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Polymerized phosphonium-based ionic liquids as stationary phases in gas chromatography: performance improvements by addition of graphene oxide†

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Eight new functionalized, polymerizable phosphonium ionic liquids were prepared and applied as polymeric stationary phases in gas chromatography (GC). These coated GC columns exhibit high thermal stability compared to other ionic liquids (220–380 °C), and column efficiencies between 2700 and 3700 plates per m. The new columns have been characterized using the Abraham model in order to understand the effects of the polymeric cations and anions on the behavior of the system. These stationary phases show unique selectivity for several types of organic compounds such as alcohols, amines, pesticides and polycyclic aromatic hydrocarbons (PAHs), with good peak symmetries in some cases. Moreover, graphene oxide (GO) sheets have been covalently bonded onto the inner wall surface of fused silica capillary columns using 3-aminopropyl-diethoxymethylsilane (3-AMDS) as a cross-linking agent. The use of GO in the preparation of the capillary columns enhances their efficiency, improving peak symmetries because of the reduction of the unspecific absorption.

1. Introduction

The term "ionic liquid" (IL) is currently used to describe a broad class of salts with wide liquid ranges.

Ionic liquids have been developed for a wide variety of applications in different areas due to their unique properties.[1–11] An emerging application of ILs is as stationary phases in gas-chromatography, which is the subject of this paper. The common properties of the ILs, such as high thermal and redox stability, high viscosity and negligible vapor pressure, make these types of compounds very attractive as stationary phases in gas chromatography. The vast majority of ILs previously applied in GC are based on imidazolium cations.[12–22] In contrast, studies focused on novel classes of ILs achieved by a modification of the chemical structure of the cations are scarce. In particular, phosphonium, sulfonium and borenium-based ILs[23–27] have not received the same literature attention as their imidazolium analogs.

The higher cost and lower air stability of most phosphines compared with amines, along with the synthetic difficulties to access multi-substituent functionalized phosphonium cations can explain the scarcity of studies focused on phosphonium-based ILs. However, some of their properties (*i.e.* less dense than water, whereas the density of the nitrogen-based ILs is higher[28]) make them more suitable for some applications such as solvents in organic and inorganic synthesis. In the field of analytical chemistry and, more specifically, in gas chromatography, the phosphonium-based ILs offer great potential due to properties such as higher thermal stability[29,30] than many nitrogen-based ILs. However, the paucity of studies carried out on phosphonium ILs is still not sufficient for a wide range of applications. It is therefore necessary to perform detailed studies on the behavior of phosphonium ILs as stationary phases in gas chromatography.

A major problem in the study of new stationary phases based on ILs is the difficulty to obtain highly homogenous coatings that would generate good profiles of peaks and more effective separations. For this reason, in recent years, developments in separation sciences have resulted in a new generation of stationary phases containing carbon nanotubes and GO, which have been found to provide homogeneous coatings. Graphene is a monolayer of sp^2-hybridized carbon atoms tightly arranged into a two-dimensional honeycomb lattice. GO is an aromatic macromolecule containing reactive oxygen functional groups such as epoxide and hydroxyl.[31,32]

Zhao *et al.*[33] demonstrated that singled-walled carbon nanotubes enhanced the enantioseparation on a chiral ionic liquid

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stationary phase, because the carbon nanotubes increased the superficial area in the inner wall, and therefore favored the interactions between the stationary phase and the analytes.

Qu *et al.* have employed graphene and GO as stationary phases for capillary electrochromatography, capillary liquid chromatography and gas chromatography, enabling effective separation of neutral, basic and protein mixtures,[34] and separation of various types of organic compounds with good separation efficiency.[35]

In order to contribute to the development and study of new stationary phases with improved selectivities, in this paper, we present a complete study of the solvation properties of eight monocationic phosphonium-based polymeric ILs (phosphonium PILs).[30] Moreover, with the aim of improving the column efficiency, to eliminate non-specific interactions due to silanol groups, sheets of graphene oxide covalently bonded to the inner wall of the column have been incorporated. For the first time, phosphonium ionic liquids have been polymerized onto this modified inner wall, giving good results. The thermal stability of the new phosphonium PIL stationary phases has been evaluated, and the Abraham model has been used to study the variation of the interactions between the new chromatographic phases and the analytes as the cations and anions are changed.

2. Material and methods

Most chemical reagents were purchased from Sigma-Aldrich and used without further purification. The PAH mixture was purchased from Restek (Bellefonte, United States). $NaBAr'_4$ (Ar′ = 3,5-bis(trifluoromethyl)phenyl) was prepared as previously reported.[36] Methanol, dichloromethane and *n*-hexane were obtained from Merck. Untreated fused silica capillaries (0.25 and 0.10 mm i.d.) were purchased from Supelco (Madrid, Spain). Dichloromethane was distilled from CaH_2 and stored under nitrogen in a Young tube and used without further purification. ^{1}H, ^{31}P and ^{13}C NMR spectra were recorded on a Bruker Advance 300, DPX-300, or Advance 400 spectrometer. NMR spectra are referred to the internal residual solvent peak for ^{1}H and $^{13}C\{^{1}H\}$, whereas phosphoric acid (H_3PO_4, 85%) is used as the external reference for ^{31}P NMR. The NMR samples were prepared under nitrogen using Konte manifolds purchased from Aldrich. All spectra are given in the ESI.†

2.1. Synthesis of polymerizable phosphonium ionic liquids

Some manipulations were performed under an inert atmosphere of dinitrogen using standard Schlenk techniques due to the air sensitivity of *n*-tributylphosphine.

