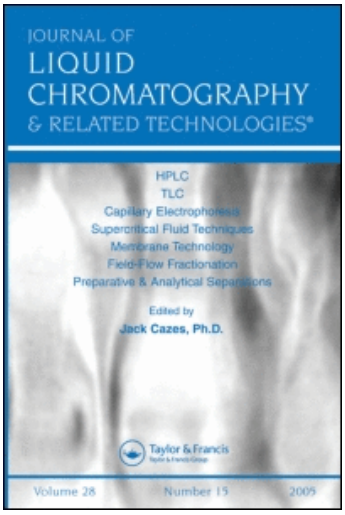

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SEPARATION AND QUANTITATION OF ANIONIC, CATIONIC AND NONIONIC SURFACTANTS BY TLC

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ABSTRACT

TLC is a potentially powerful technique for the separation of surfactants. Reversed phase thin layer chromatography (RPTLC) can be used to separate entire classes of surfactants (i.e., anionics from nonionics from cationics). Conversely, silica gel can be used to separate individual anionic or cationic surfactants from other similarly charged surfactants. RPTLC can also be used to separate individual nonionic surfactants. Using two dimensional TLC (with a special silica gel plate containing a 2.5 cm strip of reversed phase material along one edge) a complex mixture of surfactants was first fractionated into classes and then (using the second dimension) into individual components. Standard scanning densitometry was used for quantitation.

INTRODUCTION

The analysis of surfactants (e.g., detergents, soaps, etc.) can be a difficult analytical problem. Surfactants are generally somewhat soluble in both water and organic solvents. They concentrate at interfaces and tend to bind to anything available (1,2). There are a variety of spectrometric, titrimetric, atomic absorption spectrometric and ion-selective electrode methods for the analysis of surfactants (3-11). All of these techniques have

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the characteristic of being selective for certain functional groups. For example both the sodium dodecylsulfate electrode and the methylene blue complex spectrophotometric methods are selective for surfactants with sulfate or sulfonate functional groups. Consequently these techniques give positive responses for a variety of homologous, isomeric and even structurally dissimilar anionic surfactants. Another shortcoming of these techniques is that one class of surfactants cannot be effectively analyzed in the presence of another. The so-called neutralization effect of cationic with anionic surfactants is well documented (12). As a result of these limitations, the analyst has increasingly turned to physicochemical techniques which provide information on the total surfactant content in a sample (13) or to chromatography (14-16). Because most surfactants are nonvolatile without derivatization, LC or TLC methods are often preferred. The use of TLC to separate a mixture of anionic surfactants was recently demonstrated (17). In this work we not only demonstrate the separation of identically charged surfactants from each other but also the TLC separation of the three major classes of surfactants (i.e., anionic, nonionic and cationic).

MATERIALS

Whatman reversed phase TLC plates (KC18F), silica gel plates (K6F) and hybrid Multi-K plates (CS5) were activated at 115°C for two hours before use. Cetyltrimethylammonium bromide (CTAB, Sigma), cetylpyridinium chloride (CPC, Sigma), cetyltrimethyl-

ammonium chloride (CTAC, Pfaltz & Bauer), dodecylamine (DA, Aldrich), octadecylamine (OA, Eastman), sodium dodecylsulfate (SDS, Bio Rad), dodecylbenzenesulfonate (DBS, Pfaltz & Bauer), sodium dioctylsulfosuccinate (SDOS, Aldrich) and sodium laurate (SL, Pfaltz & Bauer) were recrystallized three times from ethanol-water before use. The nonionic surfactants Triton X 100 (TX 100, Bio Rad), Surfynol 465 (S 465, Air Products) and Igepol CO-530 (ICO-530, GAF) were used as received. ICO-530 is nonylphenoxypoly(ethyleneoxy)ethanol where the hydrophilic poly(ethyleneoxy)ethanol "head-group" averages five units in length. TX 100 is dodecylphenoxypoly(ethyleneoxy)ethanol. S 465 is a poly(ethyleneoxy)ethanol (averaging ten units) adduct of 2,4,7,9-tetramethyl-5-decyn-4,7-diol. Gold lable sodium tetraphenylborate (Aldrich) was used as received. Methanol, ethanol, methylene chloride and glacial acetic acid (Baker) were also used as received.

METHODS

All separations were done in a 11 3/4 in. long, 4 in. wide and 10 3/4 in. high sealed chromaflex developing tank. The plates were not pre-equilibrated with solvent vapor before use.

