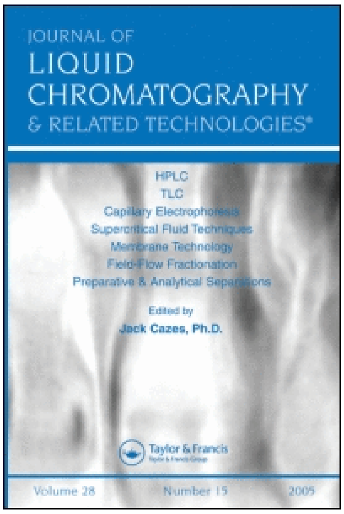

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SEPARATION AND CHARACTERIZATION OF SURFACTANTS BY HIGH PERFORMANCE THIN LAYER CHROMATOGRAPHY

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ABSTRACT

The separation of different types of surfactants of all four groups - anionics, nonionics, cationics and amphoterics, has been achieved by single development on silica plates. Ethanol and a mixture of ethanol with water have been used as the developer instead of various mixtures of much more toxic solvents (chloroform, benzene etc.). A new mode of detection with water has been applied among known agents of detection such as UV light (254 nm and 366 nm) and iodine. Anionic surfactants have shown characteristic white spots with gas bubbles after development with ethanol and detection with water. As auxiliary methods in classification of surfactants by charge type colour reactions, obtained by indicator dyes such as methylene blue, KJ_3, and bromphenol blue, have been used as simple detection tests. The reliability of the recommended TLC method has been tested on 28 different surfactants, for which the R_F values, forms and colours of spots, and gas bubbles have been determined.

INTRODUCTION

Since most of the commercial surfactant products are mixtures of several components, special separation methods are required for their identification, quality, and pollution control. Thin layer chromatography (TLC) is often used in separation of surfactants because of its simplicity, efficiency, and low material costs.

Systematic separation of surfactants by TLC has been described by many authors. Bey[1] studied different solvents, adsorbents and reagents for the detection in the separation of surfactants according to their ionic character and functional groups. König[2] used ion exchangers in pre-separation of different classes of surfactants into groups, and then used TLC to separate the compounds of one class. Frahne, Schmidt and Kuhn[3] separated the groups of electrochemically different surfactants used in textile finishing processes by electrophoresis and TLC. They used general indicating reagents for the uniform loaded groups and special reagents for the functional groups, sometimes in connection with micro splitting reactions. Hellmann[4] did interesting work by separating anionic, cationic and nonionic surfactants from waste waters and sludges by multiple chromatography on silica plates. He decomposed the complexes of cationic and anionic surfactants on thin layer before being separated. Hellmann[5] has described the application of TLC by selective mobile phases in separation of numerous groups of substances of polar and nonpolar character, among them surfactants in water, waste water and sludges. The identification was done by combination of TLC and IR. Hohm[6] introduced stable fluorescence indicators such as Thioflavin S and Primulin under long-wave UV light. Henrich[7] applied six chromatographic systems on hundred and fifty surfactants on commercial cleaning agents. He has done the reflexion spectra absorbing in UV area. Kruse, Buschmann and Cammann[8] separated different types of surfactants by four-fold development on silica plates.

This paper describes the separation of different groups of surfactants (anionic, nonionic, cationic, amphoteric) by HPTLC on silica plates. A new mode of detection on the thin layer with water is introduced after single development with ethanol.

Table 1

Anionic and Amphoteric Surfactants Investigated

Product Name	Manufacturer	Chemical Composition
Anionics:		
Cocoa soap	Lab	Sodium laurate
Na diheptyl sulfosuccinate	Merck	Sodium diheptyl sulfosuccinate
Na n-dodacyl sulfate	Merck	Sodium n-dodecyl sulfate
Texapon TN 25	Henkel	Sodium laurilether sulfate
Rewopol NOS-5	Rewo	Sodium nonylphenolpentaethoxy sulfate
Geronol ACR 9	Geronazzo	Disodium nonylphenolnona ethoxy sulfosuccinate
Emulgator RF-9P	Kutrilin	Sodium nonylphenolnonaethoxy phosphate
Hostapur SAS 60	Hoechst	Alkane sulfonate
Rhodacal 70 B	Rhone Poulenc	Calcium dodecylbenzene sulfonate
Amphoterics:		
Rewoteric AM B13	Rewo	Cocoamidopropyl betaine
Rewoteric AM KSF 40	Rewo	Sodium cocoamphopropionate

EXPERIMENTAL

Reagents

All chemicals used were of p. a. grade and were obtained from Merck, Darmstadt. As the developers, absolute ethanol, 95 %, and 90 % ethanol were used. As the reagents of detection, iodine and distilled water were used.