[(^{n}Bu)$_3$(allyl)P]Br (IL 1). Allyl bromide (0.83 mL, 9.60 mmol) was added to a solution of *n*-tributylphosphine (2 mL, 8.00 mmol) in dichloromethane (20 mL), previously cooled to 0 °C. The reaction mixture was allowed to reach room temperature and stirred for 1 h. The resulting solution was evaporated to dryness, and after aprox. 6 h under vacuum **IL 1** was obtained as a white solid (2.379 g, 92%).[23]

[(^{n}Bu)$_3$(allyl)P]NTf$_2$ (IL 2). $LiN(CF_3SO_2)_2$ (0.106 g, 0.371 mmol) was added to a solution of [(^{n}Bu)$_3$(allyl)P]Br (**IL 1**) (0.100 g, 0.309 mmol) in methanol (20 mL), and the resulting slurry was stirred for 48 h. Methanol was then evaporated under vacuum and the resulting solid residue was extracted with dichloromethane (25 mL). The solution was washed with water (3 × 20 mL) and dried overnight over magnesium sulfate. Then, the resulting solution was filtered, and evaporated under reduced pressure to yield compound [(^{n}Bu)$_3$(allyl)P]NTf$_2$ (**IL 2**) as an oil (65%).

[(^{n}Bu)$_3$(allyl)P]OTf (IL 3). To a solution of [(^{n}Bu)$_3$(allyl)P]Br (**IL 1**) (0.100 g, 0.309 mmol) in CH_2Cl_2 (20 mL), AgOTf (0.095 g, 0.371 mmol) was added and the mixture was stirred for 48 h. Afterwards, the solution was filtered through a short plug of diatomaceous earth, dried under reduced pressure, and after 6 h, **IL 3** was obtained as an oil (78%).

[(^{n}Bu)$_3$(allyl)P]BAr′$_4$ (IL 4). Compound **IL 4** was prepared as described above for **IL 3**, starting from **IL 1** (0.100 g, 0.309 mmol) and $NaBAr'_4$ (0.329 g, 0.371 mmol). **IL 4** was obtained as a white solid, with a melting point of 75 °C (yield 70%).

[(^{n}Bu)$_3$(crotyl)P]Cl (IL 5). Crotyl chloride (0.94 mL, 9.60 mmol) was added to a solution of tri-*n*-butylphosphine (2 mL, 8.00 mmol) in CH_2Cl_2 at 0 °C. The mixture was allowed to warm to room temperature, stirred for 1 hour and then the solvent was evaporated to dryness under reduced pressure. The residue was dissolved in methanol (20 mL), to which lithium bis(trifluoromethyl)sulfonamide (2.756 g, 9.60 mmol) was added and the reaction mixture was stirred for 48 h. The solvent was then evaporated under vacuum, the residue was extracted with CH_2Cl_2 (20 mL) and the organic layer was washed with distilled water (3 × 20 mL). Dichloromethane was evaporated and **IL 5** was obtained as a colorless oil (63%).

[(^{n}Bu)$_3$(crotyl)P]NTf$_2$ (IL 6). Crotyl chloride (0.94 mL, 9.60 mmol) was added to a solution of *n*-tributylphosphine (2 mL, 8.00 mmol) in CH_2Cl_2 at 0 °C. The mixture was allowed to warm to room temperature, stirred for 1 h and then the solvent was evaporated to dryness under reduced pressure. The residue was dissolved in methanol (20 mL), to which lithium bis(trifluoromethane)sulfonamide (2.756 g, 9.60 mmol) was added and the reaction mixture was stirred for 48 h. The solvent was then evaporated under vacuum, the residue was extracted with CH_2Cl_2 (20 mL) and the organic layer was washed with distilled water (3 × 20 mL). Dichloromethane was evaporated and **IL 6** was obtained as a colorless oil (2.709 g, 63%).

[(^{n}Bu)$_3$(methallyl)P]NTf$_2$ (IL 7). **IL 7** was prepared as described above for **IL 6**, starting from *n*-tributylphosphine (2 mL, 8.00 mmol), methallyl chloride (0.94 mL, 9.60 mmol) and lithium bis(trifluoromethane)sulfonamide (2.756 g, 9.60 mmol). **IL 7** was obtained as a colorless oil (57%).

[(Ph)$_2$(allyl)$_2$P]NTf$_2$ (IL 8). **IL 8** was prepared as described above for **IL 6**, starting from allyldiphenylphosphine (1.90 mL, 8.00 mmol), allyl bromide (0.83 mL, 9.60 mmol) and $LiNTf_2$ (2.756 g, 9.60 mmol). **IL 8** was obtained as a colorless oil (66%).

Schemes S1 and S2 show the structures of all the polymerizable phosphonium ILs used in this study (see ESI†).

2.2. Methods

2.2.1. Preparation of polymeric phosphonium-based IL capillary columns. All capillary columns were coated using the static method on a 10 m capillary column (0.25 mm i.d.)

at 40 °C using 0.25% (w/v) of ILs dissolved in dichloromethane. Prior to adding the solvent to the IL monomer, 3 mg of AIBN [2,2′-azobis(2-methylpropionitrile)] (∼10 wt%) were added as an initiator of the radical polymerization. Capillaries were filled with the solution of the initiator and ionic liquid. The AIBN decomposition constant is lower than the coating rate at this temperature, so polymerization was almost insignificant during the filling of the column.[37,38] After coating, the ends of the capillaries were sealed and the capillaries placed in a GC oven, where the column was heated from 40 to 80 °C at 1 °C min^{-1} and then kept at 80 °C for 5 h in order to ensure complete polymerization. Eqn (1) can be used to approximate the stationary phase film thickness (d_f) of capillary columns.[22,38]

$$d_f = d_c c/400 \tag{1}$$

where d_c is the diameter of the capillary tubing (in micrometers), and c is the percentage by weight (%) concentration of the stationary phase dissolved in an appropriate solvent.

Helium carrier gas was then flushed through the capillaries at a rate of 1 mL min^{-1}, and the capillaries were 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 determined to be higher than 3200 plates per m by using naphthalene at 100 °C.

