. The non-ionic surfactants were obtained by condensation of a mixture of natural C<sub>16</sub> and C<sub>18</sub> fatty alcohols with ethylene oxide. The mean lengths of the polyoxyethylene chains are 6, 11 and 20 ethylene oxide units for the surfactants KL 6, KM 11 and KM 20 respectively. In order to analyze these surfactants in crude oil phases, a specific and sensitive detection method, such as electrochemical detection<sup>2</sup>, is required. This paper describes the optimization of the electrochemical detection of non-ionic surfactants, achieved with a polarographic detector, and compares its performance with that of an UV detector.

## EXPERIMENTAL

*Reagents*

Acetonitrile was obtained from Prolabo (Paris, France) and tetrahydrofuran (THF) from BDH Chemicals (Poole, U.K.); both were high-performance liquid chromatography (HPLC) grade. The water was purified in a Milli RO and Millie Q system. Different mixtures of organic solvent and water, containing 0.01 *M* of a supporting salt, NaClO<sub>4</sub> or (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NClO<sub>4</sub> (Fluka, Buchs, Switzerland), were used as the mobile phases. They were vacuum-filtered through a 0.45- $\mu$ m Millipore HA filter (Millipore, Molsheim, France) prior to use. Continuous deoxygenation of the solvent reservoir was accomplished by purging with argon. The surfactant standards with six ethylene oxide units and either a C<sub>16</sub> or a C<sub>18</sub> moiety were obtained from Nikko (Tokyo, Japan). The surfactants studied, KL 6, KM 11, KM 20 and S 385 (of technical grade), were provided by Marchon France (Saint Mihiel, France) and the Institut Francais du Pétrole. The derivatization with the 3,5-dinitrobenzoyl chloride (Prolabo, RP grade) has been described elsewhere<sup>3</sup>.

*Instrumentation*

The chromatographic separation was performed on a 250 mm  $\times$  4.6 mm I.D. column packed in our laboratory with 5- $\mu$ m C<sub>8</sub> bonded silica (Nucleosil; Macherey-Nagel, Düren, F.R.G.) using the method reported by Coq *et al.*<sup>4</sup>. The 6000 A pump (Waters, Milford, MA, U.S.A.) was connected to two pulse dampers (Touzart et Matignon, Ivry, France). The mobile phase flow-rate varied from 1 to 1.5 ml/min. The injector, Model 7010 (Rheodyne, Cotati, CA, U.S.A.), was equipped with a 20- $\mu$ l sample injection loop. Detection at a dropping mercury electrode was accomplished with an EGG PAR Model 310 polarographic detector (EG/G Princeton Applied Research, Princeton, NJ, U.S.A.), which incorporated an Ag/AgCl reference electrode and a platinum auxiliary electrode. A drop size providing both sensitivity and reproducibility was selected. The 310 electrode was equipped with an argon inlet in order to deoxygenate the detection cell.

For current-potential (*i*-*E*) curves the "circulation" cell was replaced by a normal cell. The EGG PAR Model 364 potentiostat was employed in both voltammetry and detection experiments. The IFELEC IF 3802 recorder (Chauvin Arnoux, Paris, France) was used in the XY mode for polarograms and in the XT mode to obtain chromatograms.

In order to compare polarographic detection with UV detection, a Philips PU 4025 UV-VIS detector (Philips Analytical, Cambridge, U.K.) was inserted before the 310 electrode, and its signal was recorded on a recorder (Kipp & Zonen, Delft, The Netherlands).

## RESULTS AND DISCUSSION

The chromatographic analysis using isocratic elution requires *ca.* 2 h. In order to gain time, various parameters (nature and electroactivity range of the medium, electrode material) were studied by means of voltammetry.

Electrochemical detection requires the use of conducting media that offer a wide electroactivity range. Acetonitrile-water and THF-water mixtures which ap-

