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Characterization by the solvation parameter model of the retention properties of commercial ionic liquid columns for gas chromatography

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ABSTRACT

For the first time, four commercial ionic liquid columns (SLB-IL59, SLB-IL76, SLB-IL82 and SLB-IL100) for gas chromatography have been comprehensively evaluated in terms of efficiency, polarity and solvation properties. Grob tests and McReynolds constants showed that they were all high-efficiency columns of high polarity, but with low inertness to compounds with hydrogen bonding capabilities. The solvation parameter model was used to characterize the solvation interactions of the four columns in the 80–160 °C temperature range. Results revealed that all the ionic liquids studied can be considered moderately hydrogen-bond acid and highly cohesive stationary phases, on which the dominant contributions to retention were the dipolar-type and hydrogen-bond base interactions, while π–π and n–π interactions were barely significant. The SLB-IL59 column provided the best separation of homologs, while the SLB-IL76 and SLB-IL100 columns had the most basic and the most acidic phases, respectively. A principal component analysis for the commonly used stationary phases in capillary GC showed that these commercial ionic liquid columns fill an empty area of the available selectivity space, which clearly enhances the separation capacity of this technique.

1. Introduction

Over the past decade, ionic liquids (ILs) have generated great interest because of their unique and tunable physicochemical properties and their versatility for various applications [1,2]. They are organic salts with melting points below 100 °C that typically possess negligible vapor pressure, wide liquid ranges, high viscosity and good thermal stability. All these properties make them ideal candidates as stationary phases (SPs) for gas chromatography (GC) [3,4]. From the first papers published about this application of ILs [5,6] to the present, a great deal of development has been aimed at preparing columns that have higher thermal stability and different selectivity than commercial columns.

Polycationic [7,8] and polymerized [9] ILs, as well as IL bonded polysiloxanes [10,11], have shown the best characteristics as GC stationary phases.

To date, only seven different ILs have been used to prepare commercial capillary columns (SLB-IL59, SLB-IL60, SLB-IL61, SLB-IL76, SLB-IL82, SLB-IL100 and SLB-IL111). Their main advantages are that they offer different separation properties than columns prepared with polysiloxanes and poly(ethylene glycols), as well as lower column bleed, longer life time, higher thermal stability and greater resistance to damage from moisture and oxygen. Thus, they have been successfully used in the analysis of complex mixtures, as fatty acid methyl esters [12], essential oils [13], caffeine metabolites [14], pollutants [15] and haloanisoles [16] among others. Such a large number of applications suggest a wide variety of interactions, which are not completely explained by the high polarity of these commercial columns.

Polarity estimation in GC is based on the McReynolds method [17], which uses the retention indices (I) of five probes to represent a distinct interaction, and the combination of their retention indices is used to determine the polarity of the SP. However, this approach cannot fully differentiate individual interactions since the retention of probes is not driven by a single force but is most often due to several simultaneous interactions. In contrast, the solvation parameter model (SPM) [18,19] can quantitatively evaluate the individual intermolecular interactions between a SP and a substance. For that reason it has been extensively used to evaluate the retention characteristics of a variety of SPs, including ILs [4,20].

The aim of this work was to characterize by means of the solvation parameter model the retention properties of four commercial

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ionic liquid columns (SLB-IL59, SLB-IL76, SLB-IL82 and SLB-IL100), studying the effect of temperature on selectivity, and comparing their separation characteristics to those of conventional SPs in capillary GC.

2. Experimental

2.1. Materials and equipment

Three HP-5890A and HP-5890 Series II (Agilent, Palo Alto, CA, USA) gas chromatographs with split/splitless injection systems and flame ionization detectors (FID) were used. Data acquisition and processing were carried out using Clarity Lite chromatographic software (Data Apex Ltd., Prague, Czech Republic).

The results presented here were obtained on four fused-silica capillary columns coated with ionic liquids as stationary phases (Supelco Sigma–Aldrich, Bellefonte, PA, USA) and whose characteristics are summarized in Table 1. In order to simplify the notation throughout the manuscript, the columns will be referred to hereafter without the SLB- prefix.

All solutes were purchased from Merck (Darmstadt, Germany), Carlo Erba Reagenti (Rodano, Milano, Italy) and Sigma–Aldrich Co. (St. Louis, MO, USA), except for methane, which was obtained from natural gas.

2.2. Methods

For all experiments, the injection port and detector temperatures were 230 and 250 °C, respectively, with the exception of the IL100 column for which 180 and 200 °C were used instead.

A solution of naphthalene in undecane (10 μg μL^{-1}) was used to evaluate column efficiency at 110 °C by the maximum plate number per meter ($N_{\max}$/m). The quality of the column coating was expressed by the utilization of theoretical efficiency (*UTE*).