2.2.2. Preparation of polymeric phosphonium-based IL capillary columns incorporating sheets of graphene oxide bonded to the inner wall columns. In order to avoid the nonspecific adsorptions due to the low-stability of the graphene dispersion in dichloromethane,[30] GO sheets were covalently bonded onto the inner surface of fused silica capillary columns using 3-aminopropyl-diethoxymethyl-silane (3-AMDS) as a cross-linking agent. First, the capillaries were pretreated with 1 mL of 3-AMDS toluene solution (1 vol%) in order to modify the inner surface of the capillaries through a covalent interaction between the silanol groups and 3-AMDS.[35] Then, GO sheets were linked to the amino functionalized surface of fused silica capillary columns by rinsing the capillaries with the GO suspension. To obtain a stable homogeneous colloidal suspension of GO sheets, a long time of sonication is required (over 6 h) in an ultrasound bath, followed by centrifugation at 3000 rpm for 5 min. After coating, the ends of the capillaries were sealed and the capillaries were introduced in a GC oven, heating the columns from 50 to 120 °C at 3 °C min^{-1}. After this, the capillaries were filled with the solution of initiator and ionic liquid.

Fig. 1 shows the SEM images of capillary columns with a mixture of sheets of graphene oxide bonded to the inner wall and phosphonium PILs. As it can be seen, a homogeneous film is formed.

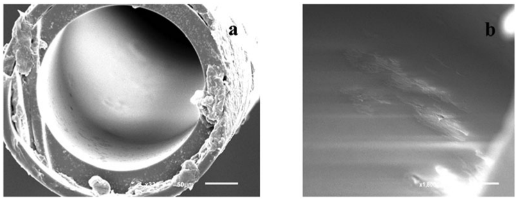

Fig. 1 SEM images of (a) the inner wall of the capillary with GO sheets covalently bonded and phosphonium PILs (b) an amplified zone of the image shown in (a).

To evaluate the capillary columns, each individual probe molecule (dissolved in dichloromethane) was injected into the columns at three different temperatures: 50 °C, 80 °C and 110 °C. At 50 °C some of the used probe molecules, (particularly the H-bond donors) showed peak asymmetries (As) higher than 1.5 and were therefore rejected from the data set. At 110 °C some probe solutes coeluted with the solvent; therefore, these results were also discarded.

For the determination of the system constants, 43 probe molecules were used, ensuring that a minimum of four test compounds were used to assess each of the parameters under study. Selected compounds differ in size, dipolarity/polarizability, and hydrogen bond donor or acceptor properties. Moreover, the peak asymmetries were from 0.9 to 2.3, and the retention times ranged from 2 to 15 min for the probe molecules at 110 °C. The solute descriptors for the 43 probe molecules are listed in Table 1.

Table 1 Probe molecules and values of solute descriptors used in the characterization of phosphonium PIL stationary phases

Probe molecules	E	S	A	B	L
1-Hexanol	0.21	0.44	0.344	0.52	3.643
Anisole	0.712	0.768	0	0.311	3.808
Cyclohexanone	0.403	0.895	0	0.53	3.759
1,2-Dichlorobenzene	0.872	0.771	0	0.054	4.516
Butylbenzene	0.595	0.499	0	0.139	4.734
Nonanal	0.121	0.636	0	0.414	4.838
Butyl acetate	0.079	0.57	0	0.438	3.409
Iodobenzene	1.182	0.784	0	0.135	4.548
1-Hexyne	0.167	0.274	0.09	0.117	2.544
1-Nitropropane	0.243	0.925	0.049	0.27	2.878
1-Pentanol	0.219	0.44	0.344	0.52	3.128
Pyridine	0.635	0.843	0	0.532	3.006
Benzonitrile	0.742	1.135	0	0.331	4.04
Phenyl acetate	0.648	1.055	0	0.521	4.378
Nitrobenzene	0.846	1.138	0	0.269	4.539
Naphthalene	1.24	0.906	0	0.193	5.154
Heptanal	0.14	0.642	0	0.441	3.856
2-Heptanone	0.123	0.662	0	0.496	3.781
1-Phenylethanol	0.823	0.819	0.351	0.648	4.424
Benzaldehyde	0.813	1.025	0	0.394	4.005
1-Octanol	0.199	0.44	0.344	0.52	4.648
1-Chloronaphthalene	1.419	0.951	0	0.135	6.175
Aniline	0.955	1.003	0.249	0.425	3.956
Fluorene	1.664	1.12	0	0.252	6.921
4-Chloroaniline	1.017	1.128	0.366	0.309	4.972
Benzyl alcohol	0.803	0.882	0.4	0.557	4.244
Butyl benzoate	0.668	0.851	0	0.393	5.974
Cinnamic alcohol	1.119	0.971	0.451	0.606	5.475
Phenol	0.769	0.759	0.716	0.319	3.844
Acetophenone	0.806	1.026	0	0.503	4.533
3-Methyl-1-butanol	0.198	0.423	0.351	0.501	2.963
1-Butanol	0.224	0.44	0.344	0.52	2.578
Ethyl benzoate	0.694	0.886	0	0.444	5.032
2-Phenylethanol	0.787	0.797	0.39	0.636	4.741
1-Decanol	0.191	0.44	0.344	0.52	5.589
Triethylamine	0.101	0.14	0	0.78	3.017
Ethylbenzene	0.613	0.499	0	0.139	3.814
1,3-Dinitrobenzene	0.079	0.57	0	0.438	3.409
Coumarin	1.269	1.61	0	0.524	6.034
Styrene	0.894	0.671	0	0.177	3.86
Undecan-2-one	0.105	0.662	0	0.496	5.732
Methyl hexanoate	0.084	0.564	0	0.456	3.970
4-Chloroaniline	1.0217	1.128	0.366	0.309	4.972

The 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 ≥ 0.97. The values of all the system constants are listed in Table 2 for phosphonium PILs.

All separations were performed using a Shimadzu GC-2010 gas chromatograph (Shimadzu, Kyoto, Japan) equipped with a flame ionization detector. Analyses of alcohols/amines, PAHs and pesticides were performed using 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 300 °C, respectively. Methane was used to measure the column hold-up time.

3. Results and discussion

Phosphonium-based ionic liquids (**IL 1–8**) have been synthesized by quaternization of phosphines, and in several cases by a subsequent methathesis reaction to allow the anion exchange. With the new ILs in hand, we have determined the influence of both cations and anions on the properties of the ionic liquids, as well as in their performance as stationary phases in GC.

