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# System map for the ionic liquid stationary phase tri(tripropylphosphoniumhexanamido)triethylamine bis(trifluoromethylsulfonyl)imide for gas chromatography

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ABSTRACT

The solvation parameter model is used to construct a system map for the retention of volatile organic compounds on the ionic liquid stationary phase tri(tripropypphosphoniumhexanamido)triethylamine bis(trifluoromethylsulfonyl)imide (SLB-IL76) over the temperature range 80–240 °C. The SLB-IL76 stationary phase is moderately cohesive and strongly dipolar/polarizable and hydrogen-bond basic but only a weak hydrogen-bond acid. Electron lone pair interactions are weak and make only a minor contribution to the retention mechanism. The separation properties of SLB-IL76 highlight the difficulty of designing new stationary phases from ion structures as the presence of amide groups in the cation don't seem to contribute significantly to the hydrogen-bond acidity of SLB-IL76. The separation properties of SLB-IL76 are closest to the bis(polycyanopropyl)siloxane stationary phases with a high percentage of bis(cyanopropyl)siloxane monomer and could be used in method development when a stationary phase with similar gross retention characteristics but different selectivity is required.



## 1. Introduction

Historically many liquids have been evaluated as stationary phases for gas chromatography but few survived as most are incapable of forming stable films on fused-silica surfaces resistant to solvents and high temperatures as well as possessing favorable diffusion properties to facilitate rapid mass transfer [1,2]. Those available as pre-coated columns are dominated by poly(siloxanes) synthesized from different monomers affording a limited range of selectivity and poly(ethylene glycols). The stringent requirements for a useful stationary phase became a barrier for stationary phase development in the 1990s with new columns being mainly application-specific columns employing conventional stationary phases with an optimized composition or phase ratio for a particular application. The desire to access a wider selectivity space than available using conventional stationary phases became possible with the development of ionic liquids with suitable properties as stationary phases for open-tubular columns at the turn of the last century [3,4]. Ionic liquids are novel organic solvents composed entirely of ions. Favorable properties for gas chromatography include the virtual absence of vapor pressure, high viscosity and a moderate surface tension facilitating film formation on fused-silica surfaces, moderate cohesion and strong polar interactions allowing retention of a wide range of compounds, and the potential to design new stationary phases with different retention properties by exploiting the diversity of available ion structures [5,6]. They complement the separation properties of conventional poly(siloxane) and poly(ethylene glycol) stationary phases by extending the column temperature operating limit and by facilitating separations that require a different selectivity to those provided by conventional stationary phases.

Sharma et al. [7] synthesized a new type of trigonal tricationic ionic liquids with favorable properties for gas chromatography that were subsequently evaluated as stationary phases by Payagala et al. [8]. Pre-coated columns of the most promising of these trigonal tricationic ionic liquids, tri(tripropylphosphoniumhexanamido)triethylamine bis(trifluoromethylsulfonyl)imide, Fig. 1, became available in 2009 (SLB-IL76). Practical applications of SLB-IL76 include the separation of long-chain fatty acid methyl esters with different chain lengths, chain branching and degree of unsaturation [9] and congener-selective separation of polychlorinated dibenzodioxins and dibenzofurans [10]. The polarity number assigned to SLB-IL76 would suggest that it has similar

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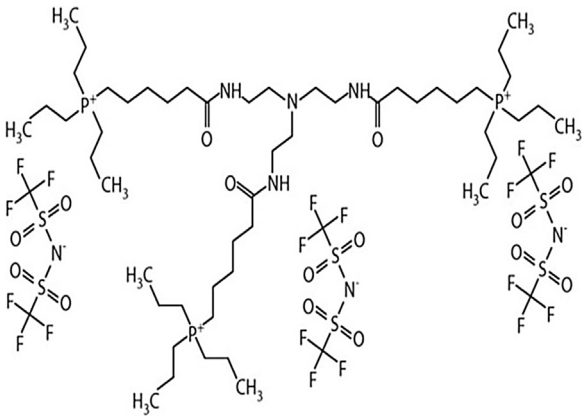

**Fig. 1.** Structure for SLB-IL76, tri(tripropylphosphoniumhexanamido)triethylamine bis(trifluoromethylsulfonyl)imide.

separation characteristics to the polar stationary phase poly(biscyanopropylcyanopropylphenylsiloxane) containing about 80% bis(cyanopropylsiloxane) monomer [11]. The polarity number is defined as the sum of the retention index differences for the first five McReynolds prototypical compounds (benzene, 2-pentanone, 1-nitropropane, *n*-butanol and pyridine) at 120 °C with squalane as a reference stationary phase. The scale is normalized such that the ionic liquid stationary phase 1,9-di(3-vinylimidazolium)nonane bis(trifluoromethylsulfonyl)imide has a polarity number of 100. However, it is doubtful if the McReynolds system of stationary phase constants provides useful information for stationary phase selection in method development [12] or whether a single value scale like the polarity number based on the same principles as the McReynolds system of phase constants would be any better [13].

