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# System maps for retention of small neutral compounds on a biphenylsiloxane-bonded silica stationary phase in reversed-phase liquid chromatography

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## ABSTRACT

The system constants of the solvation parameter model are used to prepare system maps for the retention of small neutral compounds on a biphenylsiloxane-bonded superficially porous silica stationary phase (Kinetex Biphenyl) for aqueous-organic solvent mobile phases containing 10–70% (v/v) methanol or acetonitrile. The retention properties of the biphenylsiloxane-bonded phase are shown to be complementary to an octadecylsiloxane-bonded silica (Kinetex C-18) and a pentafluorophenylpropylsiloxane-bonded silica stationary phases (Discovery HS F5). The retention properties of the Kinetex Biphenyl column are similar to an ether-linked phenylpropylsiloxane-bonded silica phase (Synergi Polar RP) with only small differences in relative retention.

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## 1. Introduction

The first choice stationary phase for reversed-phase liquid chromatography has remained an octadecylsiloxane-bonded silica sorbent with the first choice mobile phase a mixture of water or buffer containing acetonitrile or methanol since the 1970s. During this time column chemistry has continued to evolve resulting in improvements in column performance, durability, pH stability and reproducibility [1]. The hallmark feature of reversed-phase liquid chromatography is the dominant role of water in the separation process, such that the main features of a separation can be explained by the high cohesive energy and hydrogen-bond acidity of the aqueous mobile phase modulated by the solvated stationary phase [2,3]. One common approach to optimize selectivity is to utilize stationary phases with different surface chemistries created by bonding various ligands to a silica substrate and, less commonly, by utilizing non-silica based materials. Suitable ligands for bonding to

silica for reversed-phase liquid chromatography are generally, but not exclusively, limited to alkyl chains of different lengths, alkyl chains with embedded polar functional groups (e.g., amide, carbamate, urea, etc.), alkylphenyl or ether-linked alkylphenyl groups, and perfluoroalkane or perfluoroaromatic groups. Short chain alkyl ligands with polar functional groups (e.g., 3-cyanopropyl, 3-aminopropyl, spacer bonded propanediol) are little used in reversed-phase liquid chromatography because they provide only weak retention for small molecules and are mainly used with non-aqueous mobile phases for normal-phase chromatography [4,5]. This range of stationary phase chemistries is still rather limited and systems with high column efficiency are generally required to overcome the limited selectivity space for method development in reversed-phase liquid chromatography [6]. New stationary phases are introduced at frequent intervals to address this issue, of which biphenylsiloxane-bonded silica stationary phases are one such recent addition [7–9]. Biphenyl phases are stated to be more polarizable than alkylsiloxane-bonded phases and are expected to participate in dipole-induced dipole and  $\pi$ - $\pi$  interactions to a greater extent than alkylsiloxane-bonded silica stationary phases [9]. These assumptions remain largely untested in a quantitative sense, and the purpose of this study was to evaluate the retention

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properties of a biphenylsiloxane-bonded silica stationary phase with a view to shed some light on the retention mechanism and to provide further guidance for their general use in reversed-phase liquid chromatography.

Biphenylsiloxane-bonded silica phases are expected to have some properties in common with alkylphenylsiloxane- and ether-linked alkylphenylsiloxane-bonded silica stationary phases. The later have been in use for some time. Croes et al. [10] and Merchand et al. [11] used the hydrophobic subtraction model and established that additional interactions than those included in the model were required to explain the retention properties of phenylalkylsiloxane-bonded silica stationary phases. These additional interactions were ascribed to the “ $\pi$ -activity” of the phenylalkylsiloxane-bonded silica stationary phases and resulted in increased retention of polycyclic aromatic hydrocarbons and nitro-substituted aromatic compounds than was explained by the unexpanded form of the model. They also made the observation that the column “ $\pi$ -activity” was considerably suppressed for acetonitrile-containing mobile phases compared with methanol-containing mobile phases. This was also demonstrated by Appulage et al. for a biphenylsiloxane-bonded silica stationary phase [9]. In early studies of the retention properties of chemically bonded phases using the solvation parameter model for a limited range of mobile phase compositions, it was concluded that retention on alkylphenylsiloxane-bonded silica phases was less than for octadecylsiloxane-bonded silica phases due to the higher cohesion of the phenylalkylsiloxane-bonded silica stationary phases (smaller  $\nu$  system constant) which were not overcome by an increase in contributions from  $n$ - and  $\pi$ -electron lone pair interactions ( $e$  system constant) [12,13]. Our group reported more detailed studies of phenylalkylsiloxane- [14], ether-linked phenylalkylsiloxane- [15] and pentafluorophenylpropylsiloxane-bonded silica stationary phases [16] using system maps for a wide range of mobile phase compositions for both acetonitrile and methanol. System maps consist of a plot of the system constants and  $c$  term of the solvation parameter model as a continuous function of the binary mobile phase composition. A second goal of this study was to compare through system maps the differences in selectivity for the phenyl-containing stationary phases and the biphenylsiloxane-bonded silica stationary phase chemistries to provide further guidance for their use in method development.