3.1. Optimization of film thickness capillary columns

The variation of the column efficiency as a function of the film thickness was evaluated using naphthalene as a probe solute. As can be seen in Fig. 2, a percentage of 0.25% w/v PIL provides greater separation efficiency. This percentage corresponds to a PIL film thickness of about 0.16 microns. Therefore, capillary columns were prepared with a thickness of approximately 0.16 microns film (0.25%, w/v) for all subsequent studies.

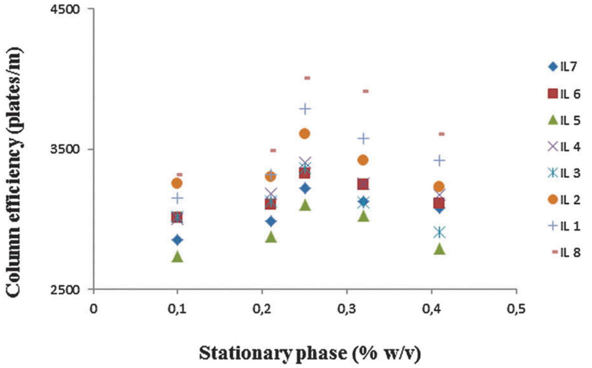

Fig. 2 Representation of efficiency variation of phosphonium PIL stationary phases.

3.2. Thermal stability

Thermal stability is highly dependent on both anions and the cations of the ILs, and directly determines the operating temperature range and lifetime of the GC columns.

Fig. 3 shows the loss of the stationary phase due to the IL decomposition or volatilization. As seen in Fig. 3, PIL 8, which has two allyl groups, shows the highest thermal stability, presumably due to crosslinking during polymerization. PILs 1, 4, 5 and 7 show lower thermal stability. It is well known that

Table 2 Regression parameter coefficients of phosphonium PILS

IL	*T* (°C)	*c*	*e*	*s*	*a*	*b*	*l*	R^2	*n*	SE	*F*
IL 1	50	−4.68 (0.12)	−0.20 (0.09)	1.83 (0.12)	5.68 (0.19)	0.09 (0.14)	0.72 (0.03)	0.99	28	0.05	338
	80	−4.32 (0.16)	−0.23 (0.14)	1.74 (0.16)	4.83 (0.20)	−0.64 (0.22)	0.59 (0.02)	0.99	32	0.07	212
	110	−4.61 (0.15)	−0.28 (0.12)	1.22 (0.17)	3.60 (0.26)	−0.66 (0.29)	0.48 (0.03)	0.98	24	0.09	188
IL 2	50	−3.39 (0.19)	−0.12 (0.14)	2.22 (0.19)	1.85 (0.32)	1.28 (0.29)	0.52 (0.05)	0.98	24	0.12	123
	80	−4.32 (0.14)	−0.23 (0.18)	1.27 (0.13)	1.69 (0.16)	0.70 (0.16)	0.58 (0.03)	0.98	27	0.08	175
	110	−4.35 (0.23)	−0.80 (0.13)	1.15 (0.23)	1.32 (0.28)	−1.07 (0.22)	0.55 (0.04)	0.97	32	0.1	66
IL 3	50	−4.73 (0.19)	−0.32 (0.14)	1.80 (0.20)	4.21 (0.32)	−0.37 (0.24)	0.77 (0.05)	0.98	28	0.08	124
	80	−3.99 (0.08)	−0.15 (0.07)	1.74 (0.09)	3.14 (0.16)	−0.64 (0.15)	0.61 (0.02)	0.99	34	0.04	461
	110	−5.48 (0.10)	−0.04 (0.07)	1.31 (0.09)	2.15 (0.11)	−0.79 (0.12)	0.40 (0.02)	0.99	33	0.04	802
IL 4	50	−3.98 (0.11)	−0.14 (0.07)	1.57 (0.08)	4.22 (0.14)	1.27 (0.10)	0.62 (0.03)	0.99	25	0.07	216
	80	−3.38 (0.13)	−0.28 (0.08)	0.96 (0.12)	3.75 (0.18)	0.90 (0.15)	0.55 (0.02)	0.98	26	0.06	120
	110	−5.33 (0.22)	−0.35 (0.16)	0.94 (0.19)	2.93 (0.22)	0.29 (0.23)	0.41 (0.02)	0.98	21	0.11	174
IL 5	50	−4.70 (0.25)	0.09 (0.18)	1.87 (0.25)	7.23 (0.46)	−0.21 (0.28)	0.67 (0.06)	0.97	23	0.15	77
	80	−4.36 (0.09)	−0.28 (0.07)	1.80 (0.10)	5.56 (0.14)	−0.33 (0.15)	0.56 (0.02)	0.99	31	0.04	544
	110	−4.55 (0.13)	−0.36 (0.11)	1.78 (0.15)	4.79 (0.23)	−0.39 (0.28)	0.49 (0.02)	0.99	25	0.07	239
IL 6	50	−3.52 (0.13)	−0.20 (0.09)	1.28 (0.12)	0.97 (0.17)	1.72 (0.11)	0.49 (0.03)	0.98	32	0.08	137
	80	−3.85 (0.11)	−0.21 (0.07)	1.05 (0.08)	0.91 (0.11)	0.97 (0.10)	0.42 (0.02)	0.98	35	0.07	171
	110	−3.99 (0.12)	−0.24 (0.08)	0.90 (0.10)	0.88 (0.11)	0.55 (0.14)	0.40 (0.03)	0.98	30	0.07	116
IL 7	50	−3.86 (0.14)	−0.12 (0.09)	1.57 (0.14)	1.62 (0.21)	0.81 (0.16)	0.67 (0.03)	0.99	31	0.07	214
	80	−3.94 (0.10)	−0.13 (0.03)	1.56 (0.08)	1.42 (0.11)	0.51 (0.07)	0.58 (0.02)	0.99	36	0.03	450
	110	−3.83 (0.16)	−0.24 (0.10)	1.00 (0.16)	0.66 (0.19)	0.04 (0.21)	0.45 (0.03)	0.98	33	0.07	106
IL 8	50	−3.90 (0.20)	−0.06 (0.15)	1.39 (0.21)	1.42 (0.32)	1.40 (0.26)	0.63 (0.04)	0.97	29	0.12	91
	80	−4.26 (0.13)	−0.10 (0.09)	1.33 (0.13)	1.07 (0.16)	1.09 (0.17)	0.51 (0.03)	0.98	32	0.1	193
	110	−3.74 (0.10)	−0.43 (0.08)	1.27 (0.12)	0.08 (0.14)	0.14 (0.16)	0.39 (0.02)	0.98	30	0.06	221

