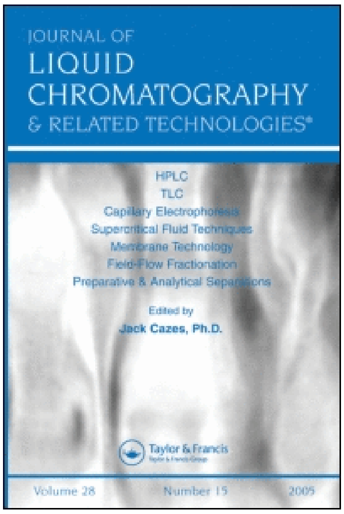

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ADSORPTION OF AN ANIONIC SURFACTANT ON AN OCTADECYL BONDED PHASE FROM A PURE AQUEOUS MOBILE PHASE

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ABSTRACT

Difficulties encountered when using pure aqueous mobile phases in ion pair reversed phase liquid chromatography are described.

The results presented in this paper show the influence of the structure and wettability of the stationary phase surface on the adsorption of an anionic surfactant (sodium octyl sulfate).

INTRODUCTION

Reversed-phase ion-pair chromatography has been well established as a method of choice for the separation of ionic or ionizable organic compounds. The main parameter for controlling the separation is the counter-ion concentration in the mobile phase. Much attention has been focused on the mechanism underlying this type

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of chromatography. Although there has been considerable disagreement on the subject, most authors agree with the fact solute retention mainly depends on the surface concentration of the surfactant (1-7) adsorbed on the stationary phase. Vital to this determination of adsorbed surfactant concentration is the establishment of an adsorption isotherm. Numerous studies have been and are being carried out on these adsorption isotherms : the shape of the isotherm depending on :

1 - the nature and the charge of the amphipilic ion (3,8)

2 - its relation with the concentration of remaining silanols

3 - its dependence on other parameters of ion pair chromatography (7,9) (nature of organic modifier, characteristics of stationary phase, nature of buffer).

Adsorption isotherms of sodium octyl sulfate (S.O.S.) were established in a wide range of chromatographically meaningful concentrations of surfactant and methanol using Hypersil ODS 5 μm as stationary phase. Ionic strength, pH of mobile phase and temperature were kept constant. Specific difficulties (i.e. non-reproducibility in the amount of adsorbed surfactant) encountered when using pure aqueous mobile phases are related in this paper. The dependence of surfactant adsorption on alkyl-bonded silica surface structure and wettability is described. These data are interpreted in terms of the "entrapment model" previously suggested by Gilpin (10,11) in which changes in solute retention were attributed to phase rearrangement solvent, the polar and non-polar nature of the solvent, the unreacted surface silanol groups, etc...).

This kind of rearrangement of hydrocarbon moieties is also described (12) as a result of the interaction between the hydrocarbon surface and other alkyl ions.

EXPERIMENTAL

The chromatographic apparatus consisted of two chromatem 380 pumps (Touzart & Matignon, Paris), a thermotemp thermostated bath (Lauda) and a model 70-10 six-part Rheodyne injection valve.

. Reagents - Sodium octylsulfate hyamine 1622 (surfactant analysis quality grade) and methanol BDH,LC grade, were purchased from Merck. H_3PO_4, NaCl and NaH_2PO_4, R.P. Normapur grade were from Prolabo. Solvents and mobile phases were filtered through PTFE (Millipore) and degassed in an altrasonic bath before use.

. Columns - Columns dimensions were 5 cm x 4.6 mm I.D. They were packed with Hypersil ODS 5 μm (Shandon-Touzart & Matignon, Paris) and Partisil 5 ODS 3 (Whatman, Interchim, Montluçon).

The known characteristics of the two packings are the following :

- Partisil 5 ODS 3 is a polymer-type, octadecyl-bonded silica. The silica had been prepared with trifunctional octadecylsilane and further capped with trimethylsilane. The carbon coverage is 10.5 %.
- Hypersil ODS is a monolayer bonded silica that has also been capped. The carbon coverage is 9 %.

. Column packing procedure - The slurry was prepared in 1.butanol (7 g bonded silica in 10 cm^3 1.butanol). The packing procedure has already been published (14). When 500 cm^3 MeOH has been passed through the column at 400 bars, the pressure is gradually decreased. Columns are then eluted with 1 liter MeOH and 1 liter H_2O.

