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Polymeric imidazolium ionic liquids as valuable stationary phases in gas chromatography: Chemical synthesis and full characterization

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ABSTRACT

Seven new functionalized polymerizable ionic liquids were chemically prepared, and later applied for the preparation of polymeric stationary phases in gas chromatography. These coated GC columns, which exhibited good thermal stabilities (240–300 °C) and very high efficiencies (3120–4200 plates/m), have been characterized using the Abraham solvation parameter model. The chromatographic behavior of these polymeric IL columns has been deeply studied observing excellent selectivities in the separation of many organic substances such as alkanes, ketones, alcohols, amines or esters in mixtures of polar and non polar solvents or fragrances. Remarkably, the challenging separation of xylene isomers has been possible using a bis(trifluoromethylsulfonyl)amide based imidazolium IL coated column as a gas chromatography stationary phase.

1. Introduction

Ionic liquids (ILs) have attracted great attention in recent years due to their unique properties such as high thermal stability, negligible vapor pressure, recyclability and electrical conductivity [1,2]. These properties and the possibility to modify their chemical composition by simple synthetic strategies have allowed their use in different chemistry areas (e.g. electrochemistry [3,4], extractions [5–7], mass spectrometry [8], reaction solvents [9,10], catalysis [11–16], analytical separations [7] and others) their use as stationary phases in chromatography being one of the most important with analytical purposes [17–19].

ILs show a dual nature when used as stationary phases for gas chromatography, making possible the interaction with both polar and non-polar compounds when acting as polar or non-polar stationary phases, respectively [20]. Thus, a myriad of ionic liquids have been synthesized and applied as stationary phases in recent years, unfortunately most of them possess low thermal stabilities compared with currently commercially available columns. Increasing operating temperatures is nowadays highly demanding aim when designing novel stationary phases; however the viscosity of ILs can then dramatically decrease, which implies a loss of film homogeneity of the stationary phase and therefore a loss in the separation efficiency of analytes and also poor reproducibility of their retention times.

In order to overcome these limitations, different authors have satisfactorily achieved the synthesis and application of new families of ILs able to operate at temperatures up to 400 °C [21–23]. To optimize the wetting ability of the ILs on fused-silica capillaries, and improve the thermal stability of stationary phases, Armstrong and co-workers prepared by cross-linking, an ionic liquid stationary phase, using a small amount of free radical initiator, maintaining the column stability up to 280 °C [24]. Later, Hsieh et al. conducted the polymerization of ILs before coating the silica capillary reaching thermal stabilities up to 350 °C [25]. On the basis of our research experience in the preparation of novel monocationic [26] and polycationic [27] imidazolium-based gas chromatography stationary phases, we have moved forward to the design and characterization of polymeric ionic liquids (PILS). Thus, a total of seven new stationary phases have been studied using the Abraham model, trying to rationalize the effect of cation/anion nature on the retention factors for selected mixtures of analytes.

2. Materials and methods

Most of the chemical reagents were purchased from Sigma–Aldrich (Madrid, Spain) and used without further purification. Methanol, dichloromethane and *n*-hexane were obtained

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from Merck (Darmstadt, Germany). Untreated fused silica capillaries (0.25 and 0.10 mm i.d.) were purchased from Supelco (Madrid, Spain).

The coating of the GC columns was performed using the static method on a 10 m (5 m thermal stability evaluation) capillary column (0.25 mm i.d.) at 40 °C using 0.31% (w/v) of ILs dissolved in dichloromethane. Before performing the static coating, the capillaries were pre-treated with sodium hydroxide (NaOH 1 M) and hydrochloric acid (HCl 1 M) however any chromatographic efficiency improvement was observed so for further experiment non pretreatment was done. Prior to adding the solvent to the monomer, 3 mg of AIBN [2,2′-azobis(2-methylpropionitrile)] (∼10 wt%) were added. Capillaries were filled with the solution of initiator and ionic liquid. The AIBN decomposition constant (K_d) at the coating temperature can be considered low, so polymerization was almost invaluable during the filling of the column [28]. After coating, the ends of the capillary were sealed and the capillaries placed in a GC oven, heating the column from 40 to 80 °C at 1 °C min^{-1} and kept at 80 °C for 5 h in order to ensure complete polymerization. Silica and ILs composition made us think that the polymer film formed on the capillary wall is immobilized mainly by adsorption phenomena. Helium carrier gas was then flushed through the capillary at a rate of 1 mL min^{-1} and the capillary was then conditioned from 30 to 120 °C at 3 °C min^{-1} and held at 120 °C for 2 h. A triplicate of each column was prepared and the efficiencies of the IL columns were found higher than 3000 plates/m by using naphthalene at 100 °C.

The solvation parameter model developed by Abraham [29–31], has been used to characterize interactions between solute molecules and stationary phases. This is based on a linear free energy relationship. In this case, the different types of solvent–solute interactions are evaluated separately. This model is described by Eq. (1) [31–33].

