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Ionic liquids as stationary phases for gas chromatography—Unusual selectivity of ionic liquids with a phosphonium cation and different anions in the flavor, fragrance and essential oil analyses

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ABSTRACT

Room-temperature ionic liquids (ILs) have been shown to be successful as stationary phases (SPs) for gas chromatography in several fields of applications because of their unique and tunable selectivity, low vapor pressure and volatility, high thermal stability (over 300 °C), and good chromatographic properties. This study has been focused on two ILs based on a phosphonium cation (trihexyl(tetradecyl)phosphonium, P_{66614}) combined with different anions, previously shown to be suitable as gas chromatography (GC) SPs. In particular, trihexyl(tetradecyl)phosphonium bis[(trifluoromethyl)sulfonyl]imide ($[P_{66614}^+]$ $[NTf_2^-]$) and trihexyl(tetradecyl)phosphonium chloride ($[P_{66614}^+]$ $[Cl^-]$) were investigated, as the Abraham linear solvation energy relationship has shown their ability to interact with the solute(s) when tested with a set of 26–34 probe analytes. The chromatographic performance were investigated on narrow bore and conventional test columns using the following: i) Grob test, ii) a group of model mixtures of compounds characteristic of the flavor, fragrance and essential oil fields (FFMix), iii) a standard mixture of 29 volatile allergens (AlMix), and iv) two essential oils of different complexity (sage and vetiver essential oils). The columns coated with the investigated IL SPs were characterized by similar polarity (Polarity Number (PN): 37 for $[P_{66614}^+]$ $[Cl^-]$ and 33 for $[P_{66614}^+]$ $[NTf_2^-]$), high efficiency and highly satisfactory inertness. The two IL SPs also exhibited a completely different separation performance, with $[P_{66614}^+]$ $[Cl^-]$ test columns mainly characterized by high retention and selectivity based on the analyte functional groups, and $[P_{66614}^+]$ $[NTf_2^-]$ test columns featured by short retention and selectivity mainly related to the analyte volatility and polarity. These results were also confirmed with the analysis of sage and vetiver essential oils.

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1. Introduction

The interest of room-temperature ionic liquids (ILs) as stationary phases (SPs) for gas chromatography is constantly increasing not only because of their unique and tunable selectivity but also for their low vapor pressure and volatility, thermal stability (over 300 °C), and compatibility with modern column technology (viscosity and wetting properties). The use of ILs in analytical chemistry (from sample preparation to analysis including GC), was exhaustively reviewed by Ho et al. in 2014 [1] and recently updated by Berthod et al. [2]. These articles also list a number of other reviews published over the past decade describing developments, chromatographic properties, and applications to specific fields of several ILs and polymeric ILs (PILs) in GC and MDGC. Other reviews by Hantao et al. [3], Kulsing et al. [4], Sun et al. [5], and Nan and Anderson [6] have since addressed IL applications in GC.

The popularity of IL coated GC columns was strongly influenced by their commercial introduction by Supelco in 2008. The first one of them, know with the acronym SLB-IL100, was followed by a group of others, including SLB-IL59, SLB-IL60, SLB-IL61, SLB-IL76, SLB-IL82, SLB-IL111, characterized by different polarities mainly based on nitrogen and phosphorus cations. The number distinguishing each column is the Polarity Number defined through their Mc Reynolds constants [7]. The performance and selectivity of these IL columns were of high interest for several fields, but further efforts

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had to be made in column manufacturing to reduce their activity, particularly towards polar or active analytes. The goal of inertness comparable to that of conventional columns, in particular for routine quantitative analysis, was achieved in 2016 by Sidisky and the Supelco group that developed a new generation of highly-inert columns coated with three of the most applied ionic liquids (i.e. SLB-IL60i, SLB-IL76i and SLB-IL111i) by carefully tuning the surface treatment of the fused silica during column preparation [8–12].

The peculiar selectivity of ILs made them of great interest, also for the flavor, fragrance and essential oil (EO) fields whose analysts are constantly looking for new stationary phases with unconventional selectivities compared to those currently-used based on polysiloxane and polyethylene glycol derivatives, while always maintaining good chromatographic properties in terms of efficiency and inertness [9,13,14]. This need is necessitated because samples of these fields are often complex mixtures of isomeric and/or homologous components with similar structural and physical characteristics (e.g. mono- and sesquiterpenoids in EOs) whose correct identification requires a decisive contribution of diagnostic chromatographic data (e.g. retention indices) to be combined with their mass spectra [15]. A number of applications of IL columns have already been reported in these fields, including the analysis of flavor and fragrance mixtures [16,17], allergens [9,13,14,18], coffee aroma [19] and several EOs (i.e. peppermint essential oil [20], lemon essential oil [7], fennel, cinnamon and nutmeg essential oils [21], chamomile and sandalwood essential oils [9], and cornmint and vetiver essential oils [14]). Because of their peculiar selectivity, IL stationary phases were also successfully and widely applied in multidimensional GC systems; Nan and Anderson [6] have recently exhaustively reviewed this topic. Three quite recent applications among others: i) Sciarrone et al. applied HS-SPME-Heart/Cut (H/C)-C-IRMS with simultaneous quadrupole MS detection using SLB-IL59 in the second GC dimension to authenticate and monitor the traceability of truffles (*Tuber magnatum* Pico) by measuring $\delta^{13}C$ of its odorous principle (bis(methylthio)methane) [22], ii) Wong et al. used IL columns in the second dimension in enantioselective-GC × GC-ToF-MS analysis to determine adulteration, or to detect additives affecting the enantiomeric ratios, in commercial Australian tea tree oils [8], iii) Yan et al. used a novel sequential three-dimensional gas chromatography–high-resolution time-of-flight mass spectrometry (3D GC–accTOFMS) system where a first non-polar column is on-line combined through a microfluidic heart-cutting (H/C) with a GCxGC system using an ionic liquid column as 3rd dimension ($GC_{np}-GC_{PEG}\times GC_{IL}$) to analyze oxygenated sesquiterpenes in hop (*Humulus lupulus* L.) essential oil and agarwood (*Aquilaria malaccensis*) oleoresin [23]. ILs as GC stationary phases were also used for micropreparative systems, in particular Mondello's group isolated pure components from very complex essential oils through a sophisticated multidimensional system consisting of four dimensions (LC-GC-GC-GC) including an SLB-IL59 column in one of them [24,25].

The search for new IL stationary phases with uncommon selectivity to be applied to GC separation in the flavor, fragrance and essential oil fields is therefore of high interest. The possibilities of the anion-cation combinations to obtain ILs are unlimited. Therefore, this study has been focused on ILs based on phosphonium cations combined with different anions whose fundamental characteristics (or better chromatographic properties) were already studied by Breitbach and Armstrong in 2008 [26]. They reported the results of an in-depth and comprehensive study into the solvation properties for eight monocationic and three newly synthesized dicationic phosphonium-based versus those of analogous imidazolium-based ILs by inverse GC using the Abraham linear solvation energy relationship applied to a set of 26–34 probe analytes. The Abraham linear solvation energy relationship [27] is described by the following equation: $\log k = c + eE + sS + aA + bB + lL$ where E, S, A, B, and L are solutes (analytes) descriptors representing their excess molar refraction, dipolarity, H-bond acidity, H-bond basicity, and gas–hexadecane partition coefficient, respectively. Whereas, e, s, a, b, and l are a measure of the ability for the solvent (stationary phase) to interact with the solute through π/nonbonding electrons, dipole–dipole interactions, H-bond basicity, H-bond acidity, or dispersion forces, respectively. With all investigated ILs, Breitbach and Armstrong found that the hydrogen bond basicity (a coefficient in the Abraham relationship) prevailed as a system constant while the others (i.e., e, s, b, and l) were by far less relevant [26]. The hydrogen bond basicity interaction parameter ranged from 1.55 for trihexyl(tetradecyl)phosphonium bis[(trifluoromethyl)sulfonyl]imide ($[P_{66614}^+]$ $[NTf_2^-]$), to 6.94 for tributyl(ethyl)phosphonium diethyl phosphate ($[P_{4442}^+]$ $[DEP^-]$). They also measured the physico-chemical properties and studied the thermal stabilities for all of the investigated phosphonium-based ILs.

These results and in particular the difference in the value of the a coefficient in the Abraham relationship [26] were the basis for the choice of the two ILs investigated in this study. In particular, they consisted of the same cation associated with different counter-anions, i.e., trihexyl(tetradecyl)phosphonium chloride $[P_{66614}^+]$ $[Cl^-]$, (a term: 6.60) and $[P_{66614}^+]$ $[NTf_2^-]$, (a term: 1.55) (Fig. 1a). Moreover, both ILs have viscosities and densities suitable for capillary column coating, solid/liquid transformation temperature by far below 0 °C affording very low minimum operative temperatures and good thermal stability ranging from 335 °C for $[P_{66614}^+]$ $[Cl^-]$ to 380 °C for $[P_{66614}^+]$ $[NTf_2^-]$ with zero column bleeding until 280 °C and 300 °C, respectively [26].