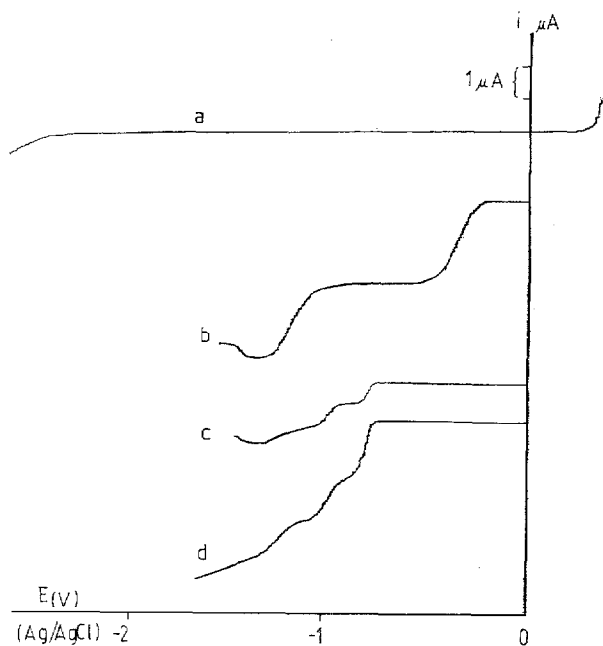


Fig. 1. Polarograms obtained in acetonitrile–water (1:1) + 0.01 M  $(C_4H_9)_4NClO_4$  with a potential scan rate of 5 mV/s in the SDC mode. (a) Supporting salt only; (b) 3,5-dinitrobenzoyl chloride; (c) derivatized standard (6 ethylene oxide units,  $C_{16}$  chain); (d) derivatized surfactant KM 20.

peared to be the best mobile phases for the reversed-phase partition chromatography of the surfactants studied<sup>1</sup> showed an electroactivity range from  $-1$  to  $-1.5$  V vs.  $Ag/Ag^+$  when using a glassy carbon electrode and 0.01 M  $NaClO_4$  or  $(C_4H_9)_4NClO_4$  as the supporting salt. The electroactivity range can be extended to  $-2.2$  V vs.  $Ag/AgCl$  when using a dropping mercury electrode in the presence of  $(C_4H_9)_4NClO_4$  (Fig. 1a). The polyoxyethylene surfactants KL 6, KM 11 and KM 20 as well as the ionic surfactant S 385 (which can be encountered in the media studied) do not show any oxidation wave on glassy carbon nor a reduction wave on mercury. This was not surprising, because the polyoxyethylene surfactants KM 11 and KM 20 possess only saturated  $C_{16}$  and  $C_{18}$  chains. The surfactant KL 6 also has an unsaturated  $C_{18}$  chain, while the ionic S 385 results from the sulphonation of a petroleum fraction, so they are also inactive. Consequently it appeared necessary to introduce an electroactive group in order to detect the surfactants electrochemically<sup>5,6</sup>. The introduction of nitro groups was accomplished by esterification of the alcohol function of the polyoxyethylene chain with 3,5-dinitrobenzoyl chloride. Derivatized surfactants showed a series of reduction waves for the standards (Fig. 1c) and for the samples (Fig. 1d), while the derivatization reagent was reduced more easily (Fig. 1b). The waves appeared more distinct in acetonitrile than in THF. Because electrochemical detection seemed more difficult on glassy carbon than on a mercury electrode, we chose a polarographic detector, although the detection in the reduction mode requires the elimination of oxygen from the medium. Although the potential reduction could be

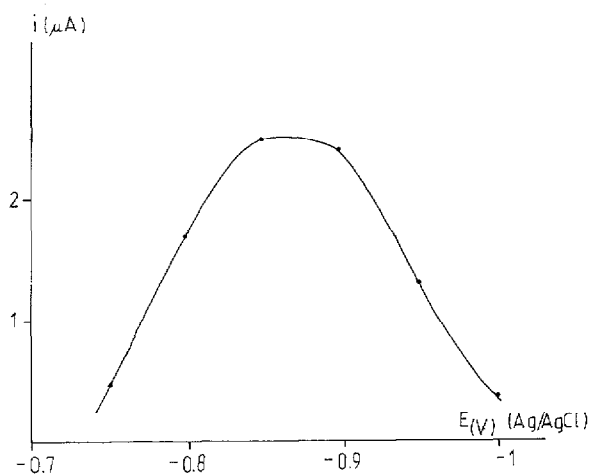


Fig. 2. Hydrodynamic polarogram of the derivatized standard (6 ethylene oxide units,  $C_{16}$  chain), obtained in the SDC mode. Chromatographic conditions: mobile phase, acetonitrile–water (3:2); flow-rate, 1.5 ml/min; column,  $C_8$  Nucleosil (25 cm  $\times$  0.46 cm,  $d_p = 5 \mu\text{m}$ ); injected volume, 20  $\mu\text{l}$ ; concentration, 100 ppm.

approximated from the  $i$ - $E$  curves, it had to be optimized under the same hydrodynamic conditions.

The polarographic detector was tested in aqueous acetonitrile and THF with percentages of the organic solvent not exceeding 65% because above this value the detector underwent deterioration. This implicated the use of a  $C_8$  column, which is less retentive than a  $C_{16}$  column. The salt  $(C_4H_9)_4NClO_4$  was preferred as supporting electrolyte to  $NaClO_4$ , which rapidly altered the performance of the column packing.

