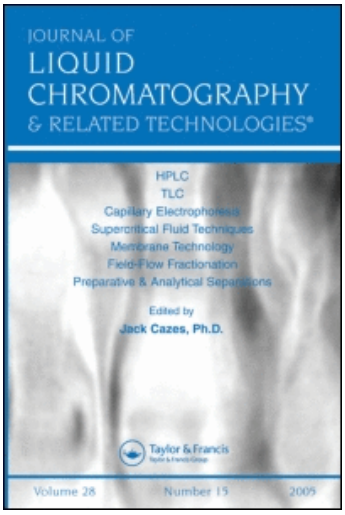

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Use of an Aqueous Micellar Mobile Phase for Separation of Phenols and Polynuclear Aromatic Hydrocarbons via HPLC

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USE OF AN AQUEOUS MICELLAR MOBILE PHASE FOR SEPARATION OF PHENOLS AND POLYNUCLEAR AROMATIC HYDROCARBONS VIA HPLC

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ABSTRACT

An aqueous solution of sodium dodecyl sulfate (SDS) micelles is shown to be a novel, highly effective mobile phase in high performance liquid chromatography. Using a reverse phase column, nine phenols and two polynuclear aromatic hydrocarbons were easily separated. The possible advantages and disadvantages of aqueous micellar solutions over traditional organic and mixed solvent mobile phases is discussed.

INTRODUCTION

The unusual properties of surfactant aggregates, or micelles, have been shown to be useful in a wide variety of analytical techniques (1-4). The use of micelles was recently extended into the field of liquid chromatography (5-7). In this paper the use of aqueous micellar solutions as the mobile phase in high performance liquid chromatography (HPLC) is reported. For some HPLC separations it is believed that the use of micellar mobile phases can offer significant advantages over traditional organic solvent or mixed solvent systems. Possible advantages are: 1. Many hydrophobic, amphiphilic, and even some hydrophilic molecules interact differentially with micelles. 2. HPLC grade organic solvents

are generally expensive, whereas dilute aqueous micellar solutions can often do as good a separation at a small fraction of the cost. 3. The elimination of trace amounts of contaminants from organic solvents is generally more difficult than purifying the water and crystalline surfactant which make up the micellar mobile phase. 4. One can simultaneously chromatograph hydrophobic and hydrophylic solutes with aqueous micellar solutions, whereas traditionally one would need an aqueous-organic gradient to accomplish the same task. 5. When using a refractive index detector with an organic mobile phase, the compressibility of the organic solvent can sometimes result in a fluctuating baseline. Aqueous solutions are, of course, relatively incompressible. 6. The addition of nonvolatile solutes to micellar mobile phases to control ionic strength, pH, buffer capacity and so on will not produce solubility problems (i.e., precipitation of salts).

There can also be some disadvantages in using micellar mobile phases in HPLC. For example, in preparative HPLC one must separate the final product from the surfactant by extraction, precipitation or some other technique. Also some compounds remain relatively insoluble in the presence of micelles (decachlorobiphenyl for example). In these instances (others will undoubtedly be discovered) traditional organic solvents or solvent mixtures would be the preferred mobile phase.

EXPERIMENTAL

A Varian Model 5020 liquid chromatograph equipped with a UV 254 nm_{max} detector was used for all runs. The stainless steel reverse phase column (Varian Micro-Pak MCH-10, 10μ, octadecylsilane) was 30 cm long and had an i.d. of 4 mm. Electrophoresis purity sodium dodecyl sulfate was obtained from Bio Rad Laboratories. The SDS was recrystallized several times from HPLC grade methanol until all UV absorbing impurities were removed. The mobile phase consisted of 0.1 M or 0.2 M $SDS_{(aq)}$ solutions. Double distilled water was used to make all stock solutions.

The temperature of all runs was 21°C. The samples (picric acid, hydroquinone, resorcinol, catechol, phenol, p-nitrophenol, o-cresol, o-isopropylphenol, o-nitrophenol, naphthalene and anthracene) were prepared for injection by dissolving the desired amount of material in either 0.1 M or 0.2 M $SDS_{(aq)}$ solution. The flow rate of the mobile phase was varied between 2.0 and 3.0 ml/min.

RESULTS AND DISCUSSION

A wide variety of phenols, many of which are positional isomers of one another, can be quickly and inexpensively separated by HPLC on a reverse phase column using aqueous solutions of micellar SDS as the mobile phase. In addition, very hydrophobic solutes such as naphthalene and anthracene can be separated from each other and the phenols under identical conditions (see Figure 1). Increasing the concentration of SDS in the mobile phase tended to decrease the retention times of all substances tested. This behavior is to be expected since increasing the surfactant concentration increases the number of micelles in the mobile phase (partitioning of the solutes is primarily and in many cases totally to the micellar pseudophase and not to the water). Varying the concentration of SDS also affected the relative separation of several peaks (Figure 1). For example, when the mobile phase is 0.1 M SDS, phenol and p-nitrophenol are completely resolved, whereas o-isopropylphenol and o-nitrophenol form one unresolved peak. With 0.2 M SDS as the mobile phase one can partially resolve o-isopropylphenol and o-nitrophneol. Phenol and p-nitrophenol, however, tend to overlap somewhat when 0.2 M SDS is used.