This study examines the chromatographic properties and selectivity of columns coated with the above ILs and the influence of their different chemical composition on separation, as well as the maximization of their performance in terms of efficiency and inertness in view of possible applications in the flavor, fragrance and essential oil fields. The results were compared to those of conventional and commercially-available IL columns.

2. Experimental

2.1. Samples and chemicals

The Grob test mixture [28], consisting of a mixture of **1:** decane, **2:** dodecane, **3:** 1-octanol, **4:** 2,3-butanediol, **5:** methyl decanoate, **6:** methyl undecanoate, **7:** methyl dodecanoate, **8:** 2,6-dimethylphenol, **9:** 2,6-dimethylaniline, **10:** dicyclohexylamine, and **11:** 2-ethylhexanoic acid in hexane and trichloromethane, was purchased from Merck (Milan, Italy) and analyzed as received.

The Polarity Number of IL SPs was calculated on a mixture (PN mixture) of pure benzene, *n*-butanol, 2-pentanone, nitropropane and pyridine (100 μL each); a mixture of pure light hydrocarbons, C5-C14 (100 μL each) was also prepared. All standards were from Merck (Milan, Italy)

The mixture of menthol isomers and derivatives contained 7 compounds: menthol, *iso*-menthol, *neo*-menthol, *neo*-*i*-menthol, menthone, *i*-menthone and menthyl acetate (Fig. 1b). Phenylpropenoids standard mixture consisted of 4 compounds: anethole, estragole, eugenol, *i*-eugenol (Fig. 1c). Both mixtures were prepared at a concentration of 200 mg/L in cyclohexane and all standards were from Merck (Milan, Italy) or from the author's standard collection.

The flavour and fragrance standard mixture (FFMix) consisted of 38 compounds: **1**:, β-pinene, **2:** limonene, **3:** nonane (ISTD), **4:** undecane (ISTD), **5:** tridecane (ISTD), **6:** 1,8-cineole, **7:** camphor, **8:** menthone, **9:** *i*-menthone, **10:** pulegone, **11:** linalyl

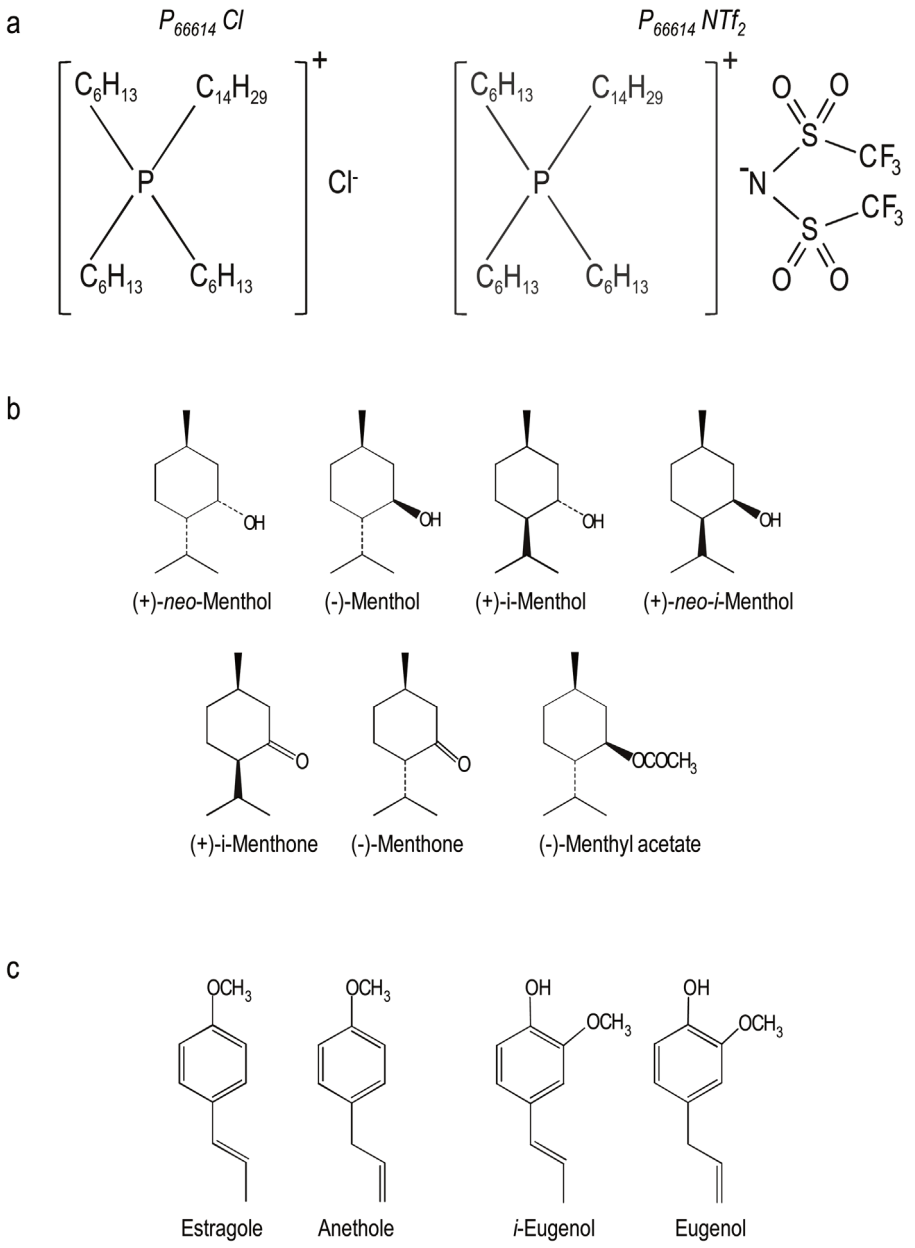

Fig. 1. Structure of a) investigated ILs, b) menthol isomers and derivatives, c) pheylpropenoids.

acetate, **12:** bornyl acetate, **13:** menthyl acetate, **14:** lavandulyl acetate, **15:** terpinyl acetate, **16:** ethyl 2-methylbutanoate, **17:** caryophyllene, **18:** estragole, **19:** anethole, **20:** γ-hexalactone, **21:** γ-heptalactone, **22:** γ-octalactone, **23:** 2-methylbutanol, **24:** 1-octanol, **25:** terpinen-4-ol, **26:** linalool, **27:** α-terpineol, **28:** *neo*-menthol, **29:** *neo-i*-menthol, **30:** menthol, **31:** *i*-menthol, **32:** lavandulol, **33:** borneol, **34:** viridiflorol, **35:** eugenol, **36:** *i*-eugenol, **37:** thymol, **38:** carvacrol. All compounds were from Merck (Milan, Italy) or from author's standard collection and were solubilized at a concentration of 100 mg/L in cyclohexane.

The suspected allergens standard mixture (AlMix) consisted of 29 compounds: **1**: limonene, **2**: linalool, **3**: estragole, **4**: phenylacetaldehyde, **5**: methyl 2-octynoate, **6**: citronellol, **7**: geraniol, **8**: benzyl alcohol, **9**: neral, **10**: geranial, **11**: α-isomethyl ionone, **12**: methyl eugenol, **13**: hydroxycitronellal, **14**: α-ionone, **15**: eugenol, **16**: lilial, **17**: cinnamaldehyde, **18**: anisyl alcohol, **19**: farnesol isomers, **20**: cinnamyl alcohol, **21**: amyl cinnamaldehyde, **22**: hexyl cinnamaldehyde, **23**: α-pentylcinnamyl alcohol, **24**: vanillin, **25**: lyral isomers, **26**: coumarin, **27**: benzyl benzoate, **28**: benzyl salicylate, **29**: benzyl cinnamate. They were solubilized at a concentration of 500 mg/L in cyclohexane.

The essential oil (EO) of sage (*Salvia officinalis* L.) was obtained by hydrodistillation following the procedure of the European Pharmacopoeia [4] while the vetiver EO (*Chrysopogon zizanioides* (L.) Roberty) was kindly provided by Robertet (Grasse, France); they were solubilized in cyclohexane at a concentration of 1 mg/ml before analysis.

All solvents were all HPLC grade from Merck (Milan, Italy).

2.2. Analysis conditions

2.2.1. Instrumental set-up

Analyses were carried out on a Shimadzu GC-FID 2010 unit equipped with Shimadzu GC Solution 2.53U software and a Shimadzu GC 2010 – Shimadzu QP2010-PLUS GC–MS system equipped with GCMS 2.51 software (Shimadzu, Milan, Italy). FID was used

to determine chromatographic parameters, while MS was used for identification purposes.

