



# Preparation and chromatographic evaluation of new branch-type diamide-embedded octadecyl stationary phase with enhanced shape selectivity



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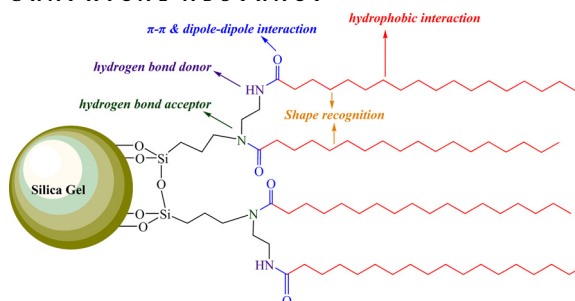
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## HIGHLIGHTS

- A new diamide-embedded octadecyl stationary phase was prepared.
- Excellent hydrophobic and aromatic selectivity.
- “Polymeric-C<sub>18</sub>” chromatographic behavior was found.
- Superior shape and planarity selectivity over C<sub>18</sub> towards isomeric PAHs.
- Carbonyl group and adjacent double C<sub>18</sub> chains impacted the retention substantially.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A novel branch-type diamide-embedded octadecyl stationary phase was prepared by facile amidation. The preparation of this new phase involves the synthesis of new bifunctional silane ligand and surface modification of spherical silica via anchoring of silane coupling agent. The obtained diamide-embedded octadecyl stationary phase demonstrated excellent hydrophobic selectivity, as well as enhanced shape and planarity selectivity in comparison to commercial polymeric and monomeric C<sub>18</sub> phases, respectively, as revealed by the systematic investigation into its liquid chromatographic retention of isomeric polycyclic aromatic hydrocarbons. The applicability of this new stationary phase was further testified by the effective separation of isomeric compounds belong to different chemical classes, including chain isomers of alkylbenzenes, and positional isomers of substituted aromatics. An in-depth analysis of the separation mechanisms other than molecular shape recognition involved in the new stationary phase was performed using a linear solvation energy relationships model and compared with its monoamide and pure C<sub>18</sub> counterparts correspondingly. The performance of the new stationary phase in quantitative analysis of phenols from real-world samples was also evaluated.

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## 1. Introduction

Stationary phases applied in high-performance liquid chromatography (HPLC) are generally prepared by chemical organic modification of the silica surface with different kinds of silane coupling agents, resulting in covalent immobilization of different ligands to the silanols [1–3]. The nature of the bonded phase formed on the surface can significantly affect the retention of solutes being eluted. The density, bulkiness, conformation, mobility and distribution of the bonded ligands can influence the interactions between the solutes and the stationary phase [4,5]. Among these modified silica materials, alkylated silica, especially that functionalized by octadecyl chain ( $C_{18}$  or ODS), is available from a wide variety of commercial origins and is the most widely used stationary phase for reversed-phase (RP) separation. There are two types of  $C_{18}$  chromatographic sorbents based on the bonding chemistry, one is monomeric, the other polymeric. The former is usually prepared by monofunctional silane, whereas, the polymeric materials are prepared via polycondensation of multifunctional silanes [6]. The monomeric phases are preferred due to its better mass transfer capability. However, polymeric sorbents offer enhanced selectivity towards molecularly rigid solutes, and therefore are more favored for the separation of constitutional isomers, such as polycyclic aromatic hydrocarbons (PAHs) [7–10].

In spite of their outstanding performance and widespread popularity, the pure alkyl stationary phases still have some disadvantages, e.g. low compatibility with highly aqueous eluent and insufficient selectivity towards polar solutes. During the past few years, a series of polar-embedded stationary phases has been developed to address the shortcomings of conventional alkyl ones [11–17]. These new phases comprise external hydrophobic segment, like  $C_{18}$ ,  $C_{16}$ , or  $C_{14}$ , and incorporated hydrophilic segment near the silica substrate, such as amide, imidazolium, urea and carbamate. Generally speaking, these polar-embedded phases are notable for their stability in highly aqueous mobile phase, improved performance in separation of polar compounds, unique selectivity but lower hydrophobicity compared to  $C_{18}$  ones. As one of the frequently used polar group, amide is often acquired through synthetic strategy. Derivatization of monoamino-silane with proper acid chloride leads to desired monoamido-silane.

