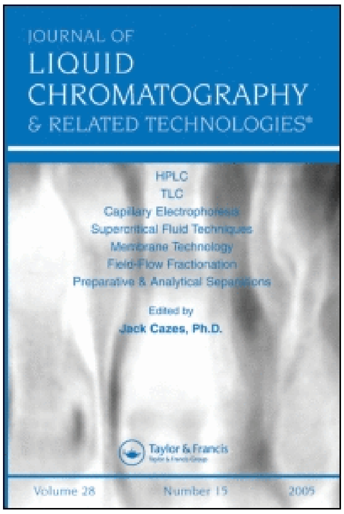

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WATER AS A DETECTING AGENT IN THIN LAYER CHROMATOGRAPHY OF SURFACTANTS

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ABSTRACT

Appearance of gas bubbles coming out from the spots of some surfactants on silica plates was examined. The plates were dipped into water after chromatograms had been developed. Experimental results had shown that only anionic surfactants gave white spots with gas bubbles (rare and slightly some nonionic surfactants, and never cationics). Therefore, this occurrence can be used for detection (and identification) of anionic surfactants, and for determination of polarity of surfactants.

On the basis of the experiments done, it was concluded that the bubbles were air bubbles liberated out of silica gel pores, influenced by water. This occurrence was caused, on one hand, by characteristic negative charge of the silica gel surface which provoked weaker binding of anionic surfactants. On the other hand, anionic surfactant molecules are built from negatively charged hydrophilic head and hydrophobic chain entities that enable foaming.

At the interface, silica gel/water anionic surfactants are oriented with hydrophilic heads toward water, and with hydrophobic tails which are poorly bonded to silica gel. Air bubbles appear; a layer of anionic surfactant is formed around the air bubble (foaming). At the water/air interface, the monolayer is formed by surfactant molecules, the surface tension of water is decreased, and emergence of air bubbles from silica gel pores is made possible (water is entering and driving air out of the silica gel pores).

INTRODUCTION

Detecting agents in thin layer chromatography are often toxic or corrosive (sulfuric acid, ammonium hydroxide, aniline-phosphoric acid, antimony chloride, etc.).[1] For this reason nontoxic detection agents, like water, in chromatography of surfactants are a great advantage.

In our previous paper[2] separation and characterization of surfactants by high performance thin layer chromatography was described. For the first time we reported on the application of water as a detecting agent. Experiments have been done on HPTLC silica plates with fluorescent indicator, 10 x 10 cm, No. 5629 and 10 x 20 cm, No. 5642 (Merck). 50 μg of surfactant was applied per spot by injection for TLC. Auxiliary methods in the classification of surfactants by charge type color reactions, obtained by indicator dyes (methylene blue, KJ_3, and bromphenol blue), have been used to determine the charge. The described HPTLC method has been tested on 28 different surfactants, for which the R_F values, forms and colors of spots, and gas bubbles have been determined.

The surfactants were developed in ethanol and ethanol-water (up 20 % of water). Developed chromatograms were 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). Then the plates stayed in the iodine chamber at room temperature overnight. The next day the plates were covered with glass and photocopied. After that the plate was dipped into distilled water in a big Petri dish while the new chromatogram appeared by reaction of water and surfactants on the thin layer. The water chromatogram is characteristic for individual and types of surfactants:

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.

Nonionic surfactants developed with absolute and 95 % ethanol and detected with iodine, give characteristic pearls similar to the pearls described by Bürger[3] 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 the plates are dipped 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 0.50 and can be seen on the iodine chromatogram under visible light. They can also be 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 the plate is dipped 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 as the dots at start.

With the experiments described in this paper we made an effort to examine causes that generate white spots and gas bubbles in contacts of silica gel and water at the presence of some surface active agents. We attempted to explain this occurrence.

MATERIALS

Reagents

All chemicals used were of p. a. grade and were obtained from Merck, Darmstadt. As the developers, absolute ethanol, ethanol-water (up to 20 % water), ethylacetate-acetic acid-water (7.5:1.5:1.5), and chloroform-methanol (6:1) were used.

As detecting agents, distilled water, water purified from air by boiling, water saturated with CO_2 (soda-water), absolute ethanol, ethanol-water (1:1), and chloroform, were tested.

HPTLC silica gel plates with fluorescent indicator, Art. 5629, Merck, were used for chromatography.

Silica gel powder for TLC Kieselgel HF_{254}, Art. 7739, Merck, was used in the experiments to the larger scale (balls).

Table 1

Investigated Surfactants

Product Name	Manufacturer	Chemical Composition
Jugopon	Kutrilin	Sodium dodecylbenzene sulfonate
Texapon N25	Henkel	Sodium laurylether sulfate
Rewoquat WE 20	Witco	Quaternary ammonium metosulfate
Rewoquat W 75	Witco	1-Methyl-2-tallow-fatty acid-acid amidoethylimidazolinium metasulfate
Brij 35	Merck	Lauryl alcohol with 23 moles EO
Tenzilin AA65	Kutrilin	Fatty alcohols $C_{16}C_{20}$ with 11 moles EO

Samples

Examined surfactants of various charge types are listed in Table 1.