2.2.2. Columns

The investigated IL SPs were [P_{66614}^+] [NTf_2^-], and [P_{66614}^+] [Cl^-],) (Fig. 1a). Trihexyl(tetradecyl)phosphonium chloride (~97%) was purchased from Strem Chemicals (Newburyport, MA, USA). The IL was purified using liquid-liquid extraction with acetonitrile and hexane. Following purification, the IL was dried under vacuum until dry. [P_{66614}^+] [NTf_2^-] was prepared by dissolving purified [P_{66614}^+] [Cl^-] in acetone followed by the dropwise addition of a 2 M excess of [Li^+] [NTf_2^-] in an aqueous solution. The crude product was dried under rotary evaporation until dry and then further purified by dissolving in diethyl ether and washing several times with water. The final product was then dried under rotary evaporation followed by extensive drying in a vacuum oven to afford the dry product.

Columns with different characteristic coatings of both IL SPs were prepared by Mega (Legnano (MI), Italy) using the static coating procedure after a proprietary deactivation process. In particular, the determination of polarity number and menthol mixture analyses were carried out with 30 m, 0.25 mm d_c × 0.25 μm d_f columns covered with the investigated SPs, while all other samples were analyzed with a test [P_{66614}^+] [Cl^-] NB column (l: 5 m, d_c: 0.1 mm, d_f: 0.1 μm) and a test [P_{66614}^+] [NTf_2^-] NB column (l: 5 m, d_c: 0.1 mm, d_f: 0.15 μm)

Commercial SLB-IL60i, SLB-IL76i and SLB-IL111i (30 m, 0.25 mm d_c × 0.20 μm d_f) from Merck (Milan, Italy) and OV1701 (30 m, 0.25 mm d_c × 0.25 μm d_f) from Mega (Legnano (MI), Italy) were used for comparative studies.

2.2.3. GC–MS conditions

GC–MS analyses were carried out under the following conditions: temperatures: injector: 240 °C; transfer line: 240 °C, ion source: 200 °C; carrier gas: He, flow control mode: constant linear velocity, flow rate for conventional columns: 1 mL/min, for 5 m narrow bore (NB) test column 0.4 mL/min. The linear velocity for PN calculation was set at 40 cm/s as recommended by Mondello et al. [7]. Injection conditions were: mode: split; split ratio: 1:50, volume: Grob test: 2 μL, all other samples 1 μL. Oven temperatures were programmed as follows: i) for PN determination: isothermal 120 °C (15 min); ii) for analysis of menthol model mixture: 50 °C // 2 °C/min // 220 °C (2 min); iii) for all samples analysed with NB test column: 40 °C // 2 °C/min // 220 °C (2 min). The MS operated in electron impact ionization mode (EI) at 70 eV, scan rate 1250 u/s, mass range: 35–350 *m/z*.

Analyte identification: when necessary, analytes were identified through their mass spectra and/or linear retention indices. Mass spectra were compared to those of authentic standards or to those of commercial or in-house libraries, or literature data. Retention indices of the available standards were calculated versus a C9-C25 hydrocarbon solution analyzed under the conditions reported above.

2.2.4. GC-FID conditions

GC-FID analyses were carried out under the following conditions: temperatures: injector: 240 °C; detector: 240 °C; carrier gas: H_2. All other analysis conditions were the same as those reported in the previous GC–MS paragraph. FID sampling rate: 40 ms.

2.2.5. Polarity Number (PN) mixture sampling conditions

A 1 μl volume of the PN and of the light hydrocarbons mixtures were sampled by headspace-solid-phase microextraction (HS-SPME) with a divinylbenzene/carboxen/poly dimethylsiloxane fiber (Merck, Milan, Italy) at 30 °C for 1 min. The sampled analytes were then recovered by thermal desorption in the GC inlet for 2 min.

PN was calculated according to the following equation: PN_x = (P_x / $P_{SLB\text{-}IL100}$) x 100 where P (Polarity) = sum of the first five McReynolds Constants and PN = polarity (P) normalized to SLB-IL100 (set at P = 100) [7].

2.2.6. Calculation of relative area % ratios

The relative area % ratio was calculated by normalizing the analytes peak areas to those of decane for the Grob test and limonene for AlMix, and then by comparing the normalized areas to those obtained with the reference columns (i.e. SLB-IL60i for the Grob test and MEGA-1701 for the AlMix). The data processed are the mean calculated over three injections; RSD for each component never exceeded 3%.

3. Results and discussion

This section consists of three parts: the first one reporting the chromatographic performance of the columns prepared with the investigated ILs, the second one discussing their selectivity and the third one showing two applications to real world samples. A set of 5 m narrow bore (NB) test columns with film thickness of 0.1 μm for [P_{66614}^+] [Cl^-] and of 0.15 μm for [P_{66614}^+] [NTf_2l^-] were used. Some experiments were also carried out with 30 m, 0.25 mm d_c, 0.25 μm d_f conventional columns. The chromatographic performance was first investigated with the Grob test together with four standard solutions consisting of i) a model mixture of menthol isomers and derivatives (Fig. 1b), ii) a model mixture of differently substituted phenylpropenoids (Fig. 1c), iii) a standard mixture of 38 volatiles characteristic in the flavor, fragrance and essential oil fields (FFMix), and iv) a standard mixture of 29 allergens (AlMix); the test NB columns were also applied to the analysis of two essential oils of different complexity (sage and vetiver essential oils) as examples of real world samples. Unless specified otherwise, all analyses are carried out under the same chromatographic conditions to facilitate comparisons.

3.1. IL gas chromatographic performance

The ILs were evaluated in terms of chromatographic properties to validate them as new stationary phases for routine gas chromatography. The Grob test was here used as a diagnostic mixture to study the GC performance of the investigated ILs.

Fig. 2 shows the GC patterns of the Grob test obtained with a) OV-1701 (reference), b) SLB-IL60i (reference), c) [P_{66614}^+] [Cl^-] and d) [P_{66614}^+] [NTf_2^-] SPs. Column efficiency and inertness were first investigated. Table 1 summarizes the chromatographic data of [P_{66614}^+] [Cl^-] and [P_{66614}^+] [NTf_2^-] test columns obtained with the Grob test. The efficiency was first measured: the [P_{66614}^+] [Cl^-] column showed a number of theoretical plates per meter (N/m), calculated by the isothermal separation of 1-octanol (**3**) at 80 °C, of 9817 N/m, while that coated with [P_{66614}^+] [NTf_2^-] of 9619 N/m. The separation power of the two columns was measured over the total Grob test pattern through the separation measure Δ*s*, i.e. the number of consecutive non-overlapping σ-intervals within an arbitrary time interval (t_b – t_a), calculated through the following equation: $\Delta s = (t_b\text{-}t_a)/[(\sigma_a + \sigma_b)/2]$, where t_a and t_b are the retention times of the first and last eluting peaks and σ_a and σ_b are their peak widths. [29]. Its value was similar for both ILs and worth highlighting, i.e., 1352 for [P_{66614}^+] [Cl^-] calculated between the first (*n*-C_{10} (**1**)) and the last (ethylhexanoic acid (**11**)) eluting peaks and 1299 for [P_{66614}^+] [NTf_2^-] measured between *n*-C_{10} (**1**) and *n*-C_{12} methyl ester (**5**).

The two columns showed very similar efficiency, but considerable difference in retention. Under the same analysis conditions, retention is drastically higher for [P_{66614}^+] [Cl^-], with the last peak (ethylhexanoic acid (**11**)) eluting with a retention time (t_R) of about

