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A system map for the ionic liquid stationary phase 1,12-di(tripropylphosphonium)dodecane bis(trifluoromethylsulfonyl)imide trifluoromethanesulfonate for gas chromatography

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ABSTRACT

The solvation parameter model is used to prepare a system map for the retention of volatile organic compounds on the ionic liquid stationary phase 1,12-di(tripropylphosphonium)dodecane bis(trifluoromethylsulfonyl)imide trifluoromethanesulfonate (SLB-IL61) over the temperature range 80–260 °C. Retention is governed by dispersion, dipole-type and hydrogen-bonding interactions each with its own temperature dependence. The exchange of a bis(trifluoromethylsulfonyl)imide anion in SLB-IL60 for a trifluoromethanesulfonate anion (SLB-IL61) results in a change in selectivity indicated by an increase in the hydrogen-bond basicity and a decrease in hydrogen-bond acidity of the stationary phase without change in either the cohesion or dipolarity/polarizability of the stationary phases. At high temperatures there are small differences in electron lone pair interactions but these are relatively unimportant in terms of selectivity differences. Since the disclosed chemical structures for SLB-IL60 and SLB-IL61 does not contain obvious hydrogen-bond acid functional groups the modest hydrogen-bond acidity of these stationary phases was unexpected but does not appear to be obviously connected to adsorption sites at the column wall. The polarity number is shown to be a poor indicator of column retention properties for SLB-IL61. Principal component analysis with the system constants as variables indicates that the retention properties of SLB-IL61 are not duplicated by any of the common poly(siloxane) and poly(ethylene glycol) stationary phase chemistries in current use for column preparation. The SLB-IL61 column is closest in separation properties to poly(cyanopropylphenyldimethylsiloxane) and poly(cyanopropylmethyldimethylsiloxane) stationary phases with a high percentage of cyanopropyl-containing monomer but the two stationary phase types are not selectivity equivalent.

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1. Introduction

Ionic liquids are a new class of solvents that have found many applications in analytical chemistry including as stationary phases for gas chromatography [1–5]. Favorable properties for gas chromatography include the virtual absence of vapor pressure facilitating their use at high temperatures with low column bleed and their capability to retain a wide range of compounds due to a combination of moderate cohesion and strong polar interactions. They complement the separation properties of conventional polar 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 [5,6].

One of the first generation of ionic liquid stationary phases to become commercially available as a precoated column was the dicationic 1,12-di(tripropylphosphonium)dodecane bis(trifluoromethylsulfonyl)imide originally synthesized by Breitbach and Armstrong [7,8]. It became available as SLB-IL59 and SLB-60 in which the two column types differed in the method employed for deactivating the fused silica column wall [9,10]. Shortly afterwards a modified version of this ionic liquid stationary phase SLB-IL61 became available in which one of the bis(trifluoromethylsulfonyl)imide anions was replaced by a trifluoromethanesulfonate anion. Practical applications of SLB-IL61 stationary phase include the separation of long-chain fatty acid methyl esters with different chain lengths, chain branching and degree of unsaturation [10,11], congener-selective separation of

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polychlorinated dibenzodioxins and dibenzofurans [12,13] and low-mass polar compounds [14]. The growth of applications for SLB-IL61 has not kept pace with SLB-IL59 and SLB-IL60. A possible contributing factor is the reliance on the polarity number as a measure of column polarity for stationary phase selection [15,16]. The polarity number is used to provide an index number for marketing ionic liquid columns such that SLB-IL60 has a polarity number of 60 and SLB-IL61 a polarity number of 61. 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) with squalane as a non-polar reference stationary phase and reference temperature of 120 °C normalized so that the ionic liquid 1,9-di(3-vinylimidazolium)nonane bis(trifluoromethylsulfonyl)imide is assigned a value of 100. This scale leads to the conclusion that the SLB-IL60 and SLB-IL61 columns would have similar separation properties and are not expected to exhibit significant selectivity differences. Thus, apart from fine tuning of nearly desirable separations it would be more profitable for method development to utilize ionic liquid columns which differ significantly in their polarity number. On the other hand, variation of the anion type is proven to be a useful method for varying the selectivity of ionic liquid stationary phases and would be expected to provide a more significant change in selectivity than indicated by the polarity number [4,17,18]. In this report we provide a quantitative description of the effect of exchanging a bis(trifluoromethylsulfonyl)imide anion for a trifluoromethanesulfonate anion on the selectivity of the SLB-IL60 and SLB-IL61 columns and further illustrate deficiencies in the polarity number for column selection in method development.