The more hydrophobic solutes, naphthalene and anthracene, had considerably longer retention times and thus are easily separated from the phenols. Both flow and concentration gradients can be used to optimize separation. At no time during this study ($Flow_{max}$ = 3 ml/min, $[SDS]_{max}$ = 0.2 M) did the column pressure become inordinately high or prohibitive. After four months of

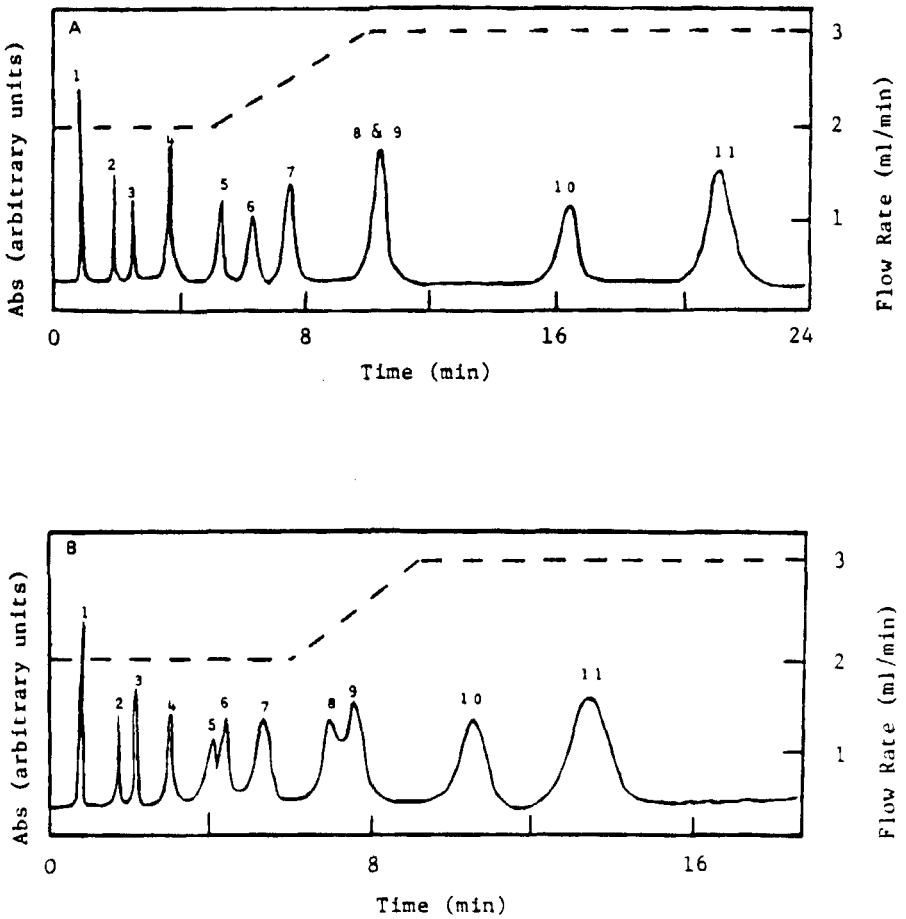

FIGURE 1. 1A shows the elution profile and retention times when 0.1 M SDS was used as the mobile phase. 1B shows the elution pattern and retention times when 0.2 M SDS was used as the mobile phase. A flow gradient was used in both cases and is indicated by the dotted line. The chart speed was 0.25 cm/min. Further details are given in the EXPERIMENTAL section. The peaks are as follows: 1. picric acid 2. hydroquinone 3. resorcinol 4.catechol 5. phenol 6. p-nitrophenol 7. o-cresol 8. o-isopropylphenol 9. o-nitrophenol 10. naphthalene 11. anthracene

use with the micellar SDS mobile phase, the reversed phase column showed no deliterious effects. When using this technique, it is advised that the column be cleaned regularly by first rinsing with

distilled water to remove the surfactant and then with methanol to remove the water and any contaminants on the column that were not easily eluted by the micellar mobile phase. To prepare a column containing methanol or some other organic solvent for use with a micellar mobile phase, simply replace the organic mobile phase with pure water, followed by the surfactant solution. Do not pump an aqueous surfactant solution directly into a column containing an organic solvent as precipitation of the surfactant might occur. For the same reason, do not pump an organic solvent directly into a column containing an aqueous micellar solution.

Although in its infancy, micellar chromatography must be considered a promising new field of study. Further research using a wider variety of surfactants and stationary phases are bound to yield interesting results on the uses and limitations of this technique.

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