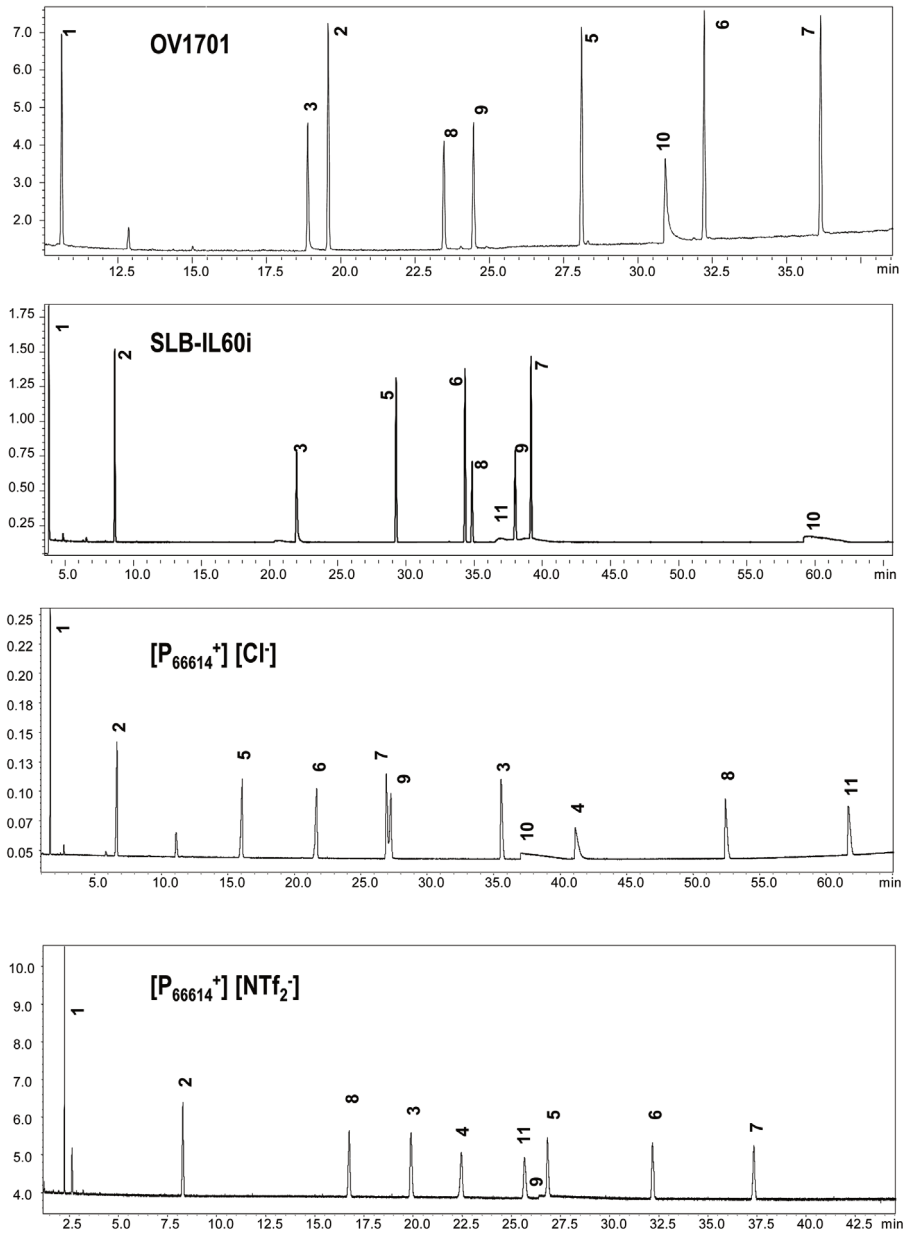

Fig. 2. GC-FID patterns of Grob test obtained with columns coated with different stationary phases: a) OV-1701, b) SLB-IL60i; c) [P_{66614}^+] [Cl^-], and d) [P_{66614}^+] [NTf_2^-]. For column characteristics, analysis conditions and peak identification see experimental.

62 min, compared to that of [P_{66614}^+] [NTf_2^-], where the last peak (*n*-C_{12} methyl ester (**5**)) elutes in 37.3 min. The difference of retention of the two investigated IL SPs is discussed in Section 3.2.

The peak width (σ), column activity, and inertness (tailing factor and relative adsorption) were then measured with the Grob test components because of their different chemical structures. In general, the average peak widths (σ) of [P_{66614}^+] [NTf_2^-] and [P_{66614}^+] [Cl^-], are rather similar, varying from 0.039 min to 0.045 min respectively. With single compounds, σ ranges from 0.010 min for *n*-C_{10} (**1**) to 0.052 min for ethylhexanoic acid (**11**) with [P_{66614}^+] [NTf_2^-], and from 0.011 for *n*-C_{10} (**1**) to 0.078 min for ethylhexanoic acid (**11**) with [P_{66614}^+] [Cl^-]. The analytes 2,6-dimethylaniline (**9**) and dicyclohexylamine (**10**) were not considered in the average σ and tailing factor determination because their peaks were too severely distorted on both columns; the only exception was 2,6-dimethylaniline (**9**) with [P_{66614}^+] [Cl^-] that had a σ of 0.042. The peak symmetry was evaluated through the tailing factors calculated at 5% of peak height. With [P_{66614}^+] [NTf_2^-], the nine peaks considered in the Grob test were inside the selected window (i.e., between 0.8 and 1.2), and with [P_{66614}^+] [Cl^-] only four peaks were outside the window; these results are highly satisfactory and compatible with those of OV-1701 and SLB-IL60i taken as reference columns [9]. Here too, 2,6-dimethylaniline (**9**) showed good peak symmetry with [P_{66614}^+] [Cl^-] (tailing factor: 1.041).

Another important representative parameter of column inertness is the relative area % ratio. Fig. 3 shows the recovery of the Grob test components relative to SLB-IL60i taken as reference because of its high inertness [9]. OV-1701 was also included for comparison purposes. With [P_{66614}^+] [Cl^-], most components presented relative areas vs. SLB-IL60i of at least 80%; and only the three linear methyl esters were below, although all were always above 70%. Some components appear to be less adsorbed compared to SLB-IL60i, in particular those with a free hydroxyl or a carboxyl group in their structure. Remarkable are the cases of i) 2,3-butanediol (**4**) that is not included in the diagram of Fig. 2 because it was fully adsorbed with the SLB-IL-60i column, and ii) ethylhexanoic

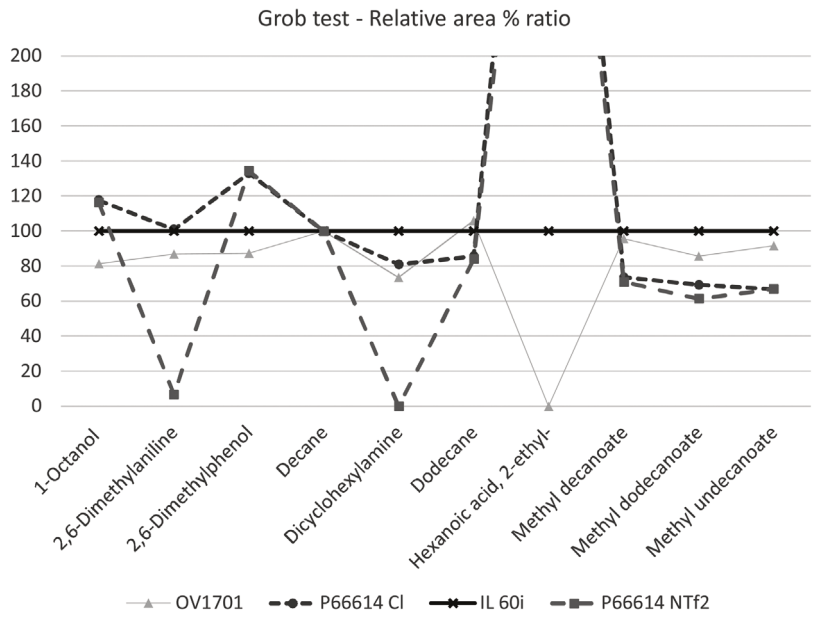

Fig. 3. Relative area % ratios of Grob Test components measured with the investigated [P_{66614}^+] [Cl^-] and [P_{66614}^+] [NTf_2^-] NB test columns, and with a OV-1701 column versus SLB-IL60i column taken as reference.

acid (**11**) that is completely adsorbed with OV-1701 and highly distorted with SLB-IL60i, while it seems not to be adsorbed at all with both of the investigated IL SPs. With [P_{66614}^+] [Cl^-], the ethylhexanoic acid (**11**) relative area % ratio vs SLB-IL60i was 530% with a peak width (σ) of 0.078 min and a tailing factor of 1.465, while the P_{66614} NTf_2, possessed an area ratio of 476% with a σ of 0.052 min and a tailing factor of 1.171. On the other hand, with this stationary phase dicyclohexylamine (**10**) was completely adsorbed and 2,6-dimethylaniline (**9**) showed a relative area ratio of about 5%.

The column temperature stability was also investigated by evaluating a 5 m NB column for each IL SP and submitting it to step conditioning by increasing the temperature by 20 °C for each step and controlling its performance with the Grob test. The two columns did not present bleeding and gave perfectly superimposable Grob test patterns up to 280°C for [P_{66614}^+] [Cl^-] and 240°C for [P_{66614}^+] [NTf_2^-]. These results are in good agreement with those reported by Breitbach and Armstrong [230] for [P_{66614}^+] [Cl^-], but significantly lower for [P_{66614}^+] [NTf_2^-] (240 vs. 300 °C).

3.2. Polarity and selectivity

In general, commercially-available room temperature IL SPs exhibit medium high to high polarities and peculiar selectivity [1,7] and these characteristics were also studied for the IL SPs investigated in this study.

Analogous to the commercial columns, the Polarity Number (PN) of these IL SPs was first determined by rigorously applying the methods and conditions described by Mondello et al [7]. Under these conditions, [P_{66614}^+] [Cl^-] gave a PN of 37 and [P_{66614}^+] [NTf_2^-], of 33. The reliability of the measured PNs was confirmed by measuring the PNs values of three commercial IL columns (SLB-IL60i, SLB-IL76i and SLB-IL111i), which provided numbers in perfect agreement with those of the column labels. The two new IL SPs showed a similar polarity, but remarkably lower than that of IL columns that are currently commercially-available (33 or 37 vs. a minimum of 59).

