

Analysis of Cationic Surfactants on the Acclaim Surfactant Plus HPLC Column

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Key Words

Acclaim Surfactant Plus, cationic surfactants, mixed mode chromatography, selectivity

Abstract

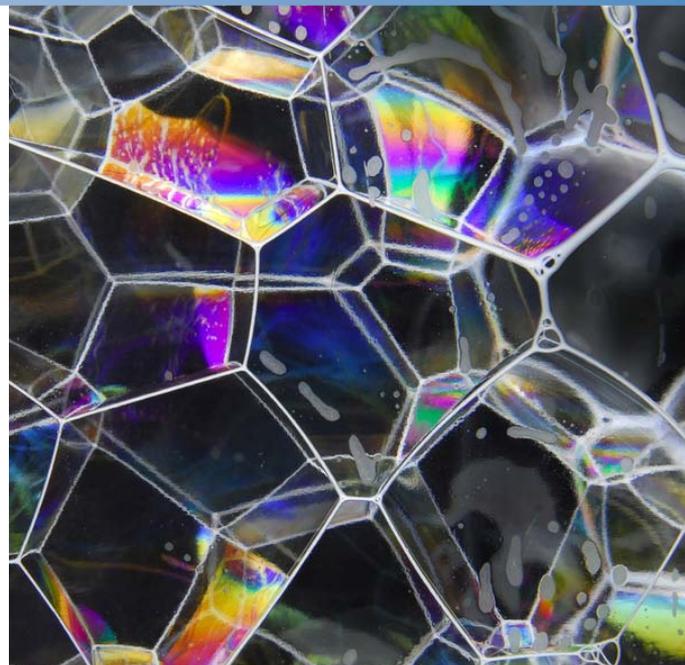
The simultaneous separation of a range of cationic surfactants using a highly selective and robust Thermo Scientific Acclaim Surfactant Plus column is described. Using a one-step gradient combined with Charged Aerosol Detection, full separation of the surfactants with baseline resolution was achieved.

Introduction

Surfactants are widely used in industrial, agricultural, and pharmaceutical markets in products as diverse as pesticides, detergent powders, petroleum products, cosmetics and pharmaceuticals. Their separation and identification can be challenging due both to the diversity of the surfactants and the complexity of the sample matrix in which they are contained. Although many different HPLC columns have been used for the analysis of surfactant formulations, none have been designed specifically for these applications in mind.

The Acclaim™ Surfactant Plus column, based on novel mixed-mode chromatography technology and advanced surface chemistry, provides both reversed-phase and anion exchange mechanisms, which is controlled by mobile phase ionic strength, pH, and/or organic solvent type and composition. This results in a specific elution order of cationic, nonionic, amphoteric and anionic surfactants and is therefore a highly selective column. In addition, the surface chemistry of the Acclaim Surfactant Plus column effectively deactivates surface silanol activity, thereby decreasing peak asymmetry by decreasing the degree of secondary analyte/silanol interaction with the stationary phase. This makes it ideally suited for the analysis of cationic surfactants such as alkyl quaternary ammonium, benzylalkylammonium and alkyl pyridinium salts.

Surfactants typically do not contain a UV chromophore, so they are measured directly with non-suppressed or suppressed mode conductivity or indirectly using photometric detection. Charged aerosol detection can measure any non-volatile and many semi-volatile compounds, typically to low ng sensitivity. Furthermore,



as response is similar for all compounds and independent of chemical structure, charged aerosol detection is ideal for measurement of surfactant species.

The purpose of this investigation is to demonstrate the effectiveness of the Acclaim Surfactant Plus column in separating a range of cationic surfactants under reversed-phase conditions.

Experimental Details

| Consumables | Part Number |
|---|--------------|
| Fisher Scientific water (HPLC gradient grade) | W/0106/17 |
| Fisher Scientific acetonitrile (HPLC grade) | A/0626/17 |
| Fisher Scientific propan-2-ol (HPLC grade) | A/4612/12 |
| Fisher Scientific ammonium acetate | A/3440/53 |
| Fisher Scientific acetic acid | A/0406/PB15 |
| Fisher Scientific Finnpiptette F2 pipettor kit (10 µL - 100 µL, 100 µL - 1000 µL, 1 mL - 10 mL) | PMP-020-220F |
| Fisher Scientific Finntip pipette tips, 200 µL | PMP-107-600F |
| Fisher Scientific Finntip pipette tips, 1000 µL | PMP-103-206K |
| Fisher Scientific Finntip pipette tips, 10 mL | PMP-107-040R |
| Thermo Scientific borosilicate glass vials (2 mL, 12 mm x 32 mm) with 8 mm black screw cap fitted with a silicone/PTFE seal | 60180-600 |