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

where log k is the solute retention factor and is determined by measuring the retention time of the analyte and dead volume of the chromatographic column. The solute descriptors (E,S,A,B,L) have been evaluated and published in the literature for a number of solutes [30]. These solute descriptors values have been optimized by Poole and co-workers [34], and are defined as E for the excess molar refraction, S is the solute dipolarity/polarizability index, A and B are the solute H-bond acidity and basicity, respectively and L is the gas-hexadecane partition coefficient at 25 °C. The system constants (e, s, a, b, l) are used to describe the solvation properties of the stationary phase and are defined as follows: the e term indicates the ability of the stationary phase to interact with the π and n-electrons of the solvent; s is a measurement of the dipolarity/polarizability of the solvent; a and b define the solvent hydrogen bond basicity and acidity, respectively; and the l term is a measurement of the phase ability to distinguish or to separate homologues in any homologous series. The intercept term, c, can be used to determine and verify the phase ratio of the column. The retention factor (k) of a given solute at a specific temperature is determined chromatographically. These values can then be subjected to multiple linear regression analysis (MLRA) to find the five coefficients and system constant.

With the aim of evaluating the capillary columns, each individual probe molecule (dissolved in dichloromethane) was injected into the column at three different temperatures: 50 °C, 70 °C and 100 °C. It should be noted that some of the probe molecules suffered high peak asymmetry factors at 50 °C and so were likewise rejected from the data set. For that reason we could not subject all the probes to multiple linear regression analysis at all temperatures examined. For the determination of solvation parameters, 41 probe molecules were used. The solute descriptors for the 41 probe molecules are listed in Table 1.

Probe molecules were injected and retention times were measured in triplicate. Multiple linear regressions were performed using Statgraphics Centurion XV for Windows version 15.2.06. The linearity regression (R^2) for all evaluations was ≥0.98. The values of all the solvation parameters are listed in Table 3.

All separations were performed using a Shimadzu GC-2010 Gas Chromatograph (Shimadzu, Kyoto, Japan) equipped with a flame ionization detector. Analyses of alcohols/amines, polar and non-polar compounds, fragrance mixture and xylene isomers were performed with helium as carrier gas at a flow of 1 mL min^{-1} and a split ratio of 100/1. The injector and detector temperatures were 250 °C and 280 °C, respectively. Methane was used to measure the column hold-up time. The temperature was programmed as follows: initial oven column temperature 35 °C for 2 min, increased at a rate of 10 °C min^{-1} to 180 °C and held at this temperature for 5 min for alcohols/amines, polar and non polar compounds and fragrance mixture. The isothermal program for xylenes isomers was 35 °C.

3. Results and discussion

3.1. Chemical synthesis of polymerizable ionic liquids

In order to develop a general and simple chemical synthetic strategy for the synthesis of a broad and novel family of imidazolium-based ILs, we have considered a tunable core structure possessing two structurally designed engineering vectors such as the imidazolium alkenyl chain of the cation and the anion nature. Following a recently described strategy for the synthesis of imidazolium ILs, cyclohexene oxide was reacted with imidazole for the synthesis of racemic 2-(1*H*-imidazol-1-yl)cyclohexanol [35,36]. This (±)-alcohol was alkylated by reaction with 4-bromo-1-butene in refluxing acetonitrile (MeCN) for 16 h yielding the corresponding bromide salt IL 1 in almost quantitative yield after a simple washing work-up with Et_2O (Scheme 1). Structural diversity can be then easily achieved in mild reaction conditions by exchanging the anion at room temperature. Thus, three room temperature ILs were obtained by reaction with lithium bis(trifluoromethane)sulfonimide ($LiNTf_2$ for IL 2), potassium thiocyanate (KSCN for IL 3) and sodium tetrafluoroborate ($NaBF_4$ for IL 4) in good to excellent isolated yields (87–96%).

This simple synthetic strategy allowed us to obtain imidazolium ILs with a different pattern substitution, in this case the nature of the anion was selectively modified, so at this point and trying to rationalize the influence of both cation and anion in the development and characterization of new gas chromatography stationary phases, we used the racemic alcohol for the synthesis of new ILs possessing different alkenyl chains linked to the N3 of the imidazolium ring (Scheme 2). Benzyl and linear alkenyl units such as allyl, 3-butenyl or 7-octenyl were considered following a general route based on the quaternization of the imidazole ring of the alcohol with allyl bromide (97%), 4-bromo-1-butene (98%), 8-bromo-1-octene (88%) or 4-vinylbenzyl chloride (78% yield), followed by anion exchange reaction to replace the halogen anion for NTf_2^-, yielding ionic liquids ILs 5–7 in high yields (88–90%) plus IL 1 and IL 2 previously obtained in Scheme 1. Quaternization reactions were carried out in acetonitrile at 80 °C for 15–24 h except for the vinyl benzyl precursor, where milder conditions (50 °C) were used to avoid undesired polymerization reactions through the vinyl position. On the other hand the anion exchange of the halogen ion (bromide or chloride) for NTf_2^- was carried out after one day of reaction at room temperature.