The Grob test was used to evaluate the overall chromatographic properties of the capillary columns, and the test mixture was prepared in-house from the pure standards [21]. The average separation number (*TZ*) was calculated as the average of the two values obtained from the methyl esters of the Grob test.

Mixtures of the McReynolds probes (benzene, 1-butanol, 2-pentanone, 1-nitropropane and pyridine) and *n*-alkanes were injected at 120 °C. In all cases, the *n*-alkanes present in the mixtures were chosen in order to bracket the McReynolds probes in the chromatograms. Hold-up times (t_M) and retention indices (I) were estimated by the LQG method [22,23], which provides reliable and reproducible t_M values and very accurate I data. McReynolds constants were obtained by subtracting the retention indices of the five McReynolds probes on the SP under study, and those in the reference non-polar SP (squalane). The polarity of the SP was calculated as the sum of the five McReynolds constants [17].

In order to cover the broad range of possible solute-stationary phase interactions, 95 solutes with varied functional groups were selected for the characterization of the IL columns by the SPM. This model is described for GC [24] by the equation:

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

where k is the retention factor of a solute on the SP at a specific temperature; c is the model intercept; the capital letters (E, S, A, B, and L) represent the solute descriptors that are probe-specific parameters determined for many substances; and the lowercase letters (e, s, a, b, and l) are referred to as the system constants, in which all information concerning the solvation properties of the SP is represented. Specifically, e defines the capability of the SP for π–π and n–π interactions and s for dipole-type interactions; while a and b, are the hydrogen-bond basicity and acidity of the SP, respectively; and l describes the overall dispersive-type interactions. The solutes selected were grouped into different mixtures and chromatographed isothermally from 80 to 160 °C at increments of 20 °C to obtain their k values. System constants, for each IL column and temperature, were calculated by multiple linear regression (MLR) analysis from experimental k values of the probes selected and their descriptor values. Table S1 in the Supplementary Data section shows the solutes selected, as well as their solute descriptors.

Radar plots for SPM data were created normalizing the total length of axes (radii) to unity. Each radius represents a system constant (e, s, a, b and l) at 120 °C and each radar plot a chromatographic column. Four radar graphs were drawn, each with data corresponding to one of the IL columns under study and to two additional columns (HP-INNOwax and SP-2340) for comparison. For these last two columns, the system constants were obtained from Poole and Poole [20].

Microsoft Office Excel (Microsoft Corp. Redmond. WA, USA) and Statgraphics Centurion XV (StatPoint Technologies, Warrenton, VA, USA) were used for data handling, basic calculations, radar plots and, non-linear and multiple linear regressions. Unscrambler X (CAMO Software AS, Oslo, Norway) was used for principal component analysis.

3. Results and discussion

3.1. Evaluation of chromatographic columns

Results showed that columns efficiency was up to about 4700 plates per meter ($k_{\text{naphthalene}} > 4.9$) at 110 °C (Table 1). The high *UTE%* values (>96%, except for the IL76 column) indicate that the columns have a very uniform film thickness, similar to those typically obtained for non-polar stationary phases [25]. The *TZ* values, between 27 and 38, agree with this behavior.

However, according to the Grob test analysis (Fig. 1), the columns showed low inertness to compounds with hydrogen bonding capabilities. Moreover, in agreement with the McReynolds constants and the polarities determined (Table 1), these IL columns are highly polar with an important acid-base behavior.

3.2. Solvation parameter model

To further understand the interactions that occur in the commercial IL columns studied, the SPM was used. Table 2 lists the system constants with their standard deviations and the goodness-of-fit statistics for each case. Very good regression models, without any significant trend in the residual plots reinforce the statistical reliability of the built models.

All the ILs studied possess the bis(trifluoromethylsulfonyl)imide anion, so differences in the system constants will mainly be attributed to the cations. Thus, dipolar-type interactions (s) are one of the most predominant forces in these columns. The s values ranged from 1.51 to 1.78 at 120 °C, falling well within the interval observed for poly(cyanopropylmethylsiloxanes) with 50–75% substitution percentages of cyanopropyl group [26]. The IL82 and IL100 columns showed higher s values than the IL59 and IL76 columns because of the polarizability of imidazolium moiety. Regarding the a system constant, a high capability for H-bond base interactions with solutes was observed. It has been described that the basicity of ILs is dominated by anion but modified by cation [27], hence, the small differences in a values must be related to the different chemical structures of cations. Imidazolium ring could act more as an H-bond acceptor than the phosphonium cation, so it could be expected that the IL59 and IL76 columns would have lower values than the IL82 and IL100 columns. However, this was only observed for the IL59 column. The higher value obtained for the IL76 column could be due to the amide groups that contribute positively