

# Articles

## New Analytical Method Using Polar Modifiers in Supercritical Fluid Chromatography and Its Application to the Separation of Fatty Alcohol Ethers

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Fatty alcohol ethers, nonionic surfactants which are used as general purpose emulsifiers were separated by use of water-modified carbon dioxide mobile phase in capillary supercritical fluid chromatography. Much greater peak intensities and improved separation were observed in the chromatogram with on-line modified mobile phase than with pure CO<sub>2</sub>. A simple method for the preparation of on-line modified mobile phase is also introduced.

### Introduction

The surfactant industry has grown considerably in the last few years. There is an increasing amount of research and development being done in this area, and many products such as detergents, emulsifiers, foaming agents and cleaners are being prepared. Supercritical fluid chromatography (SFC) has proven to be feasible techniques for the analysis of surfactants.<sup>1</sup> SFC uses the increased solubility of a substance at supercritical pressures and temperatures in order to provide highly efficient separations of high molecular weight and complex samples.

Fatty alcohol ether surfactants are usually analyzed by high performance liquid chromatography (HPLC). The main deficiency of HPLC in the analysis of surfactants is the absence of a sensitive universal detector. Kudoh demonstrated separation of fatty alcohol ether surfactants according to alkyl chain length by reverse-phase HPLC using refractive index detection.<sup>2</sup> Fluorescence detection may also be applied to fatty alcohol ether surfactants if a suitable derivatizing agents, such as 1-anthroylnitrile, is used.<sup>3</sup> Reversed-phase chromatography is then preferred even for determination of ethoxy chain length, since the excess derivatizing reagent interferes with the more common normal phase approach. Nozawa and co-workers formed the esters of fatty alcohol ethers, with 3,5-dinitrobenzoyl chloride to permit UV detection.<sup>4</sup> The resulting 3,5-dinitrobenzoyl esters were separated on a reversed-phase column (LiChrosorb RP-2) using a mobile phase of 60:40 acetonitrile/water.

For the analysis of surfactants, difficulties arise when the solutes cannot be detected easily at trace levels by a UV detector of HPLC because of lack of UV-absorbing chromophores. GC is not helpful either, because most surfactants have high molecular weights. A distinct advantage of SFC is the wide range of detector compatibility. SFC can be interfaced to simple, sensitive universal detectors (FID, Mass, NPD etc.).

The main limitation of SFC lies in the limited solubility

of compounds with polar groups in supercritical fluids such as carbon dioxide. Owing to the absence of polar single-component solvents with acceptable critical properties and safety requirements for SFC, mixed mobile phases are the only alternative when more polar fluids are needed. Organic modifiers can be introduced into the eluent system in a number of ways. Several workers<sup>5</sup> used cylinders with CO<sub>2</sub> doped with methanol, 2-propanol, or other modifiers which are commercially available. A distinct disadvantage associated with the use of such premixed fluids, is the continuous change in the composition of the residual liquid in the cylinder during usage. To permit more accurate addition of small amounts of modifier to the CO<sub>2</sub> mobile phase, further dilution is possible by plumbing the doped CO<sub>2</sub> into one pump (say pump 'B') of a dual headed pump.<sup>6</sup> Alternatively, various mixtures of modifier in CO<sub>2</sub> can be made by mixing them in a lecture bottle or a syringe pump suggested by Yonker *et al.*<sup>7</sup> Another method reported in the literature for adding modifier to CO<sub>2</sub> was by direct mixing with the use of a Waters Model 590 microflow pump and a tubing T-piece<sup>8</sup> or a home-made high pressure low-volume mixer.<sup>9</sup>

One of the simple and effective ways for the addition of modifier to supercritical fluid mobile phase reported in the literature is to use a saturator column<sup>10</sup> which is usually a silica column saturated with polar modifiers. In our laboratory,<sup>11</sup>  $\mu$ -Porasil column saturated with polar modifiers has been used successfully as a saturator column for a while. A serious disadvantage with this system is that the amount of modifiers dissolved in the mobile phase varies as mobile phase passes through the saturator column since a modifier holding capacity of the silica column is limited. Therefore, we attempted to develop a new device for the preparation of mixed fluids for SFC which can maintain the amount of polar modifiers dissolved in supercritical fluid constant for a long time. In this paper, with this mixing device, fatty alcohol ethers which are used as surfactants, with specific applications including detergents, dyeing auxiliaries, raw materials for blended emulsifier, were separated by capillary

SFC. These surfactants did not have to be derivatized prior to being analyzed by SFC. Much greater peak intensities and improved separation were observed with modified mobile phase than with neat CO<sub>2</sub>.