Sample Preparation

| | |
|-----------------------|---|
| Analytical standards: | Primary standards of cetylpyridinium chloride (CPyCl), dodecylpyridinium chloride (DdPyCl), benzalkonium chloride (BzACl), dodecyltrimethylammonium bromide (DdTmABr) and cetyltrimethylammonium bromide (CTmABr) were prepared separately in water at a concentration of 1000 µg/mL. A working standard was prepared in water by combining 2 parts CPyCl, followed by 1 part each of DdPyCl, BzACl, DdTmABr and CTmABr with 4 parts water. The concentration for CPyCl was 200 µg/mL and 100 µg/mL for the other analytes. |
|-----------------------|---|

| Separation Conditions | Part Number | | | | | | | | | | | | | | |
|--------------------------------|---|-------------|------|-------------|------|-------------------|--------|---------------|----------|--------------------------------|------------|---------|----------------------------|------|----|
| Instrumentation: | Thermo Scientific UltiMate 3000 HPLC equipped with a Charged Aerosol Detector | | | | | | | | | | | | | | |
| Column: | Acclaim Surfactant Plus 3 µm, 100 x 2.1 mm 078955 | | | | | | | | | | | | | | |
| Mobile phase A: | Ammonium acetate, 100 mM, pH 5 / propan-2-ol (95:5 v/v) | | | | | | | | | | | | | | |
| Mobile phase B: | Acetonitrile / propan-2-ol (95:5 v/v) | | | | | | | | | | | | | | |
| Flow rate: | 0.4 mL/min | | | | | | | | | | | | | | |
| Run time: | 10 minutes | | | | | | | | | | | | | | |
| Gradient: | <table border="1"> <thead> <tr> <th>Time (min)</th> <th>%B</th> </tr> </thead> <tbody> <tr> <td>0.00</td> <td>20</td> </tr> <tr> <td>0.50</td> <td>20</td> </tr> <tr> <td>4.00</td> <td>40</td> </tr> <tr> <td>7.00</td> <td>40</td> </tr> <tr> <td>7.01</td> <td>20</td> </tr> <tr> <td>10.0</td> <td>20</td> </tr> </tbody> </table> | Time (min) | %B | 0.00 | 20 | 0.50 | 20 | 4.00 | 40 | 7.00 | 40 | 7.01 | 20 | 10.0 | 20 |
| Time (min) | %B | | | | | | | | | | | | | | |
| 0.00 | 20 | | | | | | | | | | | | | | |
| 0.50 | 20 | | | | | | | | | | | | | | |
| 4.00 | 40 | | | | | | | | | | | | | | |
| 7.00 | 40 | | | | | | | | | | | | | | |
| 7.01 | 20 | | | | | | | | | | | | | | |
| 10.0 | 20 | | | | | | | | | | | | | | |
| Column temperature: | 30 °C | | | | | | | | | | | | | | |
| Injection volume: | 2 µL | | | | | | | | | | | | | | |
| Charged aerosol detector: | <table border="1"> <tbody> <tr> <td>Total flow:</td> <td>1.00</td> </tr> <tr> <td>Flow ratio:</td> <td>1.00</td> </tr> <tr> <td>Ion trap voltage:</td> <td>20.6 V</td> </tr> <tr> <td>Gas pressure:</td> <td>34.9 psi</td> </tr> <tr> <td>Nebulizer temperature control:</td> <td>ON = 25 °C</td> </tr> <tr> <td>Corona:</td> <td>Normal = 2.79 kV = 1.00 µA</td> </tr> </tbody> </table> | Total flow: | 1.00 | Flow ratio: | 1.00 | Ion trap voltage: | 20.6 V | Gas pressure: | 34.9 psi | Nebulizer temperature control: | ON = 25 °C | Corona: | Normal = 2.79 kV = 1.00 µA | | |
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Results

Under reversed-phase, gradient conditions, full separation with baseline resolution of the cationic surfactants was achieved. Separation was tightly controlled using a highly buffered aqueous mobile phase of ammonium acetate adjusted to pH 5 with acetic acid.

The repeatability in the performance of the Acclaim Surfactant Plus column for the chromatographic separation of the cationic surfactants is summarized in Table 1. It is evident that the data are matched with excellent precision, with %RSDs for the retention times and resolutions ≤ 0.10 and ≤ 1.99 for all analytes, respectively. A typical chromatogram for the six cationic surfactants is shown in Figure 1.