Separation of anionic surfactants: 1 μℓ of 0.1 M SDS, SL, DBS and SDOS was spotted 1 cm from the bottom of a 5 x 20 cm silica gel plate. The mobile phase consisted of 8:1 (v:v) methylene chloride:methanol. The addition of very small amounts of acetic acid to the mobile phase tended to increase the R_f's but did not

affect the resolution. Spots were visualized by exposure to I_2 vapor.

Separation of cationic surfactants: 1 μℓ of 0.1 M CPC, OA, DA and CTAC or CTAB was spotted 1 cm from the bottom of a 5 x 20 cm silica gel plate. The mobile phase consisted of 8:1:0.75 (v:v:v) methylene chloride:methanol:acetic acid. Spots were visualized by exposure to I_2 vapor.

Separation of nonionic surfactants: 1 μℓ of 10% TX 100, ICO-530 and S 465 were spotted on a 5 x 20 cm reversed phase (C_{18}) plate. The mobile phase consisted of 8:2 (v:v) ethanol:2% sodium tetraphenylborate$_{(aq)}$. The purpose of sodium tetraphenylborate was to prevent the spots from streaking. I_2 vapor was used for visualization.

Separation of anionic, cationic and nonionic surfactants: A Whatman CS5, Multi-K, KC18F/K5F 20 x 20 cm plate was pre-developed in ethanol and then activated at 115°C for 2 hours. Each surfactant mixture was spotted (0.5 μℓ) at a point on the reversed phase strip. The entire 20 x 20 cm plate was then developed with 75% ethanol in the direction of the reversed phase strip. Development was stopped when the solvent front was 2 cm from the top of the plate. Under these conditions, all anionic surfactants travel at or very near the solvent front (i.e., < 2 cm), all cationic surfactants remain at or near the origin of the reversed phase strip (<2.5 cm), while the nonionic

surfactants separate between the anionics and cationics. The 20 x 20 cm plate is then cut into three separate sections in a direction perpendicular to the first development. The first cut should be 2.5 to 3 cm below the solvent front. This will isolate the anionic surfactants. The second cut should be 3 cm above the origin. This will isolate the cationic surfactants. Perpendicular secondary development of the plates containing the cationic and anionic surfactants (after reactivation of the plates) will give complete separation of these species. The mobile phases for secondary development are, 8:1 (v:v) $MeCl_2$:MeOH for the anionic surfactants and 8:1:0.5 (v:v:v) $MeCl_2$:MeOH:HOAc for the cationic surfactants. If one develops the entire plate in the second direction without isolating the anionic and cationic surfactants as indicated, the nonionic surfactants tend to spread and coat the silica gel portion of the plate thereby obscuring all other components. Visualization is with I_2 vapor.

Quantitation of surfactants: Scanning densitometry was done with a Shimadzu Model 910 instrument. Surfactants could be detected directly in the absorbance-reflectance mode at 215 nm. Detection limits were lower when the developed plate was exposed to I_2 vapor and scanned at 405 nm (in the absorbance-transmittance mode).

RESULTS AND DISCUSSION

One's approach to the TLC separation of surfactants in a mixture is largely controlled by the charge of the surfactant

head-groups as well as the diversity of the sample. Silica gel is adequate for the separation of anionic or cationic surfactants from other identically charged species. Nonionic surfactants are best separated by reversed phase TLC (RPTLC). Even in RPTLC nonionic surfactants tend to streak unless a "lipophilic salt" such as sodium tetraphenylborate is added. Table 1 summarizes

TABLE I

Experimental Conditions and R_f Values of Individually Separated Anionic, Cationic and Nonionic Surfactants

Compound	Stationary Phase	Mobile Phase	R_f
Anionic Surfactants	a	c	
1. SDS			0.15
2. DBS			0.09
3. SL			0.70
4. SDOS			0.28
Cationic Surfactants	a	d	
1. CTAB			0.21
2. CTAC			0.20
3. CPC			0.27
4. DA			0.42
5. OA			0.55
Nonionic Surfactants	b	e	
1. TX 100			0.54
2. S 465			0.70
3. ICO-530			0.45