### Experimental

A Lee Scientific Series 600 supercritical fluid chromatography was used with a 100  $\mu\text{m}$  ID $\times$ 20 m capillary column (SB-biphenyl-30, film thickness 0.25  $\mu\text{m}$ ). This system was equipped with a timed split injector and a flame ionization detector. SFC grade CO<sub>2</sub> (Scott Specialty Gases) was used as a basic mobile phase. Experimental conditions for SFC separations were as the follows; supercritical CO<sub>2</sub> at 110  $^{\circ}\text{C}$ , pressure programmed from 170 atm to 400 atm at 5 atm/min, frit restrictor with a initial linear velocity of 5.5 cm/sec. High porous Teflon (40 $\times$ 8 mm, 2  $\mu$  porosity, ALLTECH, Deerfield, USA) was used in our mixing device. The mixing device was saturated with modifiers using a 50 mL hypodermic syringe. The mixing device was placed between a pump and an injector. To measure the quantity of a modifiers dissolved in supercritical fluid, a fuel cell type modifier sensor (Wonsung Electronics, Inc., Incheon, South Korea) was designed and made by depositing gold and platinum on a porous plastic disc.<sup>12</sup>

### Results and Discussion

In our previous paper,<sup>11</sup> water was used as a modifier and  $\mu$ -Porasil column was used as a saturator column with a similar system design to Engelhardt's.<sup>10</sup> With this design, a polar modifier (water) can be added to pressurized carbon dioxide fluid after the pump, and thus no modifier remains in the pump. However, when dealing with the use of a saturator column, it should be mentioned that a serious problem always arises. The problem is bad reproducibility of the amount of modifier dissolved in the supercritical carbon dioxide. When the same experiments were repeated several times, it was very difficult to obtain reproducible results in the chromatograms since the amount of modifier in the mobile phase does not stay constant with time.<sup>12</sup> For these reasons, a new mixing device (Figure 1) was developed, in which high porous Teflon material was used to hold a large

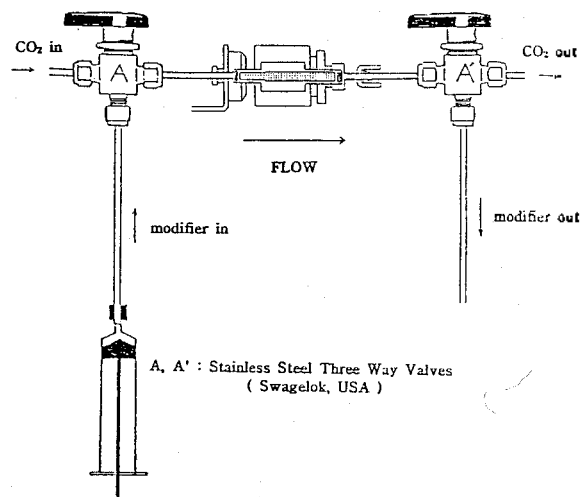


Figure 1. Mixing device.

amount of water. Two three-way valves on both sides of mixing chamber were used for adding modifier. Modifier was injected by a 50 mL hypodermic syringe. While in the saturator column,<sup>10,11</sup> water is held on the stationary phase by hydrogen bonding, with this device water is held physically inside small pores of filters. After being filled with water, the device is placed between a pump and an injector (Figure 2). With this design, supercritical CO<sub>2</sub> is delivered from the pump to the device which is filled with water. When supercritical CO<sub>2</sub> goes through the device, water held within the small pores of the filters can be dissolved in the pressurized supercritical fluids. Thus nonpolar supercritical CO<sub>2</sub> can have the characteristics of polar mobile phase because it can absorb a polar solvent, H<sub>2</sub>O. Therefore, after passing the mixing device, supercritical CO<sub>2</sub> is changed to a new mobile phase with different polarity.

To measure the amount of water dissolved in supercritical CO<sub>2</sub> after the mixing device, a similar measuring system to one in the literature<sup>12</sup> was used. The amount of water dissolved in supercritical CO<sub>2</sub> fluid after passing through the mixing device saturated with water was monitored using this sensor as a function of time.

