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Note

Purification of ethoxylated anionic surfactants by preparative high-performance liquid chromatography

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Alkyl and alkylarylalkoxyethanesulphonates are well-known surfactants which have been suggested for a variety of applications. Recent examples that have appeared in the patent literature include the application of such sulphonates to the treatment of inorganic mineral scale[1], as emulsion polymerisation surfactants[2] and as surfactant systems for the enhanced recovery of crude oil[3]. The alkylphenylethoxyethanesulphonates [$RPh(OCH_2CH_2)nSO_3Na$] were originally prepared and patented by Rohm and Haas[4] and this company also explored their surfactant properties[5] and still markets them under the "Triton" trademark in North America.

The selection of an alkylphenylethoxyethanesulphonate of correct structure for a given application depends upon a detailed structure–activity study and this can require the provision of substantial quantities of purified anionic surfactant of well-defined structure. The synthesis of such surfactants generally involves the conversion of alkylphenylethoxyalcohol in a one- or two-step process into the sulphonate, so that crude sulphonate products generally contain unreacted nonionic precursors together with anionic reaction by-products. The separation of anionic surfactant sulphonate from this crude product is a formidable task by conventional means. For example, ion-exchange chromatography is unable to separate sulphonate surfactant from anionic impurities and because alkylphenylethoxyethanesulphonates are in themselves complex mixtures containing a distribution of molecules of different ethoxy chain lengths, normal-phase gravity column chromatography results in the separation of these anionic ethoxylate oligomers and consequent overlap with non-ionics.

It has now been demonstrated that pure anionic alkylphenylethoxyethanesulphonate may be rapidly separated from crude commercial products by preparative high-performance liquid chromatography (HPLC) using a reversed-phase system. In addition, the molar ratio of anionic surfactant to non-ionic ethoxyalcohol may also be approximated by a similar system in the analytical mode and the purity of sulphonate fractions from the HPLC system rapidly monitored.

EXPERIMENTAL

Apparatus

Preparative HPLC was performed on a Waters Assoc. Prep LC/System 500A

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package. The column was a Waters Prep PAK-500/C_{18} 30 cm × 5.7 cm I.D. reversed-phase cartridge. Solutions of surfactants were injected directly onto the column and eluted products were monitored using a refractive index detector and collected manually.

The analytical HPLC system employed a Waters Assoc. Model 6000A Solvent Delivery System and RCM-100 Radial Compression Module with 10 cm × 8 mm I.D. reversed-phase C_{18} cartridge. Surfactant solution was injected onto the column via a 200 ml injection loop. Detection was performed with a Cecil CE 2112 variable-wavelength ultraviolet monitor (at 254 nm) and a Hewlett-Packard Model 3390A reporting integrator was used to record and integrate the HPLC trace.

Chemicals

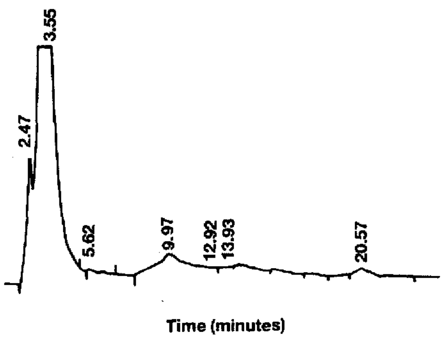
Alkylphenylethoxyethanesulphonate surfactants were BP research products and were applied to the HPLC columns as dilute solutions in the appropriate mobile phase. Methanol and isopropanol were BDH Analar grade solvents and tetrahydrofuran was obtained from Fisons as HPLC grade. Water was redistilled.

RESULTS AND DISCUSSION

Analytical HPLC

Normal-phase HPLC has recently been demonstrated[6] as a convenient technique for the separation of ethoxylate oligomers in alkylphenylethoxysulphonate surfactants. Quantification of such oligomers enables ethoxylate distribution, average ethoxylate number and anionic to non-ionic ratio to be determined. The application of a simple reversed-phase HPLC system to such alkylphenylethoxysulphonate product mixtures results in a much simpler chromatogram in which oligomer separation is largely suppressed and three regions are observable. With the HPLC apparatus detailed in the experimental section in the analytical mode and isopropanol–water (4:1) with 0.2% phosphoric acid as the mobile phase, a chromatogram similar to that shown in Fig. 1 was obtained for as-made anionic surfactant $C_{18}H_{37}Ph(OCH_2CH_2)_7SO_3Na$.