In spite of this similarity, the chromatographic behavior of these columns was completely different in terms of retention and selectivity. These properties were investigated in depth with the aforementioned standard solutions of i) menthol isomers and derivatives, ii) phenylpropenoids, iii) FFMix, and iv) AlMix. Samples iii and iv were used because they consist of compounds with different polarity, structure and functionality. The model mixture of the menthol derivatives analyzed with the 5 m NB test [P_{66614}^+] [NTf_2^-] column under the adopted conditions resulted in coelutions of *n*-*i*-menthol and *n*-menthol and *i*-menthone and *i*-menthol. The coelutions were probably due to a lack of efficiency of the test NB column (N: ∼48,000): the test column was successfully replaced with a conventional 0.25 mm d_c, 30 m column (N: ∼ 180,000) that provided a baseline separation of all analytes. A conventional [P_{66614}^+] [Cl^-] column (l: 30 m, d_c: 0.25 mm, d_f: 0.25 μm) was used also to analyze this model mixture to enable comparisons, although its seven components were baseline with the test NB column.

3.2.1. - [P_{66614}^+] [Cl^-] *column* – Fig. 4a shows the GC patterns of menthol and phenylpropenoid standard mixtures analyzed with the investigated IL SP. The GC pattern of the menthol model mixture shows that this IL SP drastically discriminates the analytes depending on their organic functional groups, i.e., first ketones (menthone isomers), then esters (menthyl acetate) and alcohols (menthol isomers) (Fig. 1b). The analyte elution temperatures with this column are very different ranging from 102 °C for menthone (i.e., the first eluting carbonyl derivative) to 163 °C for *n*-menthol (i.e., the first eluting hydroxyl derivative) resulting in a marked difference in retention (from about 26 min for menthone to above 56 min for *neo*-*i*-menthol) with a separation of more than 26 min between the clusters of carbonyl and hydroxyl-containing compounds. This pattern is completely different not only from that obtained with conventional stationary phases but also from that obtained with other IL columns [20]. The phenylpropenoid standard mixture contains phenolic ethers (estragole and anethole) and phenols (eugenol and *i*-eugenol) were each isomers differing in the position of the double bond in the C_3 side chain (i.e. propenyl or allyl groups) (Fig. 1c). The results of phenylpropenoids analysis with the test NB column confirmed those of menthol derivatives, the phenolic ethers elute far before phenols, with the elution temperature of estragole and eugenol at 62 °C and 155 °C, respectively. In this case, two groups are also clearly separated, with the t_R of estragole at about 11 min and that of eugenol at about 57 min with a difference between phenolic ether and phenol clusters of about 39 min. Within the two groups, the propenyl isomers elute before allyl iso-

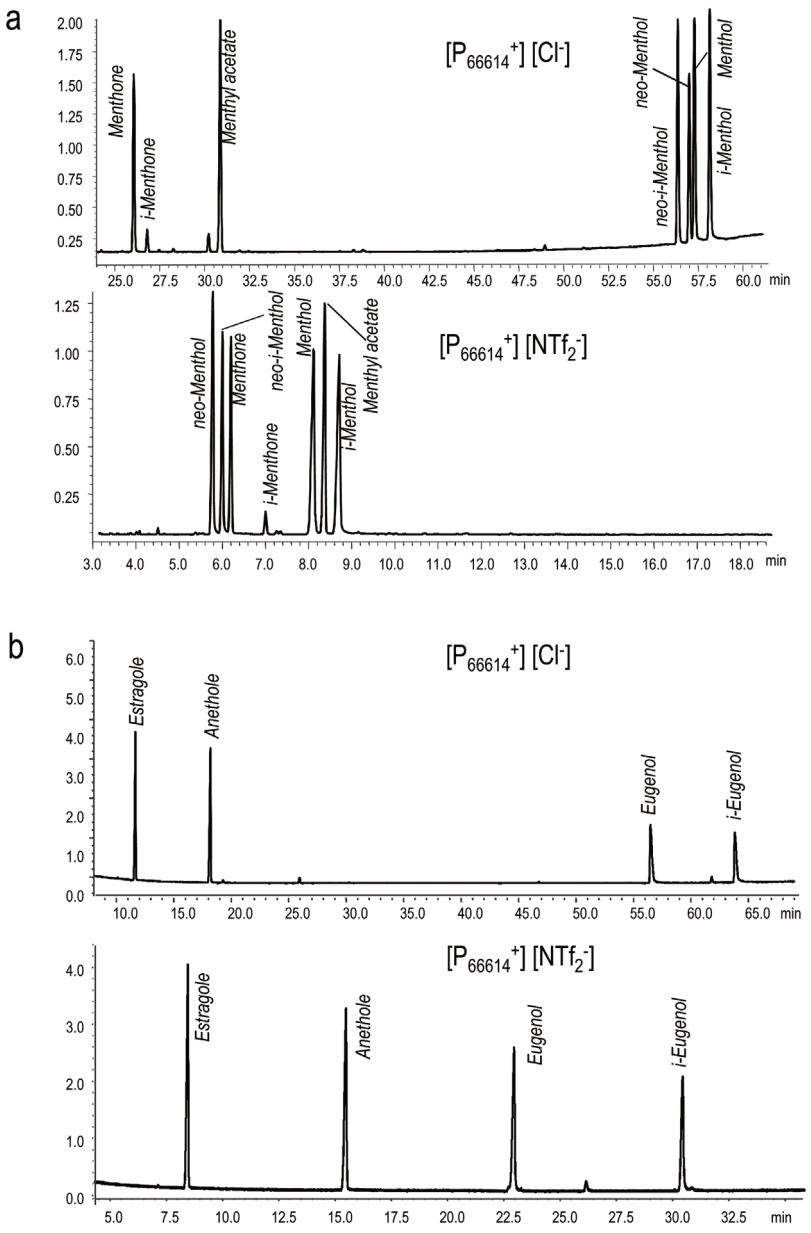

Fig. 4. GC-FID patterns of a) menthol model standard mixture analyzed with [P_{66614}^+] [Cl^-], and [P_{66614}^+] [NTf_2^-] conventional columns (l: 30 m, d_c: 0.25 mm, d_f: 0.25 μm), and b) phenylpropenoid model standard mixture analyzed with [P_{66614}^+] [Cl^-], and [P_{66614}^+] [NTf_2^-] NB test columns (l: 5 m, d_c: 0.10 mm, d_f: 0.1 μm).

mers likely because the formers can extend their aromaticity with the double bond of the side chain. This behavior where analytes are separated mainly because of nature of the functional group is in agreement with the results of the Abraham model [26] according to which the [P_{66614}^+] [Cl^-] SP is characterized by a high hydrogen bond basicity interaction (*a* coefficient of 6.60).

After analysis of the Grob test, menthol and phenylpropenoid model mixtures, other more complex standard mixtures were tested. This included the FFMix (38 components) consisting of compounds with similar structures but different organic functional groups, and the AlMix (29 components) containing compounds with randomly different structures and volatility.

Fig. 5a shows the GC pattern of the FFMix analyzed with the [P_{66614}^+] [Cl^-] test column. These results confirm those reported above with the early elution of hydrocarbons followed by carbonyl derivatives (i.e., ketones, esters and lactones in sequence), followed by alcohols. For the latter group, a clear discrimination between aliphatic alcohols and phenols is also observed. The elution order is obviously also influenced by other analyte characteristics such as volatility as indicated by the C_6-C_8 homologous series of γ-lactones (**20-22**), caryophyllene (**17**) (a C_{15} sesquiterpene hydrocarbon) and viridiflorol (**34**) (a C_{15} sesquiterpene alcohol).