To the best of our knowledge, the amino-silane used in preparation of amido-silane is 3-aminopropyltrimethoxysilane (APS). The amino group is certainly a versatile group to introduce functional group to the surface of silica. The bifunctional analogue of APS, namely *N*-(2-aminoethyl) aminopropyltrimethoxysilane (AEAPS) was never applied in preparation of RP stationary phase. In fact, AEAPS can equally participate in the surface modification of silica [18–20]. Moreover, the similar reactivity of the two amino groups (secondary and primary) contained in AEAPS makes further derivatization possible, such as di-substitution or even tri-substitution. In view of its multifunctional nature and ready availability, we believe AEAPS could be a qualified alternate for APS in preparation of multiple amide-embedded stationary stationary phases.

Herein, a new branch-type diamide-embedded  $C_{18}$  phase was proposed. Facile amidation of AEAPS with stearoyl chloride afforded the desired diamide-silane, which was then conveniently immobilized to silica to form amide-functionalized octadecyl stationary phase. Since there is a substantial amount of work already done by other authors in assessing the polar characteristics and related chromatographic behaviors of the amide-embedded phases, herein our intention was to investigate the effect of the double adjacent  $C_{18}$  chains on the chromatographic retention of isomers and the shape recognition contributed by the branched alkyl chains and amide groups. The chromatographic study on this

new stationary phase encompassed the evaluation of its hydrophobic selectivity and aromatic selectivity, a systematic investigation into its molecular shape recognition ability, including linearity and planarity selectivity towards PAH isomers. To further explore its steric selectivity, separations of other types of isomers were also successfully performed. Eventually, a comparative study on its chromatographic mechanisms with those of two reference columns was conducted via a linear solvation energy relationships model.

## 2. Experimental

### 2.1. Materials and reagents

Porous spherical silica (diameter: 5  $\mu\text{m}$ , pore size: 90  $\text{\AA}$ , surface area: 400  $\text{m}^2\text{g}^{-1}$ ) and *n*-alkylnaphthalene were synthesized in house. *N*-(2-Aminoethyl) aminopropyltrimethoxysilane (AEAPS) (98%) was a gift from Chenguang Chemical Co., Ltd. (Qufu, Shandong, China). Stearic acid (99%) and phenols of analytical grade was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). *N,N*-diisopropylethylamine (DIPEA) was purchased from Sun Chemical Technology Co., Ltd. (Shanghai, China). Fused-ring PAHs and *n*-alkylbenzenes of analytical standard were purchased from J&K Chemical (Beijing, China). Isomers of alkylbenzenes (99%) were purchased from Aladdin Industrial Inc. (Shanghai, China). Terphenyls (99%) were purchased from Tokyo Chemical Industry Co., Ltd. (Shanghai, China). Other analytes of analytical grade or better were obtained from different origins. Doubly distilled water, acetonitrile (MeCN) and methanol (MeOH) of HPLC grade were used. Solvents for organic synthesis were dried by 3  $\text{\AA}$  molecular sieves prior to use. The stock solution of three phenols (resorcinol, phenol and *m*-nitrophenol) were prepared at a concentration of 1  $\text{mg mL}^{-1}$  in MeOH (25 mL). The standard working solutions were prepared by diluting aliquots of the stock solution to obtain concentrations of 4, 6, 8, 10, 12  $\mu\text{g mL}^{-1}$ . The real-world water samples were collected from the Yellow River and water pipe, and filtered through 0.45  $\mu\text{m}$  membrane before analysis.

### 2.2. Preparation of new stationary phase

Stearic acid (4.55 g, 16 mmol) and thionyl chloride (10 mL) were mixed and refluxed in toluene (50 mL) for 8 h. After vacuum distillation of the solvent and residual thionyl chloride, stearoyl chloride was quantitatively obtained as a yellow liquid. This liquid was diluted by 10 mL of toluene, and added dropwise to a toluene solution (25 mL) of AEAPS (1.70 g, 7.5 mmol) containing slightly excessive DIPEA (2.197 g, 17 mmol) in a period of 30 min at room temperature. After another 12 h, the solution was refluxed for 4 h, and then cooled.

After filtration and washing the solid residue (DIPEA hydrochloride) by 10 mL hot toluene, the filtrate was transferred to a flask, to which silica (4 g) freshly activated in vacuum was added in one portion under mechanical stirring. The suspension was refluxed for 24 h in nitrogen atmosphere. The excessive DIPEA could act as catalyst for silylation. During silylation, a defined amount of water could be added to facilitate the hydrolysis of silane. Then the silica stationary phase (Sil-amide- $C_{18}$ ) was filtered, washed successively by hot toluene, hot ethanol, ethanol-water mixture and methanol (100 mL for each), and dried in vacuum at 80  $^{\circ}\text{C}$  overnight. The scheme was given Fig. 1.

### 2.3. Instrument and apparatus

The carbon, hydrogen and nitrogen contents of the silica material were determined by elemental analysis using a vario EL III

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