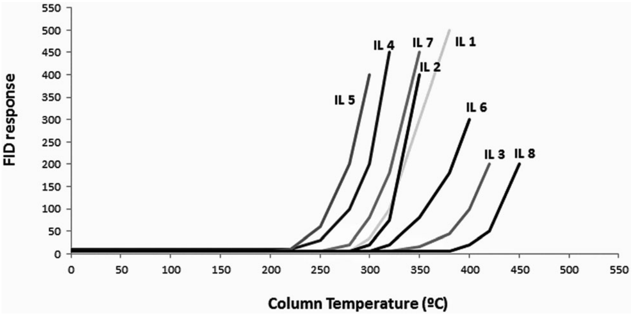

Fig. 3 Thermal stability of the phosphonium PIL stationary phases.

the presence of halides in the ILs lowers the thermal stability of the resulting stationary phases due to their nucleophilic nature, which opens the way to decomposition *via* S_N1 and S_N2 processes.[39] PIL 4 shows lower stability than PIL 1 because of the instability of the tetrakis[3,5-bis(trifluoromethyl)phenyl]borate anion. On the other hand, PILs with NTf_2^- and OTf^- anions show higher thermal stabilities, except in the case of PIL 7, a fact that could indicate instability due to the methallyl group. For PIL 6, the slight increase in the length of the aliphatic chain compared to PIL 2 makes the thermal stability somewhat higher.

These results provided a rough idea of the thermal stability of the ILs studied. To evaluate quantitatively the thermal stability of PIL stationary phases a study was conducted using an isothermal method. Thus the GC columns were held at a series of constant temperatures for at least 12 h, and the retention of probe compounds was measured at a lower temperature before and after the isothermal conditioning.

Table 3 shows the isothermal measurements for naphthalene at different temperatures with the phosphonium PILs. As it can be seen, the thermal stabilities of these PILs ranged from 220 to 380 °C, and are higher than those of other stationary phases based on ILs.[18,40,41]

3.3. IL solvation parameters: the effect of anions and cations on the system constants

A number of methods have been developed to characterize the solvation behaviour of liquids.[20,42] In this study, the solvation parameter model developed by Abraham[43] has been used to characterize the interactions between molecules of solute and stationary phases.

Table 3 Variation of the naphthalene retention factor with phosphonium PIL columns using the isothermal method

T (°C)	IL 1	IL 2	IL 3	IL 4	IL 5	IL 6	IL 7	IL 8
100	0.64	0.70	0.97	0.83	0.35	0.28	0.59	0.61
150	0.52	0.65	0.92	0.76	0.28	0.24	0.54	0.56
180	0.47	0.57	0.84	0.69	0.23	0.20	0.50	0.52
200	0.43	0.46	0.80	0.62	0.17	0.17	0.45	0.49
220	0.38	0.37	0.74	0.55	0.20[a]	0.15	0.38	0.45
250	0.31	0.31	0.69	0.59[a]	[b]	0.10	0.31	0.39
270	0.40[a]	0.27	0.61	[b]		0.08	0.39[a]	0.33
300	[b]	0.36[a]	0.52			0.22[a]	[b]	0.26
320		[b]	0.46			[b]		0.21
330			0.51[a]					0.18
350			[b]					0.11
380								0.20[a]
400								[b]

[a] Peaks tailing were observed. [b] No retention was observed for naphthalene.

The Abraham solvation parameter model equation is as follows-

$$\log k = c + eE + sS + aA + bB + lL \qquad (2)$$

According to eqn (2), the retention factor (k) of a given solute at a specific temperature is determined chromatographically. E, S, A, B, and L are solute descriptors that represent excess molar refraction, dipolarity, H-bond acidity, H-bond basicity and the gas-hexadecane partition coefficient at 298 K, respectively. Poole and co-workers[44] optimized these descriptors by gas chromatography, reversed-phase liquid chromatography and micellar electrokinetic chromatography. The system constants from eqn (2) are defined as follows: e indicates the ability of the stationary phase to interact with the π- and n-electrons of the solvent; s is the dipolarity/polarizability of the solvent; a and b define the solvent hydrogen bond basicity and acidity, respectively. Finally, l is the phase ability to distinguish between, or to separate the members of any homologous series.

The system constants for the tested stationary phases were obtained by the use of the inverse GC method and are listed in Table 2. Two of the five interaction parameter coefficients, namely s (dipole-type interactions) and a (H-bond basic interactions) have larger magnitudes for all ILs studied. This fact has been already observed for imidazolium-based ILs[19] and phosphonium PILs.[29] It is well known that hydrogen bond basicity and dipolarity of ILs are determined by the nature of the counter-anions. The cross-correlation between descriptors were checked and low correlations between descriptors (<0.5 in absolute value) were observed.

Hydrogen bond basicity values ranged from 0.66 to 5.56 at 80 °C. The values of the a-term of PILs 1 and 5 were higher in comparison with the other PILs, since the high electron density of chloride and bromide makes them strong hydrogen bond acceptors. The other studied PILs showed lower hydrogen bond basicities due to the large delocalization of the negative charge in NTf_2^-, OTf^- and tetrakis-(3,5-bis(trifluoromethyl)phenyl)-borate anions. This observation has already been made for imidazolium cations.[16,19,23,45–47]

It was observed that the values of the coefficients decrease as the temperature is increased, showing that the solute retention decreases as a function of temperature, as usually occurs in gas chromatography analysis.