The peak at 3.55 min is from surfactant sulphonate. Non-ionic alkylphenylethoxyalcohol and other non-ionic compounds appear in the region 7–21 min. Some separation of ethoxylate oligomers is observable. An anionic reaction by-product appears as a shoulder to the main anionic peak at 2.47 min. It is reasonable to assume that the extinction coefficient of the alkylphenoxy group is unaffected by the presence of hydroxyl or sulphonate groups at the end of the ethoxylate chain joined to it. Hence an approximation for molar ratio of anionic surfactant to non-ionics may be obtained from a ratio of the peak areas of the two regions of this chromatogram. An anionic to non-ionic ratio of 78:22 is obtained from the chromatogram in Fig. 1. This analytical HPLC system was designed primarily, however, for the rapid monitoring of purity of eluted sulphonate fractions from the preparative HPLC system and hinges on the rapid elution of sulphonate. A new reversed-phase system for determination of more accurate molar anionic to non-ionic ratios with higher retention of sulphonate has been developed and will be reported at a later date. This analytical HPLC technique can also be used as a rapid method for determination of approximate molar conversion of non-ionic to anionic in the sulphonation step of



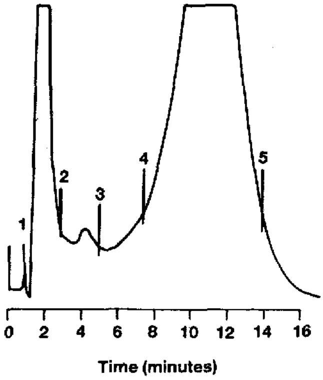


Fig. 1. Chromatogram of unpurified anionic surfactant $C_{18}H_{37}Ph(OCH_2CH_2)_7SO_3Na$. Column, 100 × 8 mm I.D. radially compressed C_{18} reversed-phase cartridge; mobile phase, isopropanol–water (4:1) with 0.2% phosphoric acid; flow-rate, 1.0 ml/min; detector, UV (254 nm).

Fig. 2. Chromatogram of as-made anionic surfactant $C_{18}H_{37}Ph(OCH_2CH_2)_7SO_3Na$. Column, 30 × 5.7 cm I.D. C_{18} reversed-phase cartridge; mobile phase, tetrahydrofuran–methanol–water (35:30:35); flow-rate, 200 ml/min; refractive index detector.

the synthesis of such surfactants. The actual surfactant sulphonate content in commercial products is generally less than this on a weight basis as the HPLC technique has not been designed to quantify inorganic salt, solvent and other non-UV-active components. The weight of surfactant sulphonate in this commercial surfactant product was 61% according to two-phase titration.

Preparative HPLC

Preparative HPLC was performed with the apparatus described in the experimental section. The mobile phase was tetrahydrofuran–methanol–water (35:30:35) and in Fig. 2 the HPLC chromatogram obtained by the injection of 10.4 g of as-made anionic surfactant $C_{18}H_{37}Ph(OCH_2CH_2)_7SO_3Na$ in 40 ml of solvent is illustrated. The numbers on the chromatogram correspond to fractions collected. Fraction 1, eluted with solvent front, contains anionic by-product, fraction 2 contains a small amount of a previously unseen material of unknown identity and fraction 4 contains pure surfactant sulphonate. The separation was complete in 15 min and 6.4 g of surfactant sulphonate and 0.9 g of anionic by-product were isolated from the 10.4 g of crude surfactant injected. This recovery of surfactant sulphonate is extremely close to the proportion estimated by weight by two-phase titration to be present in the crude product and recoveries of 85–95% of estimated proportion are routine.