. Measurement of the amount of adsorbed charged surfactant - When complex mobile phases are used, as is the case in IPC, surfactant adsorption and desorption are simultaneously accompanied by adsorption and desorption of the other eluent components (9,15). This is easily verified by the shape of breakthrough patterns. For this reason, the determination of breakthrough curves did not lead to sufficiently accurate and reproducible values. A single-step procedure was adopted for the determination of adsorbed C_8 sulfate concentrations : when surfactant had been adsorbed by eluting with the mobile phase and a given surfactant concentration, the adsorbed amount was then desorbed by eluting with water and further titrated using a specific reagent (hyamine 1622) (16).

The mobile phase composition used during the adsorption step was the following : 0.02M NaH_2PO_4, pH 2.0 (H_3PO_4) ; the total sodium concentration was adjusted to 0.1M with sodium chloride ; sodium octylsulfate concentration ranged from 10^{-3}M to 80 x 10^{-3}M. The column was immersed in a thermostated bath (30°C). Adsorption and desorption flow-rate was 2 $ml.min^{-1}$.

When 70 ml mobile phase had been passed through the column, the adsorbed amount of surfactant was constant. Then, the mobile phase volume corresponding to the adsorption process was fixed at 70 ml.

Using the same procedure, the mobile phase volume for the surfactant desorption was fixed at 50 ml. Total desorption was verified by measuring : the total amount of surfactant passed through the column, the adsorbed amount and the remaining amount in the mobile phase after adsorption. The desorbed amount of octylsulfate was selectively titrated (16) and corrected from the dead volume. The column dead volume was determined by injecting $NaClO_4$ and fructose dissolved either in the mobile phase or in water.

RESULTS - DISCUSSION

. Non-reproducibility in the determination of the adsorbed amounts of octyl sulfate

The adsorbed amounts of S.O.S. determined with a pure aqueous mobile phase are irreproducible over a period of time, when large volumes of eluent have been passed through the column between two adsorption-desorption measurements (Table 1). An adsorption isotherm of S.O.S. was established from the standard eluent under the conditions specified above. Octylsulfate concentrations in the mobile phase (C_m) range from 10^{-3}M to 80×10^{-3}M. For $C_m = 20 \times 10^{-3}$M, 290 $\mu mol.g^{-1}$ of S.O.S. (C_s) were adsorbed onto the C 18 bonded phase (Table 1). Complete plotting of adsorption isotherm required ∿ 2 l mobile phase. When 2 l mobile phase has been passed through the column, the isotherm point for $C_m = 20 \times 10^{-3}$M was measured again and was found to be 270 $\mu mol.g^{-1}$. Then 20 l phosphate buffer were eluted through the column and the same measurement was made

Table 1

Evolution of adsorbed amounts (μmole.g^{-1}) of C 8 sulfate as a function of aqueous solvent volume passed through the column (hypersil ODS). Each measurement is an adsorption with 70 ml of 0.02 mole/l S.O.S. and desorption with 50 ml of pure water.

	C 8 sulfate (μmole.g^{-1})
initial adsorbed amount, measurement 1 ...	290
2 l of aqueous solution passed through the column.......................	
measurement 2 ...	270
20 l phosphate buffer passed through the column	
measurement 3 ...	245
20 l H_2O passed through the column	
measurement 4 ...	230
100 ml MeOH + 100 ml H_2O passed through the column	
measurement 5 ...	230

again : the C_s value was 245 µmol.g^{-1}. After 20 l H_2O had been passed through the column again, the amount of adsorbed S.O.S. decreased again down to C_s = 230 µmol.g^{-1}. This decrease in C_s value was not observed when methanol-water mobile phases were operated.

Scott and Simpson (17) have shown that monolayers (brush-type) and polymeric-type bonded phases may exhibit very different behaviour when pure aqueous mobile phases are used. The explanation that has been put forward by these authors is that hydrocarbon chains can only exhibit dispersive interactions, so that hydrocarbon-hydrocarbon interactions will be much stronger that hydrocarbon-water interactions. This would result in a collapse of hydrocarbon chains at the bonded phase surface ; therefore, a decrease in the effective chromatographic surface may be noticed. This abnormal behaviour was observed when water-rich mobile phases containing up to 4 % W/W MeOH were used. With polymeric phases, dispersive interactions between hydrocarbon chains cannot occur because of the more rigid structure of the bonded phase. Looking at our results (Table 1), we put forward the following explanation : as Hypersil ODS is a brush-type material a slow diffusion of surface physisorbed methanol from the surface into the aqueous mobile phase may occur, resulting in a slow decrease in the effective surface area and therefore, of the amount of adsorbed surfactant.

As can be seen from Table 1, this hypothesis was verified and a regular decrease in the concentration of adsorbed surfactant was observed when passing large volumes of aqueous solutions through the column. These results can be related to those of Gilpin and coll. (10, 11) who observed significant changes in solute retention which were interpreted in terms of alkyl arrangement (from a "bristle state" into a "collapsed" state) and solvent entrapment.