The AlMix exhibits a similar behavior, although the discrimination is less clear-cut because several components are multifunctional. Fig. 6a shows the GC pattern of the AlMix analyzed with the [P_{66614}^+] [Cl^-] test column. Three main groups can be identified: hydrocarbons, ethers and carbonyl containing derivatives, and hydroxyl derivatives. Even here, the elution order also depends on other analyte characteristics besides their organic functional groups, such as molecular weight and volatility. Clear examples are i) the three benzyl esters (benzoate (**27**), cinnamate (**28**) and salicylate (**29**) in order of elution) where the salicylate derivative elute later likely because of the free hydroxyl moiety on the aromatic ring, ii) the hydroxyaldehydes (hydroxycitronellal (**13**), and lyral a and b (**25a, 25b**)) that elute with the hydroxyl derivatives, probably due to the prevalent interaction of the hydroxy group with the

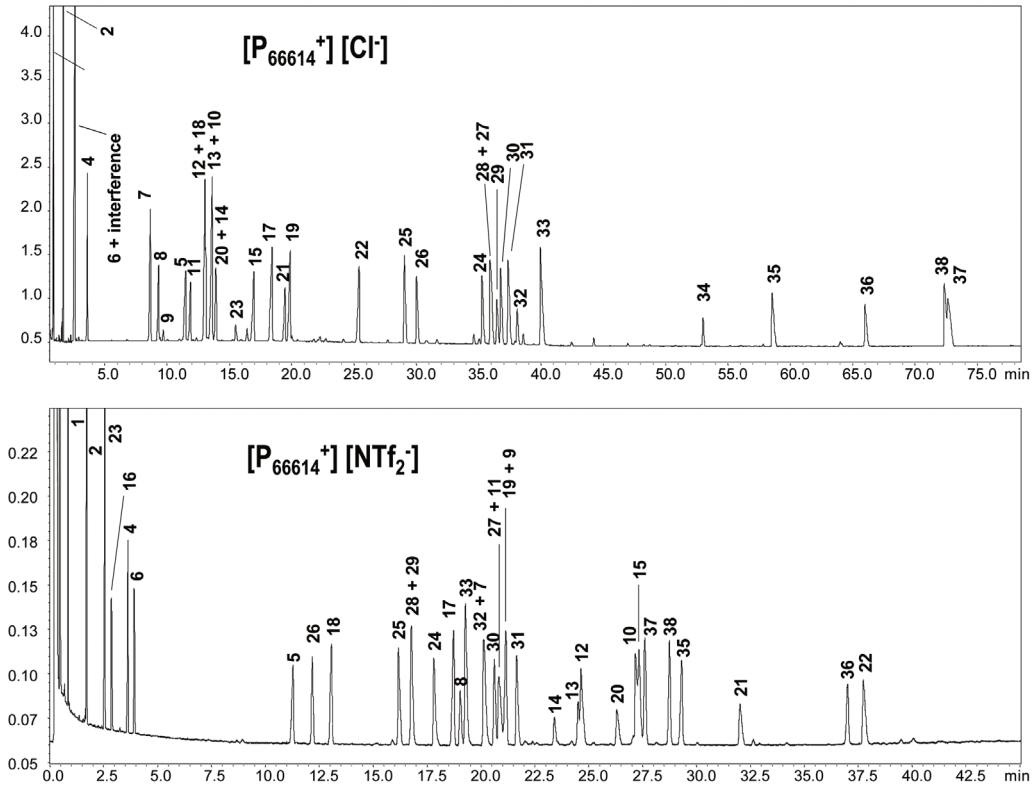

Fig. 5. GC-FID patterns of FFMix obtained with NB test columns coated with different stationary phases: [P_{66614}^+] [Cl^-], and [P_{66614}^+] [NTf_2^-]. For column characteristics, analysis conditions and peak identification see experimental.

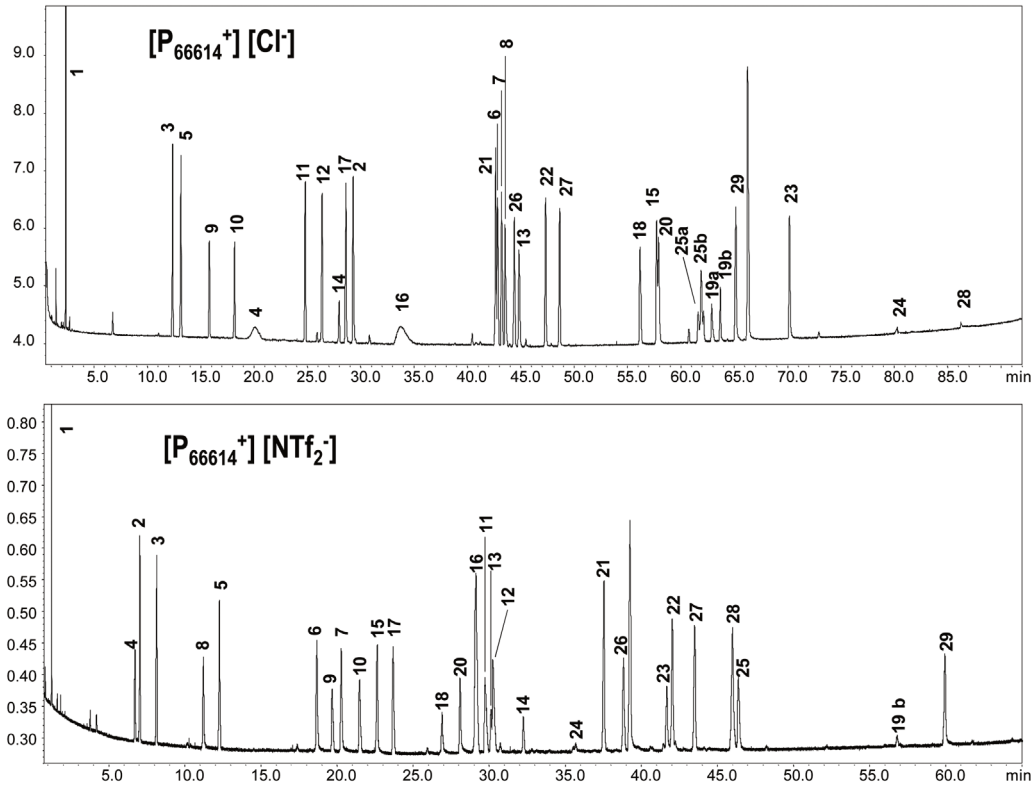

Fig. 6. GC-FID patterns of AlMix obtained with NB test columns coated with different stationary phases: [P_{66614}^+] [Cl^-], and [P_{66614}^+] [NTf_2^-]. For column characteristics, analysis conditions and peak identification see experimental.

Table 1
Chromatographic performance of the investigated stationary phases calculated on the analysis of the Grob test standard mixture.

PN			N		N/m		Δ *s*		Average σ	
[P_{66614}^+] [Cl^-]	[P_{66614}^+] [NTf_2^-]	[P_{66614}^+] [Cl^-]	[P_{66614}^+] [NTf_2^-]	[P_{66614}^+] [Cl^-]	[P_{66614}^+] [NTf_2^-]	[P_{66614}^+] [Cl^-]	[P_{66614}^+] [NTf_2^-]	[P_{66614}^+] [Cl^-]	[P_{66614}^+] [NTf_2^-]
37	33	49083	48096	9817	9619	1352	1299	0.045	0.039

	Compounds	Retention time		σ (min)		Tailing factor	
		[P_{66614}^+] [Cl^-]	[P_{66614}^+] [NTf_2^-]	[P_{66614}^+] [Cl^-]	[P_{66614}^+] [NTf_2^-]	[P_{66614}^+] [Cl^-]	[P_{66614}^+] [NTf_2^-]
1	Decane	1.66	2.26	0.011	0.010	0.833	0.822
2	Dodecane	6.67	8.29	0.027	0.027	0.818	0.818
3	1-Octanol	35.56	19.89	0.041	0.042	1.296	1.188
4	2,3-Butanediol	41.12	22.45	0.070	0.051	3.291	0.857
5	Methyl decanoate	16.08	26.84	0.039	0.042	0.844	1.200
6	Methyl dodecanoate	26.93	37.33	0.046	0.044	0.942	1.099
7	Methyl undecanoate	21.69	32.18	0.041	0.044	0.810	1.133
8	2,6-Dimethylphenol	52.42	16.74	0.052	0.038	1.568	0.987
9	2,6-Dimethylaniline	27.27	26.55	0.042	*N.C.*	1.041	*N.C.*
10	Dicyclohexylamine	37.09	*N.D.*	*N.C.*	*N.D.*	*N.C.*	*N.D.*
11	Hexanoic acid, 2-ethyl-	61.68	25.67	0.078	0.052	1.465	1.171

N.C. not calculable because highly distorted.
N.D. not detectable.

IL SP, and iii) homologs with longer side chains (amylcinnamaldehyde (**21**) and hexylcinnamaldehyde (**22**)) eluting with hydroxyl compounds because of their long retention due to high molecular weight.

3.2.2. - [P_{66614}^+] [NTf_2^-] *column* – Fig. 4b shows the GC patterns of menthol and phenylpropenoid model mixtures with this column. This IL SP shows immediately a different behavior from [P_{66614}^+] [Cl^-], mainly highlighted by a very low retention and a selectivity not depending on the organic functional group of the analytes investigated. After the preliminary experiments, the film thickness of the [P_{66614}^+] [NTf_2^-] test NB column was increased to 0.15 μm, while keeping constant the column length and inner diameter; the conventional column used with the menthol model mixture was not modified. For instance, *i*-menthol (the last peak eluting of menthol model mixture) elutes at 67 °C (about 9 min) on the [P_{66614}^+] [NTf_2^-] IL and at 166 °C (about 58 min) on the [P_{66614}^+] [Cl^-] IL, and *i*-eugenol in the phenylpropenoid mixture elutes at 113 °C (about 36 min) with [P_{66614}^+] [NTf_2^-] and at about 169 °C (65 min) with [P_{66614}^+] [Cl^-]. Moreover, all menthol derivatives elute in a time range of about 3 min with [P_{66614}^+] [NTf_2^-] and in 33 min with [P_{66614}^+] [Cl^-]. The selectivity within the phenolic ether and phenol groups is maintained. In the case of the [P_{66614}^+] [NTf_2^-] IL, the separation between allyl and propenyl derivatives almost doubles in terms of elution temperature and retention times.