It was found that sample size could be increased to 20 g in a single injection without loss of resolution in the separation. Alkylphenylethoxyalcohol and other non-ionics move extremely slowly on the reversed-phase C_{18} column in this mobile phase and in fact do not appear in Fig. 2. Only after 12 column volumes do non-ionics appear in the effluent, so it was possible to perform more than one preparative cycle before elution of the non-ionic compounds occurred. In practice, non-ionics were washed from the column by backflushing with methanol after each cycle and with tetrahydrofuran–methanol after 5 cycles so that contamination of surfactant

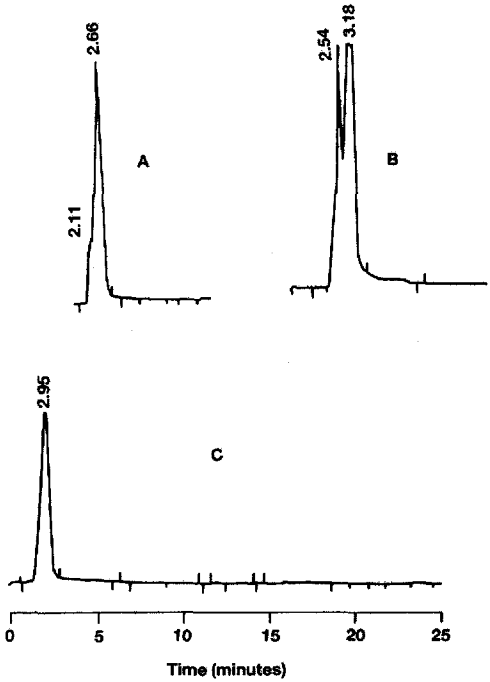


Fig. 3. Chromatograms of fractions of as-made anionic surfactant $C_{18}H_{37}Ph(OCH_2CH_2)_7SO_3Na$ purified by preparative HPLC. Column, 100 × 8 mm I.D. radially compressed C_{18} reversed-phase cartridge; mobile phase, isopropanol–water (4:1) with 0.2% phosphoric acid; flow-rate, 1.0 ml/min; detector, UV (254 nm). (A) anionic by-product; (B) anionic by-product with added surfactant sulphonate; (C) surfactant sulphonate.

sulphonate was not a possibility. A 4.6-1 volume of mobile phase was required per cycle.

Fig. 3 shows analytical HPLC chromatograms of certain of the separated fractions. Fig. 3A indicates that anionic by-product was obtained free from surfactant sulphonate in fraction 1. Addition of pure surfactant sulphonate (Fig. 3B) gives a chromatogram with two distinct peaks. Fig. 3C shows pure surfactant sulphonate isolated in fraction 4. The identity of surfactant sulphonate, together with a confirmation of the absence of non-ionic components, was obtained by NMR spectroscopy.

The final stage in the isolation of pure surfactant sulphonate involves the removal of considerable volumes of solvent, one component of which is water. It is therefore necessary to employ an efficient and rapid evaporation system and a modification of the falling film evaporator described by Bretherick[7] was found to be suitable for this application.

Application of the techniques described have allowed the separation of pure anionic surfactants $RPh(OCH_2CH_2)_nSO_3Na$ from as-made products. As much as 100 g of crude material may be processed in one day. It is also to be expected, with little fine tuning of the solvent system, that this separation procedure could be applied to a wide variety of anionic surfactant structures.

CONCLUSIONS

A reversed-phase preparative HPLC system has been developed for the separation of surfactant sulphonate from non-ionic precursor and anionic by-products in as-made alkylphenylethoxyethanesulphonate surfactant products $RPh(OCH_2CH_2)_nSO_3Na$. Purification to 100% anionic surfactant may be efficiently achieved on 10–20 g batches of injected mixture in less than 0.5 h.

Molar ratios of anionic surfactant to alkylphenylethoxyalcohol non-ionic may be approximated by an analytical HPLC system also in the reversed-phase mode for the unpurified products. This technique has been used to monitor sulphonate fractions and is a useful criterion of purity for separated surfactant.

It is anticipated that these HPLC techniques would be applicable to a wide variety of different anionic surfactant structures.

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