With our mixing device, the time period of keeping a cons-

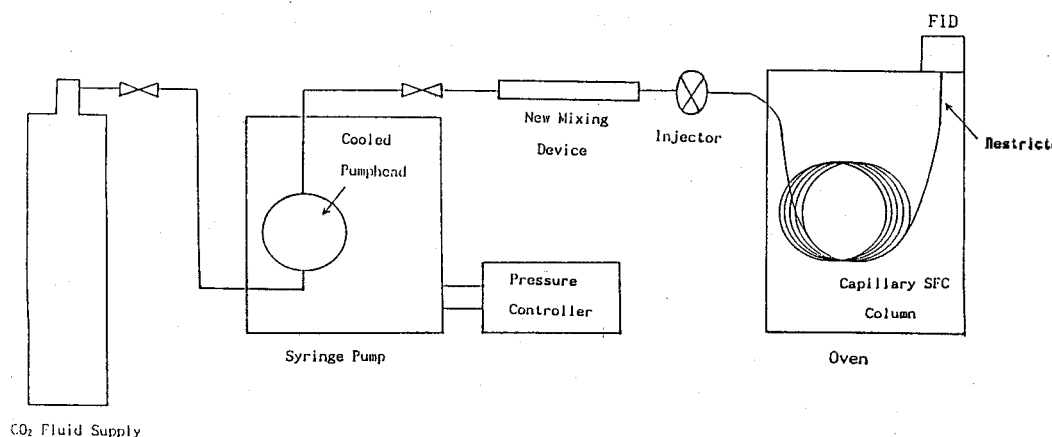
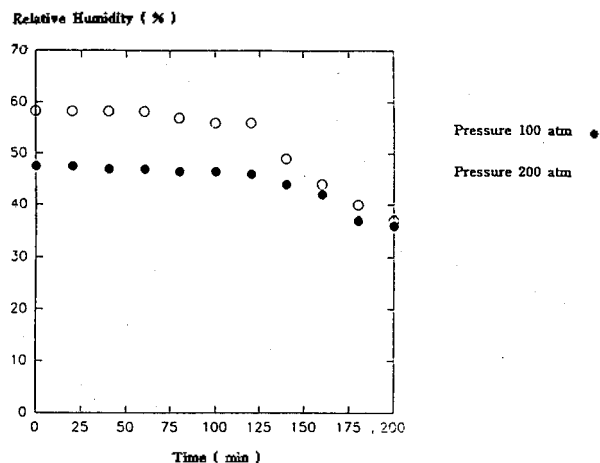
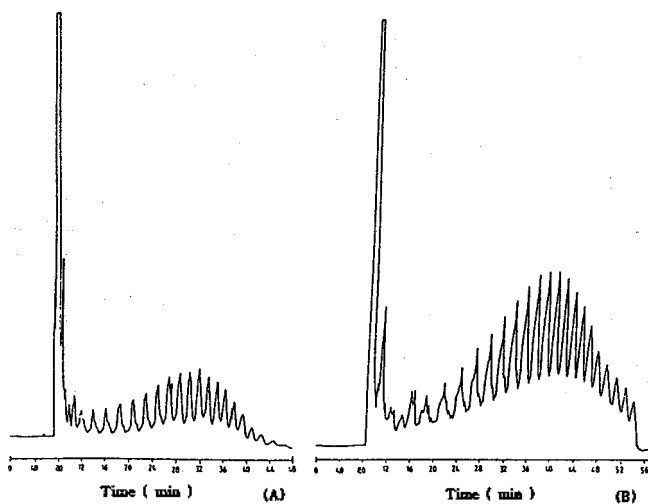


Figure 2. Schematic diagram of the apparatus used for adding a polar modifier to the supercritical fluid mobile phase.



**Figure 3.** Measurements of the water content in supercritical  $\text{CO}_2$  as a function of time with our mixing device (temperature  $24.5^\circ\text{C}$ ).



**Figure 4.** The SFC chromatograms of fatty alcohol ethers. Conditions:  $20\text{ m} \times 100\ \mu\text{m}$  i.d. capillary column; pressure programed from 170 atm to 400 atm at 5 atm/min; Oven Temperature at  $110^\circ\text{C}$ ; frit restrictor with a initial linear velocity of 5.5 cm/sec. (A) with pure  $\text{CO}_2$ ; (B) with water-saturated  $\text{CO}_2$ .

tant concentration of water was much longer (about 120 minutes, "Figure 3") than with the saturator column (about 35 minutes<sup>12</sup>). Figure 3 demonstrates that the mixing device can be used successfully to generate water-modified carbon

dioxide mobile phase. For about two hours, supercritical  $\text{CO}_2$  was changed to a more polar mobile phase, going through this mixing device, thus it was possible to separate polar samples using this new mobile phase. As an example of the ability of SFC to analyze polar polymers using our mixing device, one surfactants, fatty alcohol ether was chosen. This material contains pure ethoxylated  $\text{C}_{18}\text{H}_{35}\text{OH}$  with a small amount of the free alcohol. This sample is one example of a material which requires derivatization prior to analysis by GC or HPLC, but which was run by SFC underivatized. Figure 4 demonstrates the SFC results obtained from a fatty alcohol ether surfactant sample. Figure 4A is a chromatogram of being used with pure  $\text{CO}_2$  and Figure 4B is a chromatogram of being used with modified  $\text{CO}_2$  at the same conditions. The addition of water to supercritical  $\text{CO}_2$  using our mixing device improved the peak shape, peak intensity and resolution, and these results are matched with previous reports.<sup>8,10</sup> The stationary phase (SB-biphenyl-30) used is not polar, yet provides some selectivity due to the mobile pi electrons of the phenyl rings. The chromatogram in Figure 4B verified this polymeric surfactant has 24 ethylene oxide units. All twentyfour oligomeric units are visible on the chromatogram of Figure 4B, although only 20 ethylene oxide units are visible on the chromatogram with pure  $\text{CO}_2$ .

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