The values obtained for the b-term were negative for some of the PILs tested. Negative values of the b-terms have been also reported for some of the imidazolium ILs, despite the fact that the imidazolium cation possesses the ability to act as a hydrogen bond donor. In this case, it seems that these unrealistic values cannot be explained by the structure of the PILs because none of them have acidic hydrogens that could act as strong hydrogen bond donors. Therefore, b-term was forced to be zero and the regression was performed using e, s, a and l terms. The results obtained for the correlation coefficient and system constants remained unchanged, implying that the b-term does not affect the model. It is important to note that this phenomenon has been reported previously for other phosphonium ILs.[29,30]

On the other hand, all the PILs that we have studied have shown low values for non-bonding and π-electron interactions (*e*-term). The negative values of this system constant are related to the way in which the solute descriptor E is determined.[42] The comparison of phosphonium and imidazolium ILs shows that the *e*-term values are lower for phosphonium ILs tested here, due to the π-electron-rich imidazolium cations, implying that the *e*-term is dominated by the cations. Other phosphonium PILs studied show similar values for the *e*-term (from −0.28 to 0.12 at 70 °C). The positive values are due to the presence of lone pair electrons on the oxygen atoms of the ether chain.[29]

In the case of PIL 8, which contains two phenyl groups in its structure, negative values of the *e*-term can be explained by the presence of π-stacking interactions between the phenyl groups.

The values obtained for the *s*-term were similar for all PILs studied. For PILs 1–4, the anions change, whilst the cations remain constant. There are no major changes in the *s*-term and this implies that the dipolar interactions did not appear to be significantly influenced by the anion type. When the cations are changed (PILs 6–8), no changes were observed and it can be concluded that all phosphonium PILs interact through dipole-type interactions.

The *l* coefficient is a combination of exoergic and endoergic processes. The magnitude of this term indicates how well the IL separates compounds in a homologous series. As the studied PILs had positive *l* coefficients and the dispersion interactions seem to dominate. The term values fall within the range 0.61–0.42 at 80 °C. These values are similar to those of most of the studied phosphonium PILs. Therefore, dispersion interactions must not be significantly influenced by the cations, and the dipolarities (*s*-term) of these PILs are nearly identical.

3.4. Separation of complex mixtures

In order to study the chromatographic behavior of these IL columns, different standard mixtures were prepared and injected on phosphonium PILs stationary phases.

As an example, the chromatograms of a mixture of amines and alcohols using PIL 1 and PIL 6 coated columns are displayed in Fig. 4. Good symmetries for PILs 1 (0.8–1.9) and 6 (0.8–1.5), compared to those obtained with other stationary phases based on imidazolium and phosphonium ILs[17,18,21,35] are diagnostic of a homogeneous distribution of the polymerized ILs on the capillary inner wall. The higher tailing peaks for PIL 1 compared to those for PIL 6 are in agreement with the higher values of *a*- and *b*-terms observed for PIL 1, due to the presence of the bromide anion, which make this PIL a relatively strong hydrogen bond acceptor. Moreover, variations of the retention factor are observed for some analytes. Alcohols exhibited an increase in the retention time on the **IL 6** stationary phase compared to **IL 1**, due to the presence of hydrogen bond-donating moieties.

The chromatograms obtained for the other phosphonium PILs studied are in the ESI.† As it is shown there, some stationary phases (PILs 4 and 8) show high peak asymmetries (As > 2.0) for alcohols, which is indicative of a non-homogeneous IL film on the capillary wall. Moreover, PIL 5 shows the highest retention times for polar compounds due to their increased ability to interact through hydrogen bonds with this stationary phase (higher value of the *a*-term).

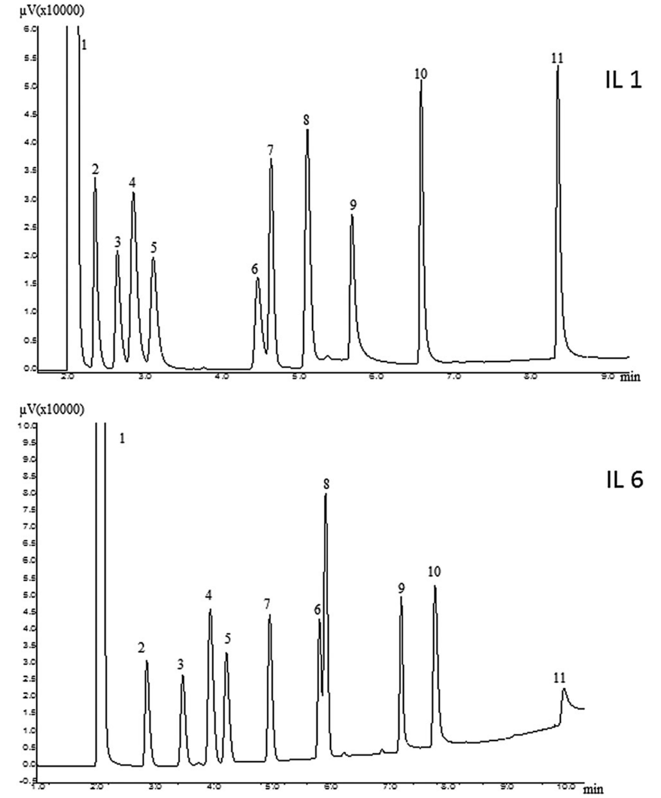

Fig. 4 Separation of a mixture containing alcohols and amines using **IL 1** and **IL 6**: (1) hexane; (2) 1-butanol; (3) 1-pentanol; (4) 2-methylpentanol; (5) 1-hexanol; (6) 1-octanol; (7) aniline; (8) diisopropylamine; (9) 1-decanol; (10) 2-phenylethanol; (11) cinnamic alcohol. Program temperature: initial oven column temperature 100 °C for 2 min, increased at a rate of 25 °C min^{-1} to 200 °C and then held at this temperature for 2 min.