[a]Silica Gel [b] C_{18} reversed phase

[c]8:1(v:v) $MeCl_2$:MeOH [d]8:1:0.75 (v:v:v) $MeCl_2$:MeOH:HOAc

[e]8:2 (v:v) EtOH:2% sodium tetraphenylborate$_{(aq)}$

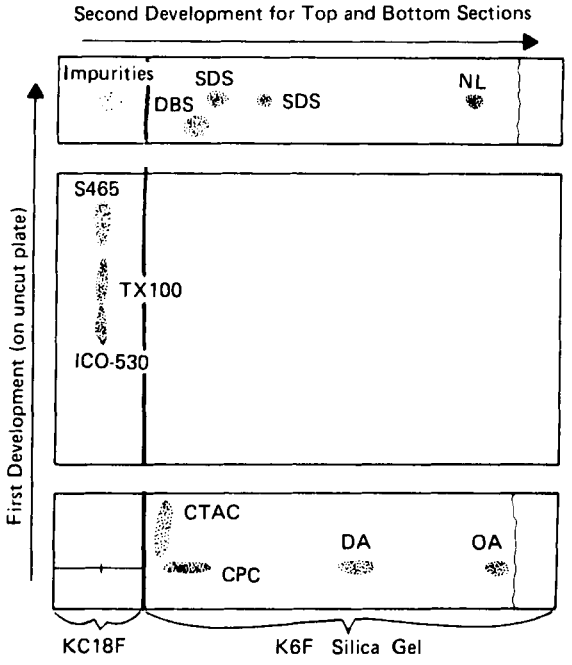

Figure 1: Schematic of a two dimensional TLC separation of eleven surfactants on a composit reversed phase-silica gel plate. The first development (on the reversed phase strip) separated the surfactants according to class. Secondary development of the top and bottom sections of the plate results in complete separation of individual surfactants. SDS = sodium dodecylsulfate, DBS = dodecylbenzenesulfonate, NL = sodium laurate, S 465 = Surfynol 465, TX 100 = Triton X100, ICO-530 = Igepol CO-530, CTAC = cetyltrimethylammonium chloride, CPC = cetylpyridinium chloride, DA = dodecylamine, OA = octadecylamine.

the separation conditions for each class of surfactants. The R_f's of the cationic surfactants can be altered (i.e., increased) considerably with a slight increase in the concentration of acetic acid in the mobile phase. The separation of surfactants with identical hydrophylic head groups (i.e., DA and OA or Tx 100 and ICO-530) is dependent on the size of the hydrophobic "tail". Generally the larger the hydrophobic portion of the surfactant, the greater the R_f.

The analysis of solutions containing surfactants of different charge can be a difficult process because of precipitation and "neutralization" effects (12). RPTLC, however, can be used to separate surfactants by class (see Figure 1). A 75% ethanol mobile phase tends to carry anionic surfactants with the solvent front and leave cationic surfactants near the origin. Perpendicular secondary development of plate sections near the solvent front and origin will then separate the anionic and cationic surfactants into individual compounds. The secondary development carries the surfactants from the reversed phase strip into the silica gel portion of the plate where fractionation occurs (Figure 1). Secondary development of the whole TLC plate or the section of plate containing the nonionic surfactants produced indistinguishable smears over much of the plate.

Quantitation of surfactants by scanning densitometry is a relatively straight forward process. It is possible to directly scan untreated spots at wavelengths from 200 to 215 nm. Sensitivity and selectivity can be enhanced by using a variety of

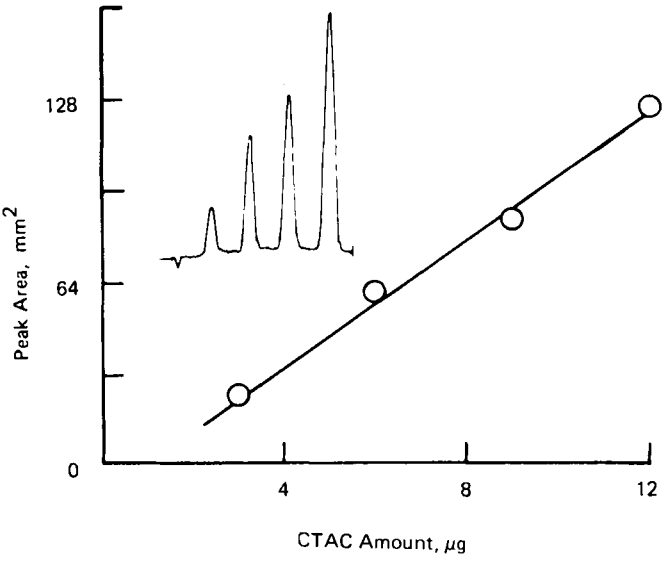

Figure 2: Calibration plot of peak area versus amount of the standard surfactant (CTAC) chromatographed. The insert shows the actual peaks obtained from scanning densitometery (at 405 nm).

visualization or charring techniques (17, 18). Figure 2 shows a scan of four CTAC standards (λ = 405 nm after visualization with I_2 vapor) and the corresponding calibration curve.

It is apparent from the literature that exhaustive chromatographic separations are presently the most effective means of analyzing complex surfactant mixtures. TLC is shown to be a highly efficient and inexpensive technique for the analysis of a variety of surfactant and surfactant mixtures.

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