The approach for characterizing the retention properties of siloxane-bonded silica stationary phases using system maps is based on the solvation parameter model set out below for use in reversed-phase liquid chromatography [2,3,17–20]

$$\log k = c + eE + sS + aA + bB^\circ + \nu V \quad (1)$$

where  $k$  is the retention factor. The lower case letters on the right-hand side of Eq. (1) are system constants that describe the complementary interactions of the system with the solute descriptors. The solute descriptors are indicated by the capital letters and are defined as excess molar refraction,  $E$ , dipolarity/polarizability,  $S$ , hydrogen-bond acidity,  $A$ , hydrogen-bond basicity,  $B^\circ$ , and McGowan's characteristic volume,  $V$ . Solute descriptors are known for several thousand compounds [17,19,20] but are not the focus of this report. The system constants are determined by multiple linear regression analysis of the experimental retention factors for a group of compounds with known descriptor values. Although the solvation parameter model does not contain a specific term to account for  $\pi$ - $\pi$  interactions, studies of  $\pi$ - $\pi$  complex formation by gas chromatography indicate that the contributions from dispersion interactions associated with the additional polarizability of loosely bound electrons are subsumed by the  $e$  system constant and those interactions of a dipole-induced dipole type by the  $s$  system constant [21]. Thus, the solvation parameter model can be used

without expansion to describe retention in systems expected to contain  $\pi$ -acid and/or  $\pi$ -base functional groups.

## 2. Experimental

### 2.1. Materials

Common chemicals were reagent grade and obtained from several sources. Methanol, acetonitrile and water were HPLC grade from Sigma-Aldrich (St. Louis, MO, USA). The Kinetex Biphenyl columns, 50 mm  $\times$  4.6 mm, 5  $\mu$ m particle diameter, and 10 mm pore diameter (part number 00B-4627-E0) were supplied by Phenomenex (Torrance, CA, USA).

### 2.2. Instrumentation and measurements

An Agilent 1200 series liquid chromatograph (Santa Clara, CA, USA) consisting of a G1312B binary pump, G1314B variable wavelength detector, G1367C Hip-ALS SL autosampler and G1316B TCC SL column oven was used for the measurement of retention factors. All measurements were made with a column flow rate of 1.5 mL/min and temperature of 45 °C. Solutes were injected (10  $\mu$ L) individually from solutions containing 0.5–2.0 mg mL<sup>-1</sup> of analyte made up in either the mobile phase composition or organic solvent component of the mobile phase depending on solubility. The column hold-up time was determined by injection of an aqueous solution of sodium nitrate (26 mg/mL) and confirmed by injection of an aqueous solution of thiourea (3 mg/mL). In all cases, sodium nitrate eluted just before thiourea (retention factor for thiourea < 0.1). Extracolumn residence times were measured by replacing the column by a zero-volume connector and used to correct all retention factors [22]

### 2.3. Calculations

Multiple linear regression analysis and statistical calculations were performed on a Dell Dimension 9200 computer (Austin, TX, USA) using the program PASW Statistics 22 (SPSS, Chicago, IL, USA). The descriptor values for a varied group of 50 compounds were taken from [23] and provide an even distribution throughout the descriptor space ( $E = 0.3$ – $2$ ,  $S = 0.5$ – $2$ ,  $A = 0$ – $1.2$ ,  $B^\circ = 0$ – $1.3$ , and  $V = 0.6$ – $1.8$ ). Further criteria for compound selection are outlined elsewhere [2,19,24].

## 3. Results and discussion

The solvation parameter model does not consider secondary interactions from steric repulsion [25,26] or electrostatic interactions [6,14–16]. The retention factors for the 50 compounds data set were evaluated initially to identify contributions from these interactions which might contribute to the uncertainty in the system constants for the retention models. For both aqueous acetonitrile and methanol mobile phases all plots of the retention factor ( $\log k$ ) against the volume fraction of organic solvent ( $\phi$ ) conformed to the general relationship, Eq. (2), without the observation of a plateau region or discontinuity in the plots associated with steric repulsion for bulky compounds.

$$\log k = a_0 + a_1\phi + a_2\phi^2 \quad (2)$$

In Eq. (2)  $a_0$ ,  $a_1$  and  $a_2$  are numerical constants without any assigned physical meaning. Next, we constructed the solvation parameter models to describe the retention factors for all compounds with inclusion and then exclusion of the weak bases (e.g., pyridine, aniline, 2-aminobiphenyl, diphenylamine,  $N,N$ -diethylaniline, etc). These models are summarized in Table-S1 (supplementary

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