Fig. 5 shows the chromatograms for the separation of a PAH mixture employing PILs 1 and PIL 6. It has been demonstrated[48] that some PAHs display high carcinogenic and mutagenic activity, and have been listed as contaminants in waste water, solid waste and sediments.

As can be seen in Fig. 5, the PIL 1 column allowed to separate indeno(1,2,3-*cd*)pyrene, dibenz(*a*,*h*)anthracene and benzo(*g*,*h*,*i*)perylene in less than 30 min, with a resolution of 3.4 for indeno(1,2,3-*cd*)pyrene and dibenz(*a*,*h*)anthracene; and a resolution of 1.2 for dibenz(*a*,*h*)anthracene and benzo(*g*,*h*,*i*)-perylene. It is important to stress that this column is able to give good results for the separation of PAHs using only 10 m of the column.

The presence of the fronting peaks 12, 15, 16 and 17 with PIL 6 may be due to a strong interaction between these compounds and the column, saturating the column even at low concentrations.

The chromatograms obtained for other phosphonium PILs under study herein are showed in the ESI.† All stationary phases show the same elution order, except for the stationary phase based on PIL 4. In this case, dibenz(*a*,*h*)anthracene

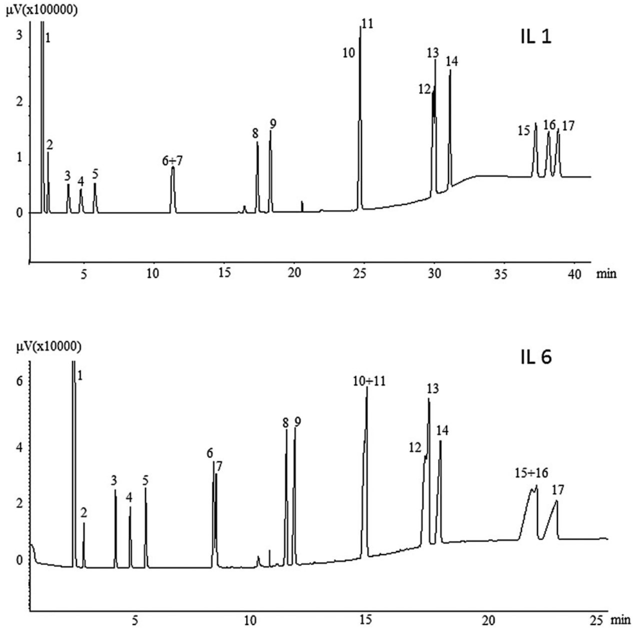

Fig. 5 Separation of a polycyclic aromatic hydrocarbon mixture using **IL 1** and **IL 6**. (1) Hexane; (2) naphthalene; (3) acenaphthylene; (4) acenaphthene; (5) fluorene; (6) phenanthrene; (7) anthracene; (8) fluoranthene; (9) pyrene; (10) benz[*a*]anthracene; (11) chrysene; (12) benzo[*b*]fluoranthene; (13) benzo[*k*]fluoranthene; (14) benzo[*a*]pyrene; (15) indeno(1,2,3-*cd*)pyrene; (16) dibenz(*a*,*h*)anthracene; (17) benzo(*g*,*h*,*i*)perylene. Program temperature: initial oven column temperature 90 °C for 2 min, increased at a rate of 15 °C min^{-1} to 255 °C and held at this temperature for 20 min.

eluted before the indeno(1,2,3-*cd*)pyrene. This behaviour could be explained due to the nature of the anion ($\mathrm{BAr'_4}^-$) having four aromatic rings in its structure. Steric effects seem to be the responsible of this inverted elution order, as for the non-linear indene compound it would be more difficult to go through the PIL 4 column than for the less bulky dibenz(*a*,*h*)anthracene, the former being therefore more retained than the latter.

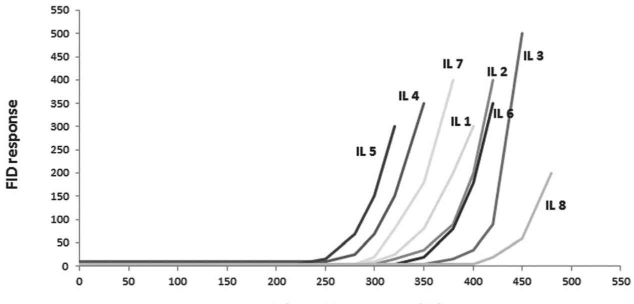

Fig. 6 Thermal stability for the mixtures of phosphonium PILs and GO sheets covalently bonded to inner wall stationary phases.

3.5. Incorporation of graphene oxide on phosphonium-based polymeric ionic liquids

The addition of a GO dispersion to the phosphonium PILs prior to use for separating a pesticide mixture by GC analysis improves the chromatographic profile notably.[30] The elution order remains the same for all pesticides, indicating that the employment of GO does not change the nature of the stationary phase, although it increases the surface area, affording a more homogeneous film of polymer ionic liquid along the capillary wall.

Despite these improvements, the GO dispersion in dichloromethane exhibited a low stability against agglomeration and sedimentation, and this implies that the GO film along the capillary wall was far from homogeneous. Considering that a more homogeneous GO coating would further improve the column performance, GO sheets were covalently bonded onto the inner surface of fused silica capillary columns using 3-aminopropyldiethoxymethylsilane as a cross-linking agent. The column efficiencies of these new stationary phases have been evaluated, and in all cases an improvement of the efficiencies has been observed, so that impressive 4200 plates per m were found for some PILs. When naphthalene was injected at 100 °C, the retention time was measured after every 50 runs, and the results indicated that the columns coated with the new phases endured a series of 450 runs without loss of activity.

The thermal stabilities of these new stationary phases were evaluated. As shown in Fig. 6, when GO sheets are covalently bonded to the inner wall of capillary columns, a slight increment of the thermal stability is observed, compared to that of the phosphonium PILs capillary columns. This phenomenon could be explained because GO displays hydroxyl (–OH) and carboxylic groups (–COOH) that allow π–π, n–π and halogen–π interactions with phosphonium PILs. This fact implies that the adsorption of the PILs onto the GO is stronger than onto silica.