Samples

The surfactants used were of p. a. grade, Merck, commercial products of different producers and the samples made in the laboratory. The composition of the samples was controlled by IR and ^{1}H-NMR spectra. Tables 1 and 2 show the investigated surfactants with their commercial names, manufacturers, chemical composition and charge type.

Table 2

Nonionic and Cationic Surfactants Investigated

Product Name	Manufacturer	Chem. Composition
Nonionics:		
Dehydol 3	Henkel	Fatty alcohols $C_{12}C_{14}$ + 3 EO
Brij 35	Merck	Fatty alcohols C_{12} + 23 EO
Tenzilin AA 65	lab	Fatty alcohols $C_{16}C_{20}$ + 11 EO
Tenzilin 1086	lab	Unsaturated fatty alcohols $C_{16}C_{18}$ + 3EO
Tenzilin 676	lab	Stearic acid + 20 EO
Tenzilin 65UR	lab	Castor oil +40 EO
Rokafenol 9	Rokita	Nonylphenol + 9 EO
Marlophen 814	Huls	Nonylphenol + 15 EO
Marlophen 830	Huls	Nonylphenol + 30 EO
NF + 100 EO	lab	Nonylphenol + 100 EO
Synperonic OP 40/70	ICI	Mixture of octylphenol with 40 and 70 EO
Span 20	Atlas	Sorbitan monolaurate
Dehypon LS 54	Henkel	Fatty alcohols $C_{12}C_{14}$ + 5EO + 4 PO
Cationics:		
N-cetyl-N,N,N-trimethyl ammonium bromide	Merck	N-cetyl-N, N, N-trimethyl-ammonium bromide
N-dodecylpyridinium chloride	Merck	N-dodecylpyridinium chloride
Lorocid	Kutrilin	Benzyldodecyldimethyl-ammonium chloride
Arquad 12.50	Akzo	Dodecyltrimethylammonium chloride

Chromatography

Chromatographic equipment: HPTLC silica plates with fluorescence indicator, Merck: 10 x 10 cm, No. 5629; 10 x 20 cm, No. 5642. Microsyringe for TLC, Hamilton, 5 µL, No. 7005. Double chromatographic chambers, Camag (23.5 x 8.2 x 22.5 cm and 13.0 x 5.5 x 13.4 cm). UV lamp with wavelength 254 nm and 366 nm, Camag, UV-cabinet II. Glass Petri dish, diameter = 24.0 cm. Photocopy machine, Canon, NP 1215.

Chromatography was performed on 10x10 cm and 10x20 cm silica plates for HPTLC. The silica plates were prewashed with 95 % ethanol. The samples of the surfactants were solved in ethanol + water 1:1, v/v mixture to give concentrations of 50 mg/mL. The injection for TLC was used to apply the surfactant solutions 1 μL (50 μg) at the point of exactly 1 cm above the edge of the plate. The chromatograms were developed up to 6.5 cm height. The developing time was about half an hour.

As the reagents of detection UV light 254 nm and 366 nm, iodine vapour and water were used. The plates were exposed to iodine vapour in closed chambers overnight at room temperature. Iodine chromatogram was visualized under VIS and UV light, photocopied, and the plate was dipped into distilled water in a big Petri dish. The spots with gas bubbles can be observed on the water chromatogram. The number, the form, the colour and R_F values of the spots are to be observed on the water chromatogram under VIS and UV light.

Detection Of Surfactants By Charge Type[9]

Determination of charge type of surfactants was done in an ordinary way described in the literature. Anionic surfactants were detected by colour reaction with methylene blue, nonionics with KJ_3 by colour and reaction of precipitation, and cationics with bromphenol blue.

RESULTS AND DISCUSSION

By following the described separation method it is possible to achieve complete separation of the four classes of surfactants, as well as the separation of single members in the class.