Two general approaches have been used to characterize the retention properties of ionic liquid stationary phases [3–6]. The Rohrschneider-McReynolds approach based on retention index differences for prototypical solutes on the ionic liquid stationary phase and squalene at 120 °C has become immortalized in the gas chromatography literature but has known deficiencies and its use cannot be recommended [19–22]. In particular, the retention index differences for the prototypical compounds are largely determined by the retention difference for the *n*-alkane standards on the compared phases with polar solute-stationary phase interactions making only a minor contribution. For further discussion see [20]. The solvation parameter model provides a thermodynamically sound approach for column selection in gas chromatography [4–6,22–24]. It is set out below in the form suitable for gas chromatography

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

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*. Descriptor values for several thousand compounds are available and those recommended for column characterization by gas chromatography are summarized in [25–29].

The system constants for a number of ionic liquid stationary phases are summarized in [4,5,18]. Weber and Anderson [30] provided system constants at 60 and 100 °C for SLB-IL61. A system map for SLB-IL60 for the temperature range 80–280 °C was provided by Lenca and Poole [31]. Rodriguez-Sanchez et al. [32] provided system constants for SLB-IL59 at 100–160 °C. In each case the ionic liquid stationary phases are indicated as possessing moderate hydrogen-bond acidity although the disclosed structure of the stationary phases contains no obvious hydrogen-bond acid functional groups. This is of interest for method development since conventional non-ionic commercially available stationary phases

do not exhibit a hydrogen-bond acid capability [6,33]. In this report we have studied the retention properties of the SLB-IL61 column over a much wider temperature range than before, 80–260 °C, with the view to provide a system map to describe its retention properties over its full operating temperature range and to evaluate the influence of substituting a trifluoromethanesulfonate anion for a bis(trifluoromethylsulfonyl)imide anion on the characteristic retention properties of 1,12-di(tripropylphosphonium)dodecane bis(trifluoromethylsulfonyl)imide stationary phases.

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-IL61 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 300 °C and detector temperature 300 °C. Methane was used to determine the column hold-up time. Retention factors were measured at 20 °C intervals over the temperature range 80–260 °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 were taken from [31] with additional values for polycyclic aromatic compounds [35], flavor and fragrance compounds [36] and plasticizers [37] added to minimize descriptor cross-correlation and to ensure adequate cover of the descriptor space and retention factor range. The selected compounds cover the descriptor space *E* = 0–3.0, *S* = 0–2.3, *A* = 0–1.50, *B* = 0–1.50, and *L* = 2.0–15.0. The protocol for compound selection is outlined in [31,34].

3. Results and discussion

The system constants at 20 °C intervals for the temperature range 80–260 °C were determined for groups of varied compounds selected to meet the chemical and statistical requirements to construct robust models using multiple linear regression analysis on the SLB-IL61 column. The results are summarized in Table 1 together with the model statistics for each temperature. The statistics for the individual models indicate that the fit of the retention factors to the solvation parameter model is satisfactory with multiple correlation coefficients >0.995, standard error of the estimate <0.057, and Fisher statistic >1680. The system constants in Table 1 were used to construct a system map for general interpretation, Fig. 1. As expected, polar interactions are less effective at retaining compounds at higher temperatures. Of particular note is that

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