Methods

Surfactants were separated and characterized as was described in the previous paper[2] and shortly in the introduction. Silica plates with developed chromatograms were dipped into various kinds of water (water was in Petri dishes): in regular distilled water, in water purified from air by boiling, and in water saturated with CO_2. The plates with developed chromatograms were also dipped into absolute ethanol, in ethanol-water (1:1), and in chloroform.

Experiments to a larger scale were made. The balls made from surfactant (2.35 g) and silica gel powder (1.20 g) were formed by hand. These balls were dipped into glasses with water to observe occurrence of gas bubbles. Water and air temperature was 15°C.

There were six glasses, in every glass of 40 mL distilled water pH 6. Into each glass one ball made from the mixture of surfactant and silica gel powder was placed to observe the occurrence of gas bubbles. Six balls were made from the six surfactants listed in Table 1.

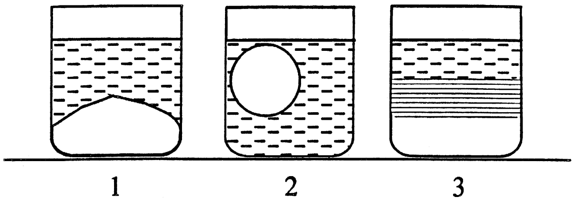


Figure 1. Experiment with balls of surfactants and silica gel in water the next day. 1. Solution of anionic surfactant in water, and silica gel at the bottom (sodium dodecylbenzene sulfonate). 2. Ball of cationic surfactant with silica gel floating in water (quarternary ammonium metosulfate). 3. Solution and emulsion of nonionic surfactant with water, and silica gel at the bottom (lauryl alcohol ethoxylate with 23 moles EO).

RESULTS

After developing of chromatograms with two representatives of surfactant classes (2 anionics, 2 cationics, and 2 nonionics), dipping the plates into distilled water, into water purified from air by boiling, and into water saturated with carbon dioxide, always at the places with anionic surfactants, in all cases, white spots with gas bubbles appeared. Each plate was dipped several times into the water and dried. Generation of bubbles was reversible.

In the experiments where developed chromatograms were dipped into absolute ethanol, into ethanol-water (1:1) mixture, and into chloroform, bubbles never appeared.

In the experiments with balls made from powder silica gel and surfactants, thrown into water, the following was observed:

After throwing single balls into the water different occurrences could be seen. For the first 30 minutes bubbles were coming intensively out of two balls with anionic surfactants. With cationic surfactants balls no bubbles were coming out at all. With nonionic surfactants balls bubbles were coming out slightly and very slowly.

Appearance of balls in water, solutions, and emulsions was characteristic the next day (Figure 1). The balls with anionic surfactants were strewed down in the cones at the bottom of the glasses. The balls with cationic surfactants stayed formed. The balls with nonionic surfactants were solved and emulsified. The next day in the glasses with nonionic surfactants, a flat layer of silica gel at the bottom, white emulsion above it, and clear solution at the top, could be seen. Measured pH in all solutions was 6 the next day. Not until ten days were the balls with cationic surfactants flattened and fell down to the bottom.

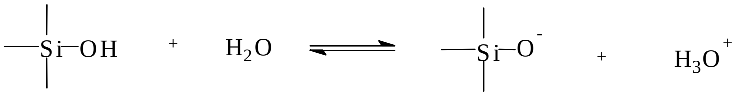
DISCUSSION

Results of the experiments made, clearly show that after development of surfactants on thin silica layer with the developer ethanol-water followed by dipping the plates into water, white spots and gas bubbles generate only where anionics are present. The same way, the experiments with the balls show that the bubbles develop in the presence of anionics, very slightly in some cases of nonionics, but never cationics. The results also show that the bubbles occur only in water, never in another solvents like ethanol or chloroform. There is a question: Why do anionic surfactants have such an influence in contact with water?

Considering the observed results of the experiments, consulting the corresponding literature, it can be supposed that detection tests with water on a thin silica gel layer can be based on physical and chemical properties of surfactants and silica gel, their interface acting, and the action of other participants in the process at silica gel/surfactant/water/air interfaces.

Silica gel is a sorbent with a large specific surface area, large specific pore volume, and a high energy surface. Work for adhesion at interface water/SiO_2 is 388 erg/cm^2.[4] Average pore radius is 2,5 nm.

Some authors[4] consider silica gel negatively charged in water, because they suppose there is -OH ionization:



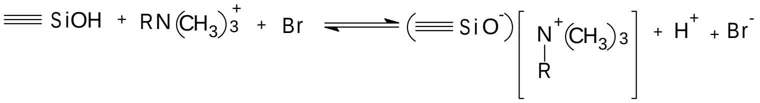
$$\equiv Si{-}OH + H_2O \rightleftharpoons \equiv Si{-}O^- + H_3O^+$$

But, a higher degree of ionization is not likely, because the constant of this balance reaction was determined to be 10^{-6}-10^{-8} values, which means really low values.[5] Beside that, it was experimentally determined that even strong acids, respectively their H^+, were strongly bonded to silica gel.[6]

Thus, it was confirmed that silica gel strongly bonds positive ions, but this bonding cannot be based on ionization of silica gel.