Similar observations were made by Morel and Serpinet (19) when studying the influence of temperature on the retention of a solute chromatographed on a C 22 bonded phase which has (or has not) been dried previously to remove any trace of sorbed solvent.

The presence of physisorbed MeOH at the bonded phase surface has been confirmed by Bayer and coll. (20) using ^{13}C CP-MAS NMR determinations. The signal corresponding to physisorbed MeOH disappeared when the silica had been heated up to 120°C under vacuum. All earlier studies (10,11,17,19) report changes in retention related to alkyl arrangement and/or solvent release by the alkyl phase. Our aim here is to demonstrate that the decrease in specific surface due to alkyl rearrangement in a collapsed state results in a decrease in the amount of adsorbed octylsulfate onto the stationary phase. The following experiments were carried out to confirm this hypothesis.

. Influence of methanol release on C 8 sulfate adsorption - The concentration of octylsulfate in the mobile phase was 0.02 M ; adsorbed amounts were determined before and after drying the column for 8 hours with N_2 at 70°C. Two similar experiments where carried

Table 2

Adsorbed amounts of sodium octyl sulfate on two reversed-phase packings with (or without) elimination of adsorbed MeOH. Each measurement is an adsorption with 70 ml of 0.02M S.O.S. and desorption with 50 ml of pure water.

	(μmol.g^{-1}) adsorbed amount of C 8 sulfate on :	
	Hypersil ODS	Partisil 5 - ODS-3
STEP 1 initial adsorbed amount	278	310
STEP 2 N_2 (70°C, 8 hours)	20	203
STEP 3 200 ml MeOH + 100 ml H_2O	276	296
STEP 4 N_2 (70°C, 8 hours)	18	

out when the bonded phase surface (previously dried or not) had been regenerated with MeOH. All the columns used in this study where freshly packed either with Hypersil ODS or with Partisil 5 ODS 3. The results are shown in Table 2. It can be seen from Table 2 that when the column has been dried with N_2, the decrease in the amount of adsorbed octylsulfate is 93 % in the case of Hypersil ODS and 35 % with Partisil 5 ODS 3. When 200 ml MeOH + 100 ml H_2O have been passed through the column (Step 3) the initial amounts are again observed so that the surface modification seems to be reversible.

It is assumed that dry N_2 eliminates every trace of MeOH or remaining 1.butanol (slurry packing solvent). The phenomenon appearing to be reversible once the bonded phase has been wetted by MeOH, one can consider that the observed differences in the amounts of adsorbed C 8 sulfate result from the presence or the absence of remaining surface MeOH, even when the column has been rinsed with large amounts of water.

The great decrease in the adsorbed amounts on Hypersil ODS is in agreement with the hypothesis of Scott and coll. (17) i.e. in presence of water, the hydrocarbon chains of the brush-type bonded phase interact, resulting in a decrease in the effective surface area.

In these extreme conditions (i.e. drying the bonded phase surface with N_2), the stationary phase does not exhibit its normal conditions observed in usual chromatographic experiments. Nevertheless , the previous results seem to prove that the regular removing of MeOH from the stationary phase surface is responsible for the regular decrease in adsorbed amounts. This phenomenon was no longer reversible after several month's use of a column (Table 1) eluted with pure aqueous mobile phases. With a polymer-type bonded phase (such as Partisil-5 ODS-3) a lower but significant decrease in the adsorbed amounts can also be noticed (this phenomenon is reversible when eluting the column with MeOH), although Scott and coll. (17) have shown that bulk phases exhibit the expected retentive characteristics according to their carbon content even in the presence of pure water. The decrease in the adsorbed amounts observed with Partisil-5 is however lower than that observed with Hypersil ODS due to its rather rigid cross-linked structure.

It is difficult to explore these particular behaviour in greater depth since little information exists on the commercial bonded phase structure, silylation reagent, etc...

Nevertheless, it is possible to underline some practical considerations : the use of pure aqueous mobile phase in practical I.P.C. utilisation seems to present some difficulties. The extensive use of these aqueous eluents, in particular with brush-type materials, leads to a significant decrease in effective chromatographic surface area and, consequently, to an irreproducibility in observed retentions. The decrease in specific surface and in adsorbed amounts of octylsulfate seems to be irreversible after several months' use. In fact the difficulties encountered when using pure aqueous phases do not exist when water-methanol mobile phases are used ; the determination of adsorption isotherms is then possible and chromatographic measurements are reproducible.

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