The EGG PAR potentiostat offered four modes of measuring current intensity, only two of which are of interest for electrochemical detection: sampled direct current (SDC) and differential pulse (DP). As the analysis of the surfactants requires *ca.* 2 h, optimization of the detection was performed with an esterified standard having six ethylene oxides and a  $C_{18}$  chain. The hydrodynamic polarogram of this compound obtained in acetonitrile–water is shown in Fig. 2. As the noise increases when the

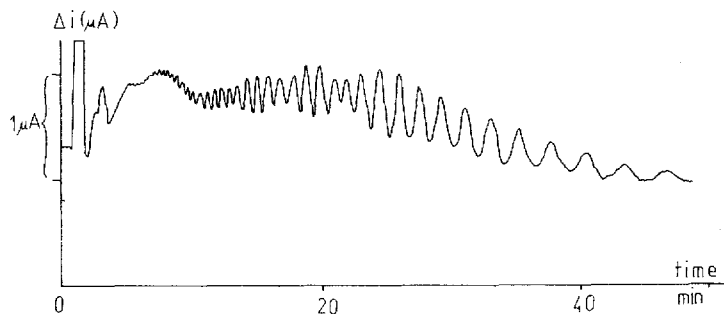


Fig. 3. Chromatogram of the derivatized surfactant KM 20, obtained in the SDC mode. Chromatographic conditions: as in Fig. 2, except flow-rate 1 ml/min, concentration 1000 ppm and detection potential  $-0.85$  V vs. Ag/AgCl.

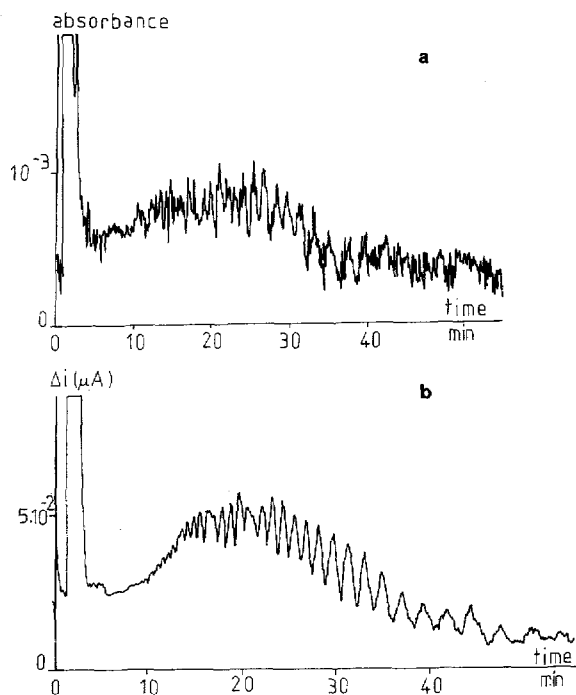


Fig. 4. Chromatograms of the derivatized surfactant KM 20: (a) polarographic detection (DP mode) potential  $-0.76$  V vs. Ag/AgCl; (b) UV detection wavelength, 254 nm. Chromatographic conditions: as in Fig. 2.

potential becomes more negative,  $-0.85$  V vs. Ag/AgCl was used for the detection in SDC mode. Under analogous conditions, a signal ten times less intense was recorded when acetonitrile was replaced by THF. This can be attributed to the weaker dielectric constant of this solvent (7.4) compared to that of acetonitrile (38.0). In the DP mode the optimum potential was  $-0.76$  V vs. Ag/AgCl, and the sensitivity was increased by a factor of ten. The surfactants analysis under the previously established conditions led to satisfactory chromatograms, as shown in Fig. 3. The presence of an ionic surfactant (S 385) and/or inorganic ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ) in the mixtures used for enhanced oil recovery did not change the appearance of this chromatogram, these species being electroinactive at the detection potential employed.

The performance of the polarographic detector in quantitative analysis was tested and compared to that of an UV detector, mounted in series before the Model 310 electrode. The dynamic ranges of the two detectors were initially established with the esterified standard (6 ethylene oxide units,  $\text{C}_{16}$  chain). The linear dynamic range extended from 0.5 to 100 ppm for the polarographic detector used in DP mode and from 5 to 10 000 ppm for the UV detector. The Model 310 electrode appeared more sensitive than the UV detector, having an absolute detection limit of 0.1 ppm compared to 1 ppm at a signal-to-noise ratio of 2.0, but it was saturated for concentrations exceeding 500 ppm.

For the surfactants studied the linear range extended from 10 to 1000 ppm, the detection limit of the polarographic detector being 10 ppm, while the UV detector

offered a linear dynamic range from 1000 to 10 000 ppm and a detection limit of 500 ppm.

In conclusion, polarographic detection is superior to UV detection in trace analysis of the surfactants KL 6, KM 11 and KM 20 (Fig. 4). Moreover, it can be used with complex mixtures, absorbing in the UV range, particularly, in the petroleum phases which we are now considering.

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