We considered that an oxygen atom in dipole group -OH possesses free electron pairs. Their negative charge is much bigger than positive H^+ charge, therefore the surface of a silica gel particle acts rather negatively than positively.

Cationic surfactants don't generate bubbles in detection test with water, because they are firmly bonded with negative surface of silica gel particles:



$$\equiv SiOH + RN(CH_3)_3^{+} + Br \rightleftharpoons (\equiv SiO^{-})\left[\begin{matrix} N^{+}(CH_3)_3 \\ | \\ R \end{matrix}\right] + H^{+} + Br^{-}$$

Silica gel/alkyl trimethyl ammonium bromide.

Strong bonds between silica gel and cationic surfactants were proven by chromatography; their spots have low R_F values or stay at the beginning.

Nonionic surfactants are bonded to silica gel by hydrogen bonds. In rare cases, when these bonds are weak, as with low ethoxylated alcohols (C_{12} with 3 moles EO), there can be an occurrence of bubbles in test with water. Ethoxylates with 6 moles or more don’t generate bubbles. Highly ethoxylated compounds with 30 and more moles EO are firmly bonded to silica gel and can be seen as tails at the beginning.

Anionic surfactants are bonded to silica gel slightly. Therefore, under influence of water, they easy liberate silica gel pores, decrease surface tension at interface water/air, and release air bubbles from silica gel pores.

It can be considered that gas, going out of the spots with anionic surfactants on thin silica gel layer after dipping the plate into the water, has to be air from silica gel pores. This opinion is based on the following:

- There is no gas which can be generated in eventual chemical reaction of anionic surfactant with silica gel and water.

- Air is coming out of silica gel, not out of water, because experiments have been made with water purified from air by boiling where bubbles have generated equaly as with the water saturated with air or with the water saturated with carbon dioxide.

Generation of bubbles is reversible. The bubbles are generated after dipping the plate with anionic surfactant on thin silica layer. After drying the plate and repeated dipping, the bubbles occurr again. The procedure can be repeated 5-6 times, while all anionics will be resolved in water (it is applied 50 μg/spot).

Water is indispensable for generation of bubbles. The bubbles don’t occurr after dipping the plate into absolute ethanol, choroform, or the mixture ethanol-water (1:1). There are more bubbles from the spots on developed chromatograms than from the spots at the beginning. The reason is bigger surface (and volume) of silica gel covered with surfactant after developing.

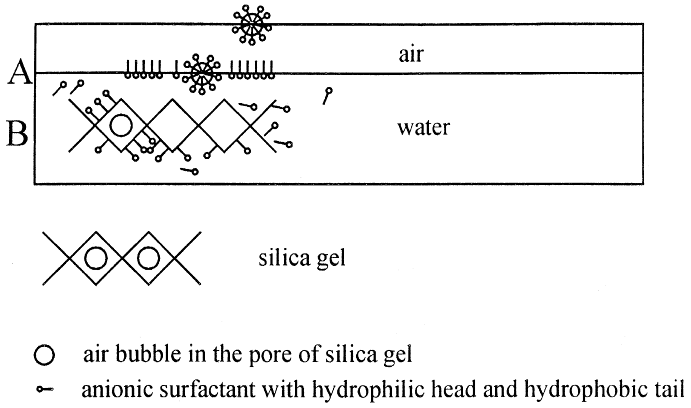


Figure 2. Orientation of anionic surfactant molecules at the air/water (A) and silica gel/water (B) interfaces.

Since anionic surfactant molecules are built from negatively charged hydrophilic head and hydrophobic chain, their physical and chemical characteristics, in combination with previously mentioned surface properties of silica gel, make possible the liberation of air out of silica gel pores in the form of visible bubbles.

In Figure 2. orientation of anionic surfactant molecules can be seen at silica gel/air/water interfaces toward experimental results in this paper, and regardless, todays knowledge in the physical chemistry field.[7-11]

At silica gel/water interface, surfactants are oriented with hydrophilic heads to water, and with hydrophobic tails to silica gel. Bubbles are coming out; at the edges of the bubbles there is a layer of anionic surfactant (foaming). Silica gel is wetting with water by help of anionic surfactants. At water/air interface surfactant molecules generate monolayer, decrease surface tension of water, and enable liberation of air bubbles from silica gel pores (also entrance of water which drives out air).

CONCLUSION

In thin layer chromatography water as a detecting agent can be applied to characterize and identify surfactants on chromatograms. Only anionic surfactants react with water (exceptionally some nonionic surfactants too).

After dipping the plates with chromatograms into water, white spots with visible air bubbles are generated. Occurrence is reversible and can be repeated 5-6 times.

By simple physical tests an explanation of generated bubbles was found. These are air bubbles from silica gel pores. This occurrence is based on properties of silica gel (more negative surface charge and weaker bonds with anionic molecules), and physical and chemical characteristics of anionic surfactants (the molecules of which composed of negative hydrophylic head and hydrophobic tail enable foaming).

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