

CHROM. 16,695

Note

Improved high-performance liquid chromatographic analysis of anionic surfactants by derivatization

MEGUMU KUDOH* and KAZURO TSUJI

Wakayama Research Laboratories, KAO corporation, 1334 Minato, Wakayama-shi, 640 (Japan)

(Received February 28th, 1984)

Since most anionic surfactants have no specific ultraviolet-absorbing functional groups, their simple and sensitive analysis by high-performance liquid chromatography (HPLC) is not possible. Gas chromatographic methods are available and can usually be carried out after methyl esterification, but their use is limited to thermally stable esters.

Recently, HPLC using an ion-pair extraction detector^{1,2} was proposed for the analysis of anionic surfactants. However, this detection system requires a solvent-delivery system for on-line extraction.

Diazoalkanes, *e.g.*, diazomethane react with the acid forms of anionic surfactants to produce methyl esters. 4-Diazomethyl-N,N-dimethylbenzenesulphonamide was synthesized by Sekiya³ and shown to react with acidic substances such as fatty acids and benzoic acid.

This paper describes a rapid and simple liquid chromatographic method for the analysis of anionic surfactants by use of derivatization with 4-diazomethyl-N,N-dimethylbenzenesulphonamide. The acidic forms of anionic surfactants such as α -olefinsulphonates, alkanesulphates, alcohol ethoxylate sulphates and alkyl phosphates react with this derivatization reagent to produce ultraviolet-absorbing derivatives which can then be separated by reversed-phase HPLC.

EXPERIMENTAL

Reagents

Standard C₁₆ α -olefinsulphonates, alcohol ethoxylate sulphates and alkyl phosphates were synthesized in our laboratories. α -Olefinsulphonates and alkanesulphates were purchased from Mitsubishi Chemical Industries (Tokyo, Japan). The derivatization reagent, 4-diazomethyl-N,N-dimethylbenzenesulphonamide, was obtained from Wako Pure Chemical Industries (Tokyo, Japan). Deionized water was further purified on an ODS column. All other reagents were analytical reagent grade.

HPLC

The chromatographic separations of the derivatives of anionic surfactants were carried out with an instrument comprising an HPLC pumping system (Hitachi Model 655), an UV detector (Hitachi Model 638-04) and a data processor (Model 655-60;

Hitachi Scientific Instruments, Tokyo, Japan). A syringe-loading sample injector (Model 7125, Rheodyne, CA, U.S.A.) was used for sample injection. A 125×4 mm I.D. stainless-steel column packed with LiChrosorb RP-18, $5 \mu\text{m}$ (Merck, Darmstadt, F.R.G.) was employed. Methanol-water mixtures were used as mobile phase; flow-rate 1.0 ml/min. The detection was performed at 240 nm; sensitivity 0.16 a.u.f.s.

The derivatization of the anionic surfactants was carried out as follows. To a 100% methanol solution of the acidic forms of the anionic surfactants (0.01 *M*), a 0.1 *M* solution of 4-diazomethyl-*N,N*-dimethylbenzenesulphonamide in methanol was added until the solution gave an orange colour indicating an excess of the derivatization reagent. The reaction was carried out at room temperature. The acidic forms of the anionic surfactants were prepared by solvent extraction between diethyl ether and an aqueous solution of 2 *M* hydrochloric acid.

RESULTS AND DISCUSSION

Fig. 1a and b shows chromatograms of the ultraviolet-absorbing derivatives of the hydroxyl and alkenyl forms of C_{16} α -olefinsulphonates, respectively. The mobile phase was to methanol-water (80:20, v/v). It was found that the hydroxyl form of α -olefinsulphonate was eluted more rapidly than the alkenyl form. The peak eluted after the hydroxyl form in Fig. 1a is the alkenyl form present as an impurity in the standard.