The solvation parameter model provides an alternative approach to the system of McReynolds phase constants to characterize the retention properties of stationary phases for gas chromatography [14–17]. System maps derived from the system constants of the solvation parameter model afford insight into the variation of column selectivity with temperature as a continuous variable [13–15,18,19]. The solvation parameter model in the form suitable for characterizing retention in gas chromatography is set out below

$$\log k = c + eE + sS + aA + bB + lL \quad (1)$$

where $k$ is the retention factor and $e$, $s$, $a$, $b$, and $l$ are system constants that describe the complementary interactions of the stationary phase with the solute descriptors (E, S, A, B, L). The solute descriptors are defined as the excess molar refraction E, dipolarity/polarizability S, hydrogen-bond acidity A, hydrogen-bond basicity B, and the gas-liquid partition constant on hexadecane at 25 °C L [20–22]. The system constants are determined from the experimental retention factors for a collection of diverse compounds with known descriptor values by multiple linear regression analysis. The identity of the test compounds for column evaluation is less important than the experimental design employed. The test compounds are selected to provide accessible retention properties, to cover a wide descriptor space with roughly even occupancy, and with low cross-correlation between descriptors.

The system constants for a number of ionic liquid stationary phases are summarized in [5,6,17]. Payagala et al. determined the system constants for a self-made open tubular column prepared from tri(tripropylphosphoniumhexanamido)triethylamine bis(trifluoromethylsulfonyl)imide at 70 and 100 °C [8]. Rodriguez-Sanchez et al. [23] determined the system constants for a commercial version of this stationary phase at 100–160 °C. At 100 °C, where a comparison of the system constants is possible, the two studies show good agreement for the contribution of dipole-type interactions to the retention mechanism but predict different properties for hydrogen-bonding interactions. This is of interest for the design of new stationary phases since the widely used poly(siloxane) and poly(ethylene glycol) stationary phases have a wide range of hydrogen-bond basicity but none are hydrogen-bond acids [18,24]. A number of ionic liquids have been identified as weak hydrogen-bond acids extending the selectivity space for separations by gas chromatography [5,6,17]. The central core of the tri(tripropylphosphoniumhexanamido)triethylamine stationary phase, Fig. 1, contains an amide group in each of the three linker arms of the cation potentially contributing to its polarity and hydrogen-bond acidity. Previous attempts to design ionic liquid stationary phases with hydrogen-bond acidity employing alkylsulfonate anions containing hydroxyl, amide, or amine groups were unsuccessful [24–26]. The problem seems to be that ionic liquids which are simultaneously strong hydrogen-bond acids and hydrogen-bond bases prefer to form internal hydrogen-bonded complexes rather than form solute-solvent hydrogen-bonds. Thus, these ionic liquids were classified as non-hydrogen bond acids with respect to their separation properties by gas chromatography. A question we wished to answer is whether the restricted flexibility of the amide-containing arms in the tri(tripropylphosphoniumhexanamido)triethylamine cation would be more favorable for promotion of solute-solvent hydrogen-bonds with the stationary phase acting as a hydrogen-bond acid. This is in addition to providing a system map for SLB-IL76 for its full operating temperature range for comparison with a database of system constants for non-ionic and ionic stationary phases [6,13,18,27,28]

## 2. Experimental

### 2.1. Materials

Common chemicals used for column characterization were of the highest purity available and obtained from several sources. The 30 m × 0.25 mm internal diameter SLB-IL76 open-tubular column, 0.20 μm film thickness, was obtained from Supelco (Bellefonte, PA, USA).

### 2.2. Instrumentation

Retention factor measurements were made with an Agilent Technologies (Palo Alto, CA, USA) HP6890 gas chromatograph fitted with a split/splitless injector and flame ionization detector using Chemstation software (rev. B04.01) for data acquisition. Nitrogen was used as the carrier gas at a constant flow rate of 1.0 mL/min. The split ratio was generally 30:1 but varied to control peak detection, septum purge 1 mL/min, inlet temperature 280 °C and detector temperature 280 °C. Methane was used to determine the column hold-up time. Retention factors were measured at 20 °C intervals over the temperature range 80–240 °C for varied compounds, selected so as to obtain experimentally accessible retention factors and statistically meaningful retention models (see Section 2.3).

### 2.3. Calculations

Multiple linear regression analysis and statistical calculations were performed on a Dell Optiplex 9020 computer (Austin, TX, USA) using the program PASW Statistics 24 (SPSS, Chicago, IL, USA). The core collection of compounds and their descriptor values for column characterization are given in [27] with additional values for polycylic aromatic compounds [29], flavor and fragrance compounds [30] and plasticizers [31] added to ensure adequate cover of

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