On the contrary, the elution order of menthol derivatives cannot reliably be explained although all components are baseline separated. The [P_{66614}^+] [NTf_2^-] behaviour is in line with the fact that any of the Abraham model coefficients (*e, s, a, b* and *l*) [26] remarkably prevails on the others.

These results are also confirmed with FFMix and AlMix. Fig. 5b shows the GC pattern of the FFMix analyzed with the [P_{66614}^+] [NTf_2^-] column. As already observed with the Grob test, hydrocarbons are also well separated from the oxygenated compounds, and within the latter group, an analogous elution sequence begins with non-aromatic hydroxyl compounds followed by esters, phenols and lactones. Fig. 6b shows the GC pattern of the AlMix analyzed with the [P_{66614}^+] [NTf_2^-] column. As already observed for [P_{66614}^+] [Cl^-], the chemical complexity of the components of this mixture makes its selectivity more difficult to rationalize. The analysis of AlMix with this IL SP confirms the results of FFMix indicating, in addition, that aldehydes elute in proximity to the corresponding alcohol, i.e., the organic functional group does not play a prevalent role in selectivity as it does with the [P_{66614}^+] [Cl^-] IL In general, the selectivity of this IL SP seems to be more conventional and is mainly driven by analyte volatility: this consideration is also in agreement with its polarity number (33), which is far lower than those of the IL columns currently commercially available.

These results are also substantiated when the separation measures (Δ*s*) of the two test columns were calculated on both FFMix and AlMix. The FFMix values of Δ*s* are significantly different (i.e., 1860 for [P_{66614}^+] [Cl^-] and 1138 for [P_{66614}^+] [NTf_2 -]). The explanation is that, under the adopted analytical conditions, the peculiar selectivity of [P_{66614}^+] [Cl^-] on different functional groups dramatically influences the retention time of the last eluting peak, i.e. thymol (**37**) accounting for about 73 min, while the limited retention power of [P_{66614}^+] [NTf_2^-] gives an elution time for the last eluting peak (γ-octalactone (**22**)) of about 38 min.

On the other hand, the AlMix values of Δ*s* are closer (i.e., 2632 for [P_{66614}^+] [Cl^-] and 2125 for [P_{66614}^+] [NTf_2^-]). This result was expected because of the significant structural heterogeneity of its components that limits the influence of the specific selectivity of [P_{66614}^+] [Cl^-] towards the organic functional groups and increases the role of polarity, which is similar for the two investigated IL SPs (PN being 37 and 33, respectively). This makes the difference of the total analysis time on the last eluted peak to be less pronounced under the adopted conditions. For example, benzyl salicylate (**28**)

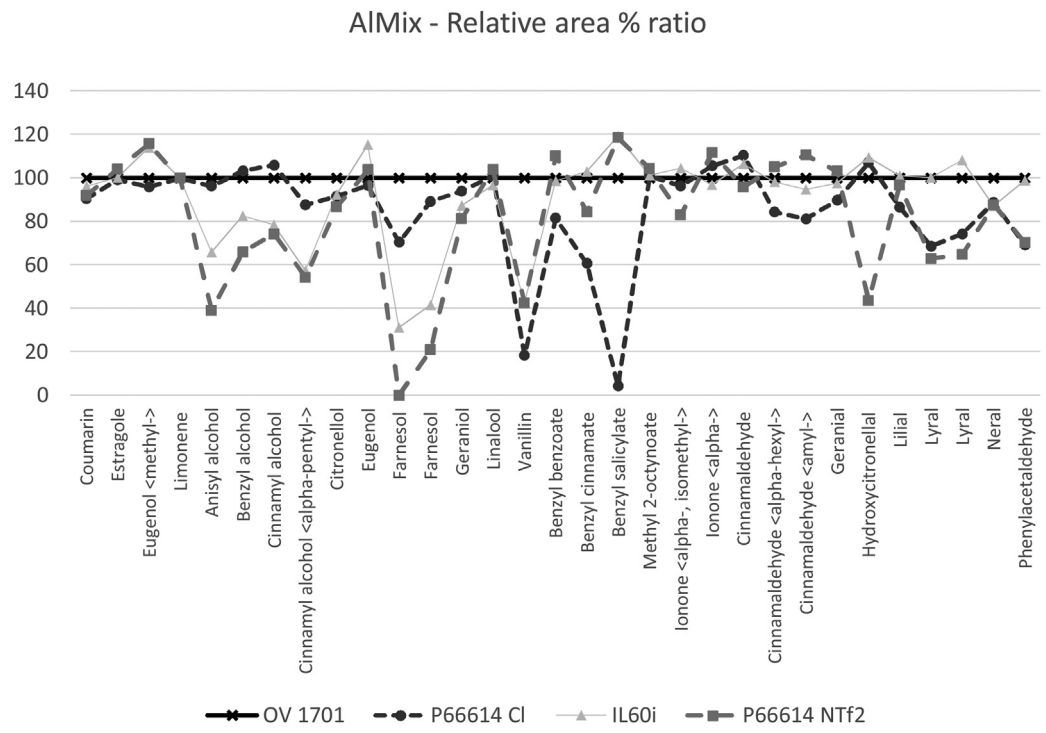

Fig. 7. Relative area % ratios of AlMix components measured with the investigated [P_{66614}^+] [Cl^-] and [P_{66614}^+] [NTf_2^-] NB test columns, and with a SLB-IL60i column versus OV-1701 column taken as reference.

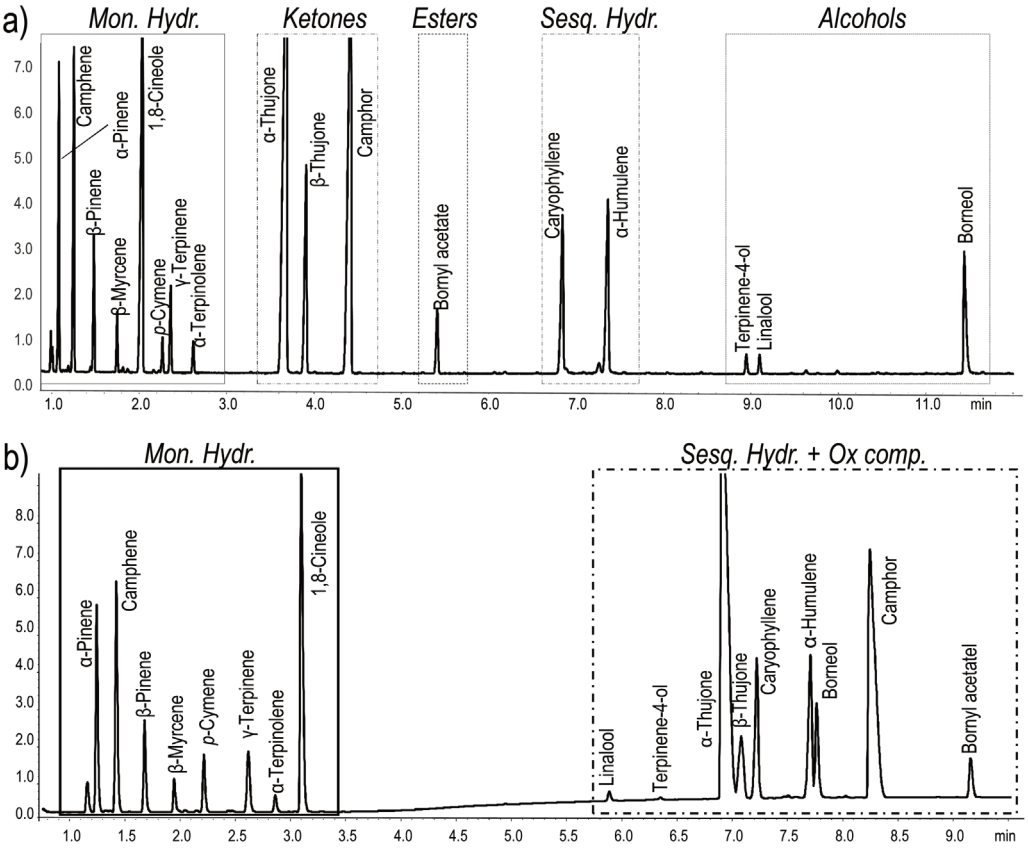

Fig. 8. GC–MS patterns of sage essential oil with [P_{66614}^+] [Cl^-] (a) and [P_{66614}^+] [NTf_2^-] (b) NB test columns. Temperature program: from 50 °C to 200 °C (5 min) at 10°/min.

on the [P_{66614}^+] [Cl^-] IL eluted at about 87 min and benzyl cinnamate (**29**) eluted at about 60 on the [P_{66614}^+] [NTf_2^-] IL.