Benzalkonium chloride is composed of a mixture of benzalkonium chlorides with various even number alkyl chain lengths. The homologs $n\text{-C}_{12}$ and $n\text{-C}_{14}$ in benzalkonium chloride products comprise the major portion of the alkyl groups¹, which would account for the two benzalkonium chloride peaks observed. The separation of the benzalkonium chloride homologs has been previously demonstrated on the Acclaim surfactant column.²

| Analyte | Analyte Name | Retention Time | | Resolution | |
|---------|-----------------------------|----------------|-------|------------|-------|
| | | Mean (min) | % RSD | Mean | % RSD |
| 1 | ddTMABr | 5.18 | 0.07 | N/A | N/A |
| 2 | DdPyCl | 5.46 | 0.05 | 2.56 | 0.76 |
| 3 | BzACl ($n\text{-C}_{12}$) | 6.32 | 0.04 | 8.61 | 0.69 |
| 4 | BzACl ($n\text{-C}_{14}$) | 7.50 | 0.05 | 11.34 | 0.83 |
| 5 | ATmABr | 7.93 | 0.06 | 3.32 | 0.86 |
| 6 | CPyCl | 8.20 | 0.10 | 1.71 | 1.99 |

Table 1: Chromatographic performance of the Acclaim Surfactant Plus column. Statistical assessments based on data derived from 10 replicate injections.

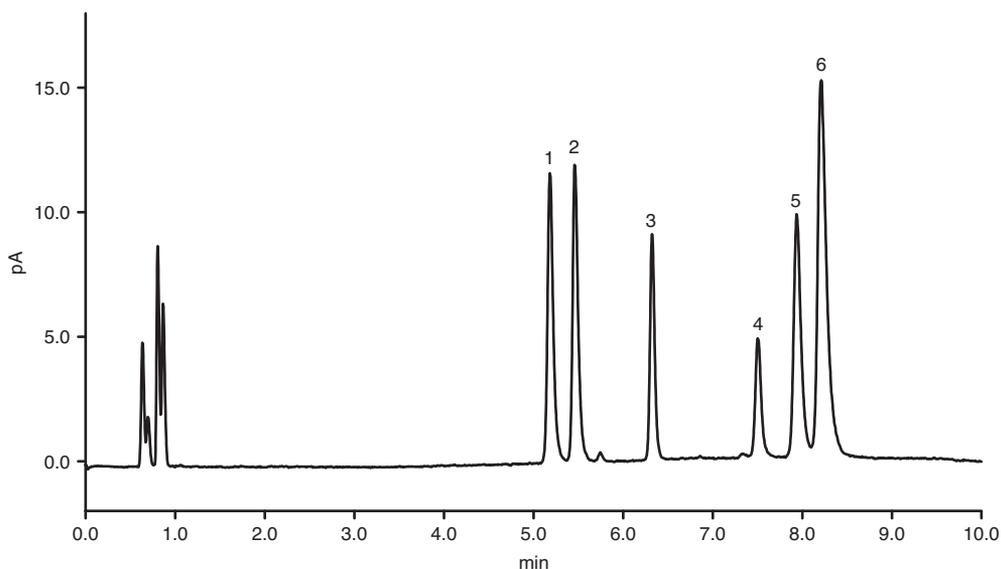


Figure 1: Separation of dodecyltrimethylammonium bromide (1), dodecylpyridinium chloride (2), benzalkonium chloride (3,4), cetyltrimethylammonium bromide (5) and cetylpyridinium chloride (6)

Conclusion

The Acclaim Surfactant Plus column can be used for the successful separation of cationic surfactants. Under reversed-phase, gradient conditions, baseline resolution with excellent peak shape is achieved for all the cationic surfactants within ten minutes.

The Acclaim Surfactant Plus column features reversed-phase and anion-exchange retention mechanisms. By modifying the ionic strength, pH, or the organic solvent type and composition, the retention and selectivity of surfactants can be optimized for total control of the elution profile. This makes the Acclaim Surfactant Plus column ideally suitable for the separation of a range of cationic, anionic, nonionic and amphoteric surfactants.

References

1. Y.W. Yang, W.Q. Zhang, Y. Zhu, Simultaneous Determination of Quaternary Ammonium Salts in Antiseptics by High-Performance Liquid Chromatography. *Chin. J. Health. Lab. Tech.* 2006, 16(7), 823-824.
2. Analysis of Benzalkonium Chloride on the Acclaim Surfactant Column by High-Performance Liquid Chromatography. Thermo Scientific (formerly Dionex), Application Note 237.

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