GO–PIL 8 was chosen to test the effect of the covalently bonded GO on the ability of the PIL columns to separate different types of compounds by GC. The choice of this PIL 8 in particular was based on it, displaying the worst symmetry peaks in the separation of the mixtures described above, so that clearly an improvement was needed.

Table 4 shows the resulting system constant values for the GO–PIL 8 stationary phase. The *a* and *b* terms are lower than those of PIL 8 (with no GO). This can be attributed to the generation of a more homogeneous film along the capillary as a consequence of the covalently bonded GO sheets to the inner wall, and to the existence of a lower number of free silanol groups thus reducing the non-specific absorption.

Table 4 Regression parameter coefficients of a mixture of PIL 8 and GO sheets covalently bonded to the inner wall stationary phase

IL	*T* (°C)	*c*	*e*	*s*	*A*	*b*	*l*	R^2	*n*	SE	*F*
IL 8	50	−3.90 (0.18)	−0.10 (0.12)	1.45 (0.18)	1.05 (0.12)	1.11 (0.23)	0.79 (0.03)	0.99	30	0.11	561
	80	−4.30 (0.12)	−0.16 (0.19)	1.21 (0.17)	0.82 (0.08)	0.86 (0.10)	0.68 (0.03)	0.98	34	0.08	227
	110	−4.68 (0.10)	−0.39 (0.10)	1.09 (0.20)	0.11 (0.14)	0.19 (0.17)	0.61 (0.02)	0.97	36	0.07	105

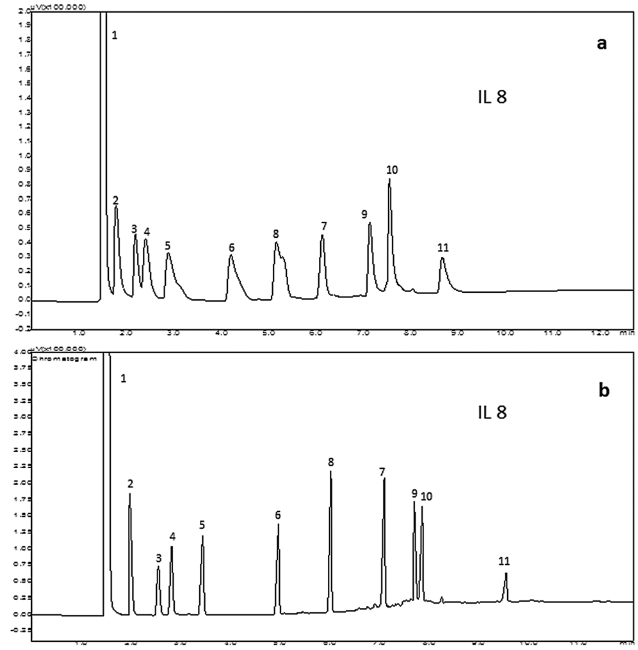

Fig. 7 Separation of a mixture containing alcohols and amines on (a) polymeric **IL 8** and the graphene dispersion column; (b) polymeric **IL 8** and the graphene oxide covalently bonded column: (1) hexane; (2) 1-butanol; (3) 1-pentanol; (4) 2-methylpentanol; (5) 1-hexanol; (6) 1-octanol; (7) aniline; (8) diisopropylamine; (9) 1-decanol; (10) 2-phenylethanol; (11) cinnamic alcohol. Program temperature: initial oven column temperature 100 °C for 1 min, increased at a rate of 30 °C min^{-1} to 200 °C and then held at this temperature for 2 min.

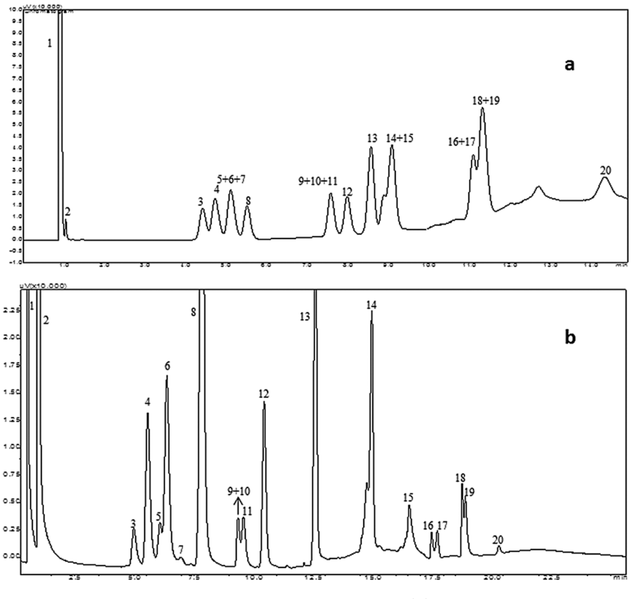

Fig. 8 Separation of a pesticide mixture on: (a) a mixture of graphene oxide dispersion and the PIL 8 column; (b) a mixture of covalently bonded graphene oxide and the polymerized **IL 8** column: (1) hexane; (2) hexachlorobenzene; (3) aldrin; (4) bromocyclen; (5) HCH; (6) heptachlor; (7) endrin; (8) isodrine; (9) chlorophenothan; (10) endosulfan; (11) 4,4-DDE; (12) dieldrin; (13) DDD; (14) metoxychlor; (15) bromacil; (16) coumaphos; (17) dialifos; (18) ruelene; (19) carbaril; (20) pyraclofos. Program temperature: initial oven column temperature 130 °C for 2 min and a heating rate of 10 °C min^{-1} to 250 °C and then held at this temperature for 15 min.

The chromatograms obtained when alcohol/amine and pesticide mixtures were injected in the column coated with covalently linked GO sheets and phosphonium PIL 8, are depicted in Fig. 7 and 8, respectively. As shown in Fig. 7, the good peak symmetries obtained (As < 1.1) compared to those observed by the use of a dispersion of graphene for the alcohol/amine mixtures constitute a clear improvement, and strongly suggest that the