Finally, the inertness of the two new IL SP columns was evaluated versus the allergen standard mixture because of the widely different chemical nature of its components. Fig. 7 shows the rel-

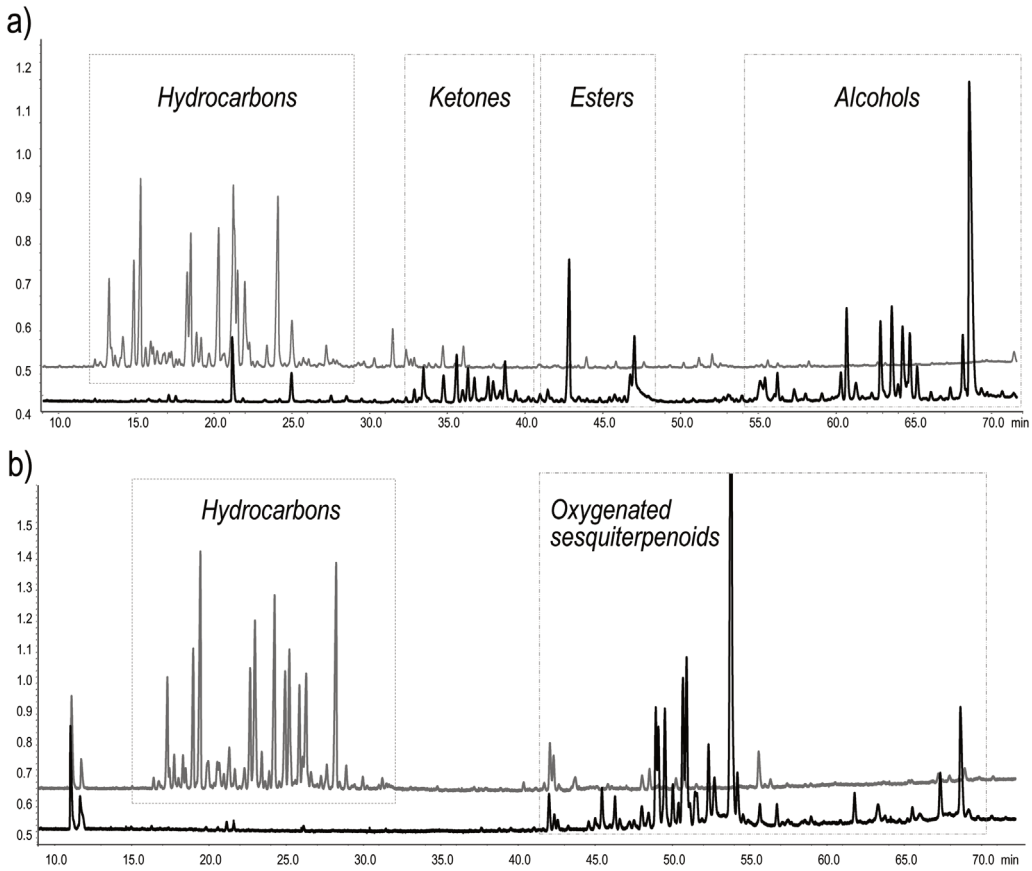

Fig. 9. GC-FID patterns of vetiver essential oil hydrocarbon (in grey) and oxygenated fractions (in black) analyzed with a) [P_{66614}^+] [Cl^-] NB test column, and b) [P_{66614}^+] [NTf_2^-] NB test column.

ative area % ratios of the components within the allergen model mixture calculated *vs*. those obtained with OV-1701 taken as reference. SLB-IL60i values are also included for comparison. The results showed that most components were recovered above 80% and some of them above 60% for both columns. The exceptions are: a) for [P_{66614}^+] [Cl^-], benzyl salicylate (**29**) (almost fully adsorbed) and vanillin (**24**) (recovered at 20%), and b) for [P_{66614}^+] [NTf_2^-], farnesol 1 (**19a**) (fully adsorbed), farnesol 2 (**19b**) (recovered at 20%), anisyl alcohol (**18**) (40%), vanillin (**24**) (42%), and hydroxyl citronellal (**13**) (42%).

3.3. Analysis of real world samples

The two proposed IL SPs have then been tested with real world samples to verify their ability in routine analysis. Two essential oils of highly different complexity were therefore chosen because these matrices mainly consist of components where a number of skeletons is substituted with different functional groups, i.e., these are samples where selectivity plays a fundamental role in the separation.

Sage (*Salvia officinalis* L.) essential oil consists of about 40 components, mainly well-known monoterpenoids (and to a lesser extent sesquiterpenoids), belonging to hydrocarbons, ketones, esters, and alcohols. Fig. 8 shows GC–MS data analyzed with [P_{66614}^+] [Cl^-] and [P_{66614}^+] [NTf_2^-] 5 m NB test columns. The [P_{66614}^+] [Cl^-] pattern shows a very clear separation between the components as a function of their organic functional groups and number of carbon atoms, for example, (in order of elution) monoterpenoids (C_{10}) including hydrocarbons and 1,8-cineole, ketones, esters, sesquiterpene (C_{15}) hydrocarbons, and monoterpene alcohols. On the other hand, the [P_{66614}^+] [NTf_2^-] pattern clearly discriminates between hydrocarbons and oxygenated monoterpenoids and also incorporates sesquiterpene hydrocarbons, with the retention of this IL SP also significantly conditioned by analyte volatility and polarity.

Vetiver (*Chrysopogon zizanioides* (L.) Roberty) essential oil is very complex and mainly consists of hydrocarbon and oxygenated sesquiterpenoids. Filippi et al. separated more than 250 sesquiterpenoids by GCxGC-MS and identified 216 of them with 122 being sesquiterpene hydrocarbons and 94 sequiterpenoids (acids, alcohols, aldehydes, esters, ethers, ketones), 49 of them being sesquiterpene alcohols [30]. Belhassen et al. recently reviewed vetiver essential oil composition and discussed its variation depending on origin and quality [31]. This essential oil was used as a representative test of the selectivity of the two investigated IL SPs mainly consisting of a highly complex mixture of C_{15} based skeleton components, although with different functional groups. The investigated essential oil was first submitted to a preliminary flash chromatography separation on a silica gel column with solvents of increasing polarity to separate hydrocarbons from oxygenated components in different fractions. The two fractions were then analyzed with the two IL coated NB columns under the same GC conditions. Fig. 9 shows the GC–MS patterns of the hydrocarbon and oxygenated fractions of the investigated vetiver essential oil analyzed with [P_{66614}^+] [Cl^-] (a) and [P_{66614}^+] [NTf_2^-] (b) 5 m NB columns. The unique selectivity on the organic functional groups of [P_{66614}^+] [Cl^-] SP was kept also on this very complex essential oil. This is clearly shown when the patterns of the two fractions are compared (Fig. 9a) where the hydrocarbon fraction does not overlap at all with the components of the oxygenated fraction; moreover, within the oxygenated fraction, the ketone group elutes separately from esters, and, in their turn, the latter are clearly sep-

arated from alcohols. Further studies are under way with longer columns that provide efficiency suitable for the complexity of the mixtures under investigation. The GC–MS analysis of the above fractions of this essential oil using the $[P_{66614}^{+}]$ $[NTf_2^{-}]$ as IL SP also confirm its properties in that hydrocarbons are well separated from oxygenated fraction components but the latter without discrimination of the analytes with different functional groups (Fig. 9b).

4. Conclusions

The reported results show that the two investigated ILs with phosphonium cation are highly useful and of high interest as SPs for gas chromatography because of their thermal stability, chromatographic properties and uncommon but complementary selectivity. In particular, the $[P_{66614}^{+}]$ $[Cl^{-}]$ SP has been shown to be able to discriminate analytes through their functional groups, while the $[P_{66614}^{+}]$ $[NTf_2$-] SP separates them as a function of their polarity and volatility. Further studies have still to be performed to make these columns suitable for routine use by: i) extending the investigated ILs to routine analysis of complex real-world samples and combining their selectivity with suitable column efficiency and characteristics (including length, inner diameter and film thickness) that have obviously limited the test columns investigated in this study, and ii) evaluating their applicability in not only 1D but also to 2D separations, planar columns and micropreparative GC.

These results are part of a wide study aiming to introduce new stationary phases for GC that exhibit uncommon analyte selectivity complementary to conventional and commercially-available IL SPs that should be highly useful in flavor (aroma), fragrance and essential oil analyses, where the analytical procedures (and analysis conditions) are well established and highly consolidated. The introduction of additional tools capable of providing different patterns of separation will extend the use of metabolomics approaches (mainly fingerprinting and profiling) to other fields. This will enable the characterization of samples with the maximum number of diagnostic representative data to achieve the searched level of information.

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