Fig. 2 shows a typical chromatogram of the ultraviolet-absorbing derivative of a commercial C_{16} α -olefinsulphonate. The amount injected was 5 μg . The two peaks eluted at around 10 min were the hydroxyl and alkenyl forms of α -olefinmonosulphonate. The two later peaks are considered to be due to the hydroxyl and

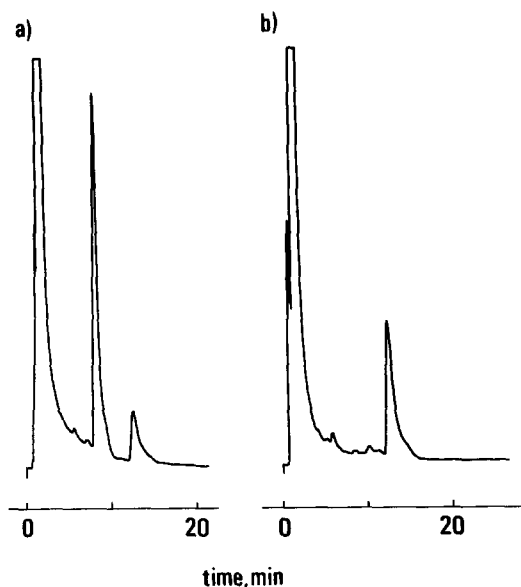


Fig. 1. Chromatograms of UV-absorbing derivatives of standard C_{16} α -olefinsulphonate in its hydroxyl (a) and alkenyl (b) forms.

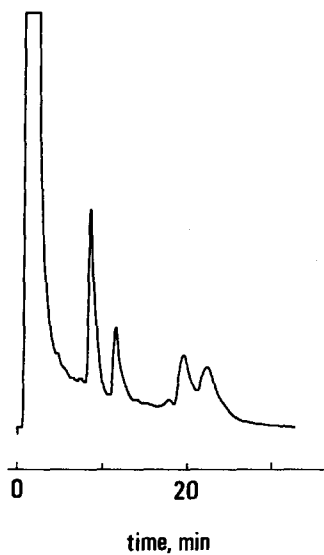


Fig. 2. Typical chromatogram of the UV-absorbing derivative of commercial C_{16} - α -olefinsulphonate.

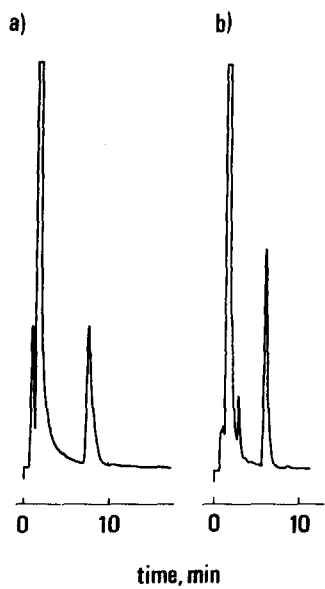


Fig. 3. Chromatograms of the UV-absorbing derivatives of monolauryl phosphate (a) and dilauryl phosphate (b).

alkenyl forms of α -olefindisulphonates produced during sulphonation, because 1 mol of α -olefinsulphonate reacted with 2 mol of the derivatization reagent and the retention time of the derivative increased relative to UV-adsorbing derivatives of α -olefinmonosulphonate. It should be noted that the hydroxyl and alkenyl forms of α -olefindisulphonate could not be separated without the derivatization of the sulphonate group, because these disulphonates were usually eluted with the solvent front.

Fig. 3a and b shows chromatograms of mono- and dilauryl phosphate derivatives, respectively. The mobile phase was methanol-water (80:20, v/v) for the mono-lauryl and 95:5 for the dilauryl phosphate derivative. The amounts injected were 0.5 μ g. As shown in Figs. 2 and 3, it is seen that the detection sensitivity is increased in comparison with a conventional refractive index detector which usually requires at least ten times more sample.

By means of the described liquid chromatographic method, the analysis of various kinds of anionic surfactants was carried out simply, rapidly and sensitively.

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