Before chromatographic procedure, tests for the detection of surfactants by charge type were done.

After detection of the charge type, development with 95 % ethanol as the best proven developer follows (among absolute, 95 %, and 90 % ethanol.). The development in 90 % ethanol has not given satisfactory results; the front has been spilt due to the high percentage of water, and the nonionic surfactants

Table 3

Description of the Chromatograms and R_F Values of Some Investigated Anionic Surfactans, Which Gave the Water Chromatograms After Developing With 95 % Ethanol. HPTLC Plates Merck No. 5629

		Detection			
	$UV_{254\,nm}$	Iodine		Water, VIS	
Surfactant	R_F	R_F	Form	R_F	Form, Colour, Gas Bubbles
Coco soap	---	0.88	round	0.89-0.46	drop, white, bubbles
Na diheptyl sulfosuccinate	---	0.91	round	0.91	round, white, bubbles
Na n-dodecyl sulfate	---	0.89 0.71	round round	0.88	ellipse, white, bubbles
Rewopol NOS-5	1.00-0.80	0.92-0.62	pearls	0.92	ellipse, white, bubbles
Hostapur SAS 60	---	0.85	ellipse big	0.83	ellipse, white, bubbles
Rhodacal 70 B	0.98-0.82	0.88	square, big	0.85	ellipse, white, bubbles

---

Forms of spots: Round, ellipse, drop, tail, pearls. --- The spot is not visible.
Bubbles: Bubbles of gas are coming out of the spot after dipping of the plate into the water.

have not shown such a clear pearl finger print with iodine. (Pearl finger print means the characteristic spots with difference in mass 44 - mass of ethylene oxide).

Tables 3 and 4 show R_F values of investigated surfactants after developing with 95 % ethanol, appearance of the spots under UV light 254 nm, appearance of the spots after reaction with iodine and water, and observation of gas bubbles on some spots after dipping of the plate into distilled water.

Table 4

Description of the Chromatograms and R_F Values of Some Investigated Nonionic Surfactans, Which Gave the Water Chromatograms After Developing With 95 % Ethanol. HPTLC Plates Merck No. 5629

	Detection				
	$UV_{254\,nm}$	Iodine		Water, VIS	
Surfactant	R_F	R_F	Form	R_F	Form, Colour, Gas Bubbles
Tenzilin 676	---	0.71-0.35 0.14	pearls	0.17-0.00	dark
Marlophen 830	0.25	0.31-0.00		0.32-0.00	dark
NF + 100 EO	0.09	0.12-0.00		0.11-0.00	dark tail
Synperonic OP 40/70	0.18	0.26-0.00		0.23-0.00	dark tail

Forms of spots: Round, ellipse, drop, tail, pearls. --- The spot is not visible. Bubbles: Bubbles of gas are coming out of the spot after dipping of the plate into the water.

At first, the developed chromatograms have been examined under UV light of 254 nm wave length and there were differences between aromatics and compounds with unsaturated bonds regarding others (unsaturated alcohols, acids, glycerides). Under 366 nm only ethoxylated castor oil can be seen. Then the plates stayed in the iodine chamber over night at room temperature. The next day the plates were covered with glass and photocopied. After that the plate with iodine chromatogram was dipped into distilled water in a big Petri dish while the new chromatogram occured by reaction of water and surfactants on the thin layer. The spots of different colours appeared, with gas bubbles coming out of some of them. The water chromatogram is characteristic for individual and types of surfactants.

The anionic surfactants: sulfates, sulfonates, phosphates, succinates and sulfosuccinates, give white spots with R_F values nearly 0.90 with gas bubbles on the water chromatogram.

Alkoxylated surfactants developed with absolute and 95 % ethanol and detected with iodine give characteristic pearls similar to the pearls described by Bürger[10] given with the developer ethylacetate-acetic acid- water (7.5:1.5:1.5). Low ethoxylated compounds have higher R_F values. Nonylphenols with a higher degree of ethoxylation from 15 moles EO have R_F 0.70 and below, so nonylphenol with 100 moles EO has R_F 0.09. After dipping the plates into the water, high ethoxylated compounds show black/brown spots from the start up to a certain height dependent upon the degree of ethoxylation.

Cationic surfactants give R_F values below from 0.50 and can be seen on the iodine chromatogram under visible light. They can be also seen at the start on the water chromatogram under UV light 366 nm, while others are not visible. Some of them show other spots (grey, white, etc.) after dipping of the plate into the water.

Amphoteric surfactants stay at the starting point, but they differ from cationics because of the special form of spots on the iodine chromatogram, such as gymns. Amphoteric surfactants can be seen also on the water chromatogram under UV light 254 nm, while they are not visible under 366 nm.

In some cases, such as Na dodecyl sulfate, Texapon TN 25 and Emulgator RF-9P (anionic surfactants), it is recommendable to do the developing in absolute ethanol, and perform identification by comparing two water chromatograms. Texapon TN 25 shows three white spots on the water chromatogram with gas bubbles after developing with absolute ethanol, and Na dodecyl sulfate only one. Phosphate, Emulgator RF-9P, after developing with absolute ethanol and dipping of the plate with iodine chromatogram into the water, has shown a white round spot with gas bubbles $R_F = 0.11$. It makes a difference by comparison with high ethoxylated compounds, because they show black/brown tails at the starting position. The length of the tails is inversely proportional to the degree of ethoxylation.

In this paper, single development has been described with simple low toxicity solvent ethanol or mixtures of ethanol with water. This represents an ecological advantage for the analyst, because, in the previous procedures, more toxic solvents such as chloroform, benzene, etc. have been used. The iodine chromatograms can be photocopied. The advantage of the described chromatographic method is also in the use of water as a new, simple and nontoxic agent in the additional detection and characterization process. Consequently, except for the efficient separation of surfactants of different chemical composition, the advantages of this method are its simplicity, low cost and ecological privilege for the analyst.

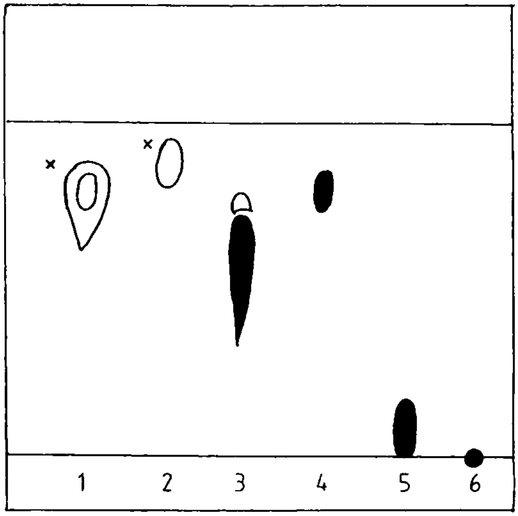

Figure 1. Water chromatogram of some tensides under UVlight 254 nm and after exposure to iodine vapour. Silicagel plate Merck No. 5629. Samples: 50 μg. Developer: 95 % ethanol.

1. Coco soap
2. Rhodacal 70 B
3. Rokafenol 9
4. Dehypon LS 54
5. Arquad 12.50
6. Rewoteric AM KSF 40

White spots signed with x give gas bubbles.

CONCLUSION

A new method for the detection of surfactants on the thin layer has been discovered and described here to assist in identification of surfactants. The anionic surfactants (sulfates, sulfonates, phosphates, succinates, sulfosuccinates) have given white spots with evolution of gas bubbles. High ethoxylated compounds have migrated in the form of black/brown tails from the start. Amphoteric surfactants differ from other groups of surfactants because they stay at the starting point and can be seen such as dark dots, after the reaction with water, under UV light 254 nm.

It has been shown that the absolute and 95 % ethanol can be successfully applied in separation of different surfactants.

As the agents of detection, UV light 254 nm and 366 nm, iodine, and water have been used. The iodine and water chromatograms have been examined under visible light and under UV light 254 nm and 366 nm.

The iodine chromatograms have been photocopied before dipping the plates into the water (Fig. 1, for example).

Experience of the chromatographer, as well as auxiliary tests for the detection of surfactants by charge type, are required. A combination of other analytical methods, such as ion exchange and TLC/IR is recommended. This method also represents a contribution to the decrease of use of toxic chemicals the analyst uses at his work.

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