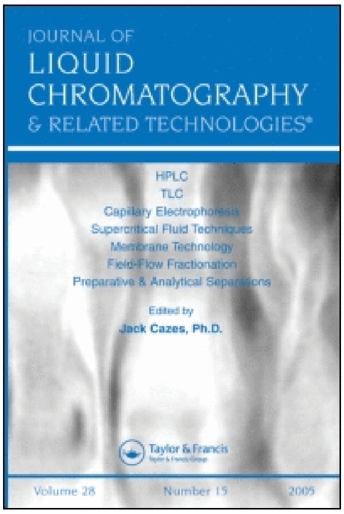

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THIN LAYER CHROMATOGRAPHIC METHOD FOR THE DETERMINATION OF SURFADONE™ QSP IN FORMULATED PRODUCTS

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ABSTRACT

Thin layer chromatography with densitometric detection is utilized for the quantitative analysis of Surfadone™ QSP in formulated products. Iodoplatinate reagent is used to derivatize the quaternary ammonium surfactant, yielding a colored species with a maximum absorbance at 525 nm. The high polarity of the surfactant is demonstrated by comparison of its chromatographic behavior to that of other commercially available materials. Prototype formulations (foaming conditioner, styling glaze) were analyzed yielding excellent accuracy and precision.

INTRODUCTION

Surfadone™ QSP (Dimethylsteramidopropyl [(2-pyrrolidonyl) methyl]ammonium chloride) is a newly developed quaternary ammonium surfactant which has a

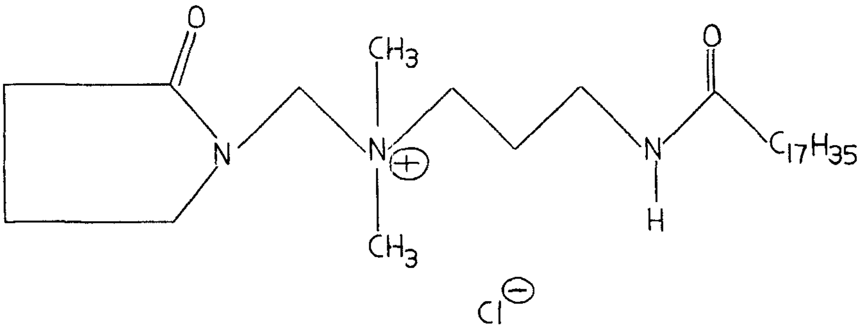

FIGURE 1 - Chemical structure of Surfadone™ QSP

multitude of cosmetic applications. Incorporation of the pyrrolidone ring into the basic structure (Figure 1) imparts various unique properties into the molecule such as clarity and compatibility with anionic surfactants, high water solubility, complexation with fragrances, and mildness to hair and skin. These properties make Surfadone™ QSP a very attractive component for clear conditioning shampoos and conditioners.

Many analytical techniques are available for the assay of quaternary ammonium surfactants based on titration (1-3), ion selective electrodes (4-6), spectrophotometry (7-9), gas chromatography (10,11), and HPLC (12-16). In general, these methods require sample pre-treatment (eg. ion exchange) in order to insure specificity. While HPLC is inherently more specific than most alternate methods, sensitive detection usually requires the presence of a UV absorbing or fluorescent chromophore which Surfadone QSP does not possess. Thin layer chromatography is an attractive technique in this case as derivatization chemistries can be employed after chromatographic separation to allow for sensitive and specific detection of the quaternary ammonium moiety.

We wish to report the development of a thin layer chromatographic method for the quantitative determination of Surfadone™ QSP. In this method, the quaternary ammonium surfactant is selectively retained on high performance silica gel TLC plates by use of a mobile phase of 6 + 3 + 0.75 (v/v/v) methanol / methylene chloride / acetic acid. Derivatization with iodoplatinate reagent and scanning densitometry (reflectance at 525 nm) are used for the quantitation. Under the analytical conditions, Surfadone™ QSP can be separated from formulation components as well as reaction precursors.

EXPERIMENTAL

Apparatus

HPTLC plates were developed in either a Camag linear development chamber (23 cm long x 14 cm high) or a Camag horizontal development chamber without pre - equilibration with mobile phase. Sample solutions were applied to the plates with disposable 5 microliter Drummond micropipettes. A Desaga dipping tank was used to derivatize the developed HPTLC plate with iodoplatinate reagent. Photometric measurements were done using a Shimadzu Model CS - 930 scanning densitometer in the reflectance mode. Zones were scanned in the direction of chromatography with a slit width of 0.2 mm and slit length of 4 mm. The analytical wavelength (determined by obtaining a visible spectrum of derivatized Surfadone QSP on the HPTLC plate) was 525 nm.

Materials

Whatman LHP - KDF silica gel 60 HPTLC plates (20 cm x 10 cm) were used for all separations. Chloroform, methanol, methylene chloride (HPLC grade), glacial acetic acid, potassium iodide, and hydrogen hexachloroplatinate (A. R. grade) were obtained from Aldrich Chemical Company. Distilled deionized water (18 megohm - cm, HPLC grade) was obtained from EM Science. HPTLC plates were cleaned by elution with 1 + 1 (v/v) chloroform / methanol and air drying. The iodoplatinate derivitizing reagent was prepared by mixing 1 mL of 5 % (w/v) aqueous H_2PtCl_6 H_2O with 9 mL of 10 % (w/v) aqueous KI and diluting to 300 mL with distilled deionized water. Surfadone™ QSP was obtained from GAF Chemicals Corporation. This material was assayed by the two phase tetraphenyl boron titration procedure of Cross (2) before use. All other chemicals were of reagent grade.

Procedure

Standards and samples were diluted with methanol and applied to the pre - adsorbent layer of the HPTLC plate using a Drummond micropipette. After air drying, the plate was developed a distance of 5 cm from the origin using a mobile phase of 6 + 3 + 0.75 (v/v/v) methanol / methylene chloride / glacial acetic acid. Air dried plates were then dipped into the iodoplatinate reagent for 5 s and allowed to drain. After air drying, Surfadone™ QSP appeared as a purple zone on a light pink background. Quantitation was accomplished by densitometric scanning (reflectance at 525 nm) and comparison of integrated peak areas to a calibration curve.

RESULTS AND DISCUSSION

Recently, the separation of quaternary ammonium surfactants from reaction precursors and formulation components has been dominated by HPLC techniques. In these cases, the molecules of interest contained aromatic moieties which allow for the use of UV and/or fluorescence detection. Surfadone™ QSP contains only amide groups which have low wavelength absorption (ca. 210 nm). The use of this wavelength is relatively non -

specific and prone to interference by many system components. Armstrong and Stine (17) demonstrated the use of TLC for the separation of cationic surfactants from anionic surfactants. In their work, the conditions allowed for such a separation without precipitation or neutralization effects. Unfortunately, iodine vapor was used for visualization which, due to its volatile nature, yielded fading zones. In the current investigation, the above mentioned TLC system was optimized for Surfadone™ QSP and coupled with the use of iodoplatinate reagent for visualization. This derivatizing reagent generates a permanent, deeply colored complex with the quaternary ammonium group (16,18), allowing for reproducible densitometric measurement. Figure 2 shows a visible spectrum of the derivatized Surfadone™ QSP on the silica gel surface. This spectrum (difference between the derivatized analyte and the blank background) indicates a broad absorption maximum (reflectance minimum) centered a ca. 550 nm. Densitometric scans of the amidoamine precursor indicated some reflectance contribution at this wavelength. A detection wavelength of 525 nm was chosen as a compromise in order to minimize the amidoamine contribution (amidoamine has a minimum absorption at this wavelength).

Using the described procedure, a 50 ppm standard generated the chromatogram shown in Figure 3. Typically,

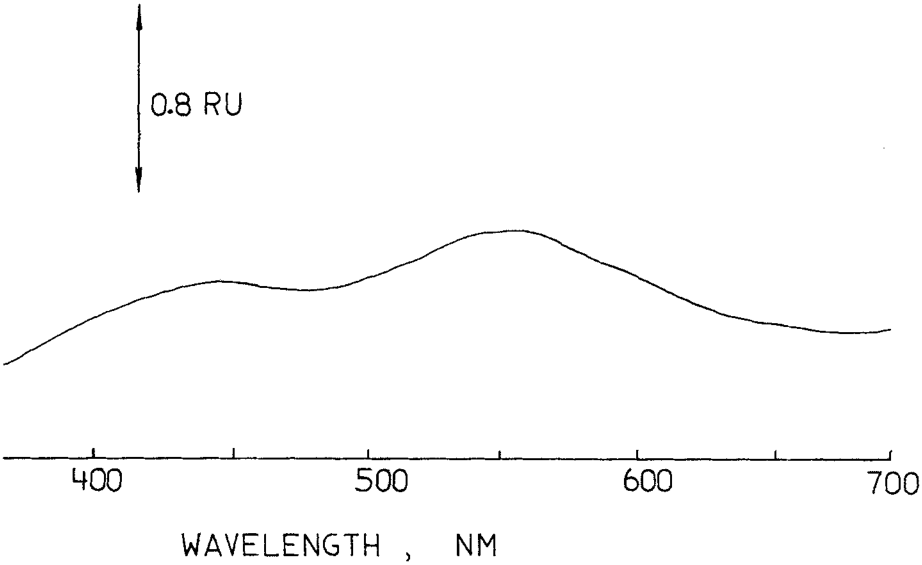

FIGURE 2 - Difference spectrum of Surfadone™ QSP after reaction with iodoplatinate reagent.

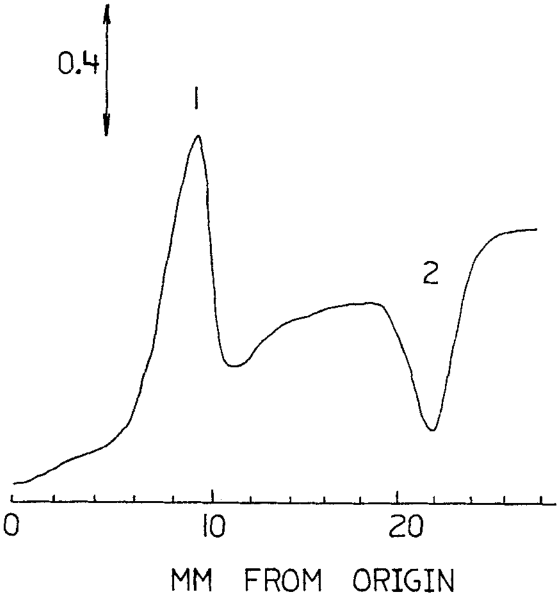

FIGURE 3 - Thin layer chromatogram of 50 ppm Surfadone™ QSP standard. 1 = Surfadone QSP; 2 = amidoamine

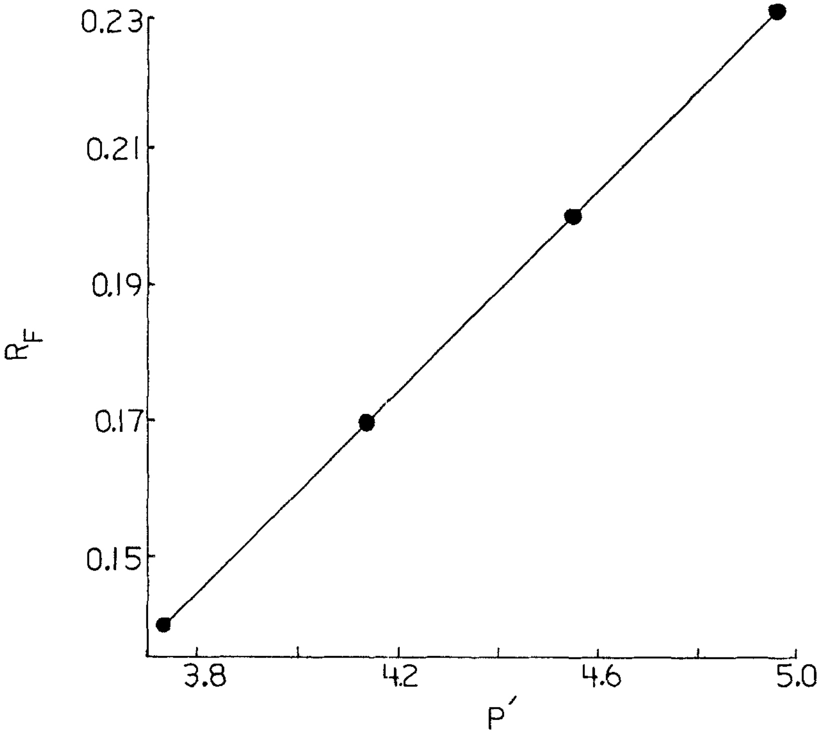

FIGURE 4 - Linear regression plot of R_f versus solvent polarity for Surfadone™ QSP.

the retardation factor, R_f, was 0.20 ± 0.1 under these conditions. The amidoamine precursor appears as a white zone (negative peak; $R_f = 0.36$) in the chromatogram. An examination of R_f versus variation in polarity of the methanol / methylene chloride / acetic acid mobile phase (shown in Figure 4) was linear (correlation coefficient = 0.9999) with low slope. This behavior suggests a single retention mechanism based on sample polarity. The high

TABLE I - Retardation Factors of Various Quaternary Ammonium Species

Sample	R_f[a]
Surfadone™ QSP	0.20
Dimethylstearylamidopropyl amine[b]	0.35
Benzyl(diisobutylphenoxyethoxy ethyl)dimethylammonium chloride	0.45
Stearyldimethylbenzylammonium chloride	0.73
t-butylammonium chloride	0.92

[a] mobile phase = 6+3+0.75 (v/v/v) methanol / methylene chloride / glacial acetic acid

[b] tertiary amine precursor for Surfadone™ QSP

polarity of Surfadone™ QSP is suggested by examining the chromatographic behavior of other quaternary ammonium surfactants under identical conditions. Table I lists the observed R_f values of selected species using the optimized mobile phase. The trend of increased retention with degree of polarity of side groups is quite evident.

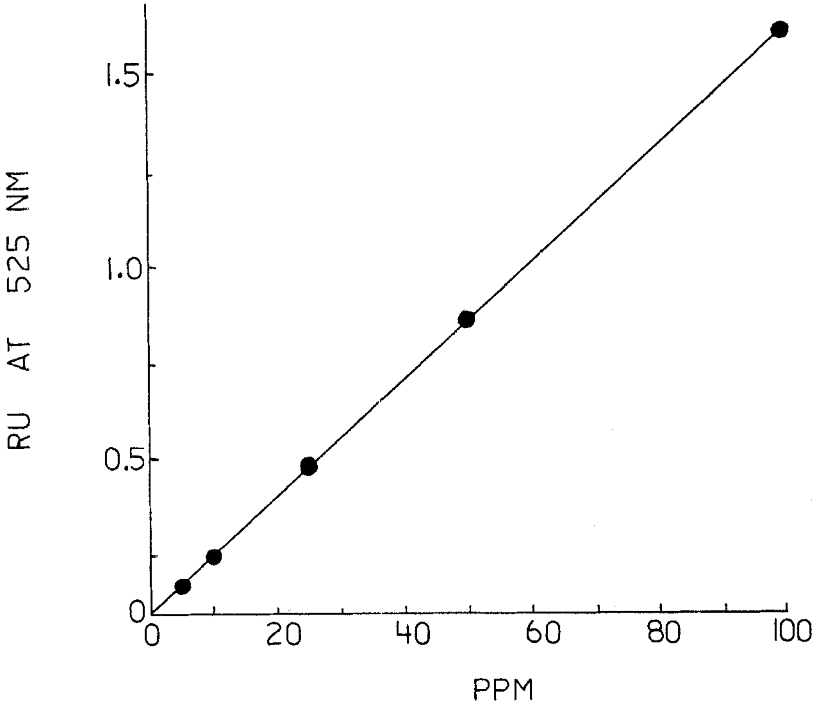

FIGURE 5 - Linear regression plot of reflectance at 525 nm versus Surfadone™ QSP concentration.

In fact, it appears that much of the apparent polarity of Surfadone™ QSP is derived from the amide functionality in its amidoamine precursor. It is believed that the high polarity of Surfadone™ QSP and the unique complexation properties of the pyrrolidone moiety are the primary factors governing observed compatibility and solubility with anionic surfactants.

TABLE II - Analysis of Prototype Formulations for Surfadone™ QSP

Sample	added,%	found, %
Foaming conditioner	3.00	2.98 ± 0.16
	3.00	2.99 ± 0.15
Styling glaze	1.00	1.04 ± 0.06
	1.00	1.01 ± 0.04

The calibration graph for Surfadone™ QSP (Figure 5) was found to be linear in the 5 ppm to 100 ppm range (25 ng to 500 ng applied to the plate) and obeyed the following equation:

$$H(\text{arb. units}) = (15.12 \pm 0.07\ \text{ppm}^{-1})C + 98.62 \pm 3.85$$

The correlation coefficient was 0.9999 with a standard error of estimate of 5.81. The detection limit (signal / noise = 3) is 2 ppm (absolute) which, depending on sample concentration and applied volume, translates to as low as 100 ppm in the formulated sample.

System precision was evaluated in two ways. A single application of a 50 ppm Surfadone™ QSP standard was subjected to multiple scanning. For eight scans, the average Surfadone™ QSP level was found to be 49.5 ppm ± 1.4 ppm at the 95 % confidence level. The coefficient of

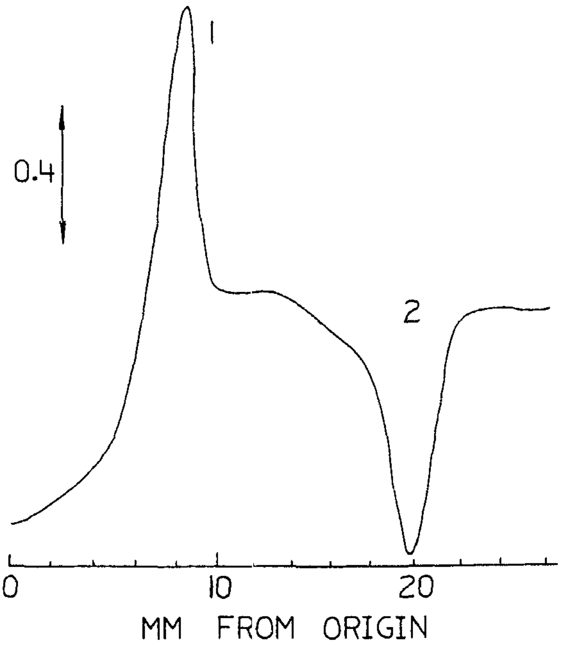

FIGURE 6 - Thin layer chromatogram of 0.20 g / mL foaming conditioner in methanol. 1 = Surfadone™ QSP; 2 = amidoamine

variation was 1.2 %. The system precision is compromised if a spray technique is used instead of the dipping method. Eight separate solutions of 100 ppm Surfadone™ QSP were analyzed and found to contain 98.0 ppm ± 4.6 ppm at the 95 % confidence level. The coefficient of variation was 2.0 %.

The procedure was utilized for the determination of Surfadone™ QSP in prototype clear foaming conditioner and styling glaze formulations. These materials were simply dissolved in methanol and applied to the pre - adsorbent layer without analyte isolation or pre - treatment. The excellent accuracy and precision of this analysis is clearly evident in Table II (four replicates at the 95 % confidence level) for representative samples. It should be noted that these formulations contain a variety of polymers, preservatives, and fragrances which are either fully retained on the pre - adsorbent layer or are eluted at the solvent front. A typical sample chromatogram is shown in Figure 6.

CONCLUSIONS

A thin layer chromatographic method was developed for the assay of Surfadone™ QSP in formulated products. This method allows for the direct analysis of hair conditioners and styling glazes without sample cleanup. The procedure should find broad applicability in quality control and identity testing of formulations containing this versatile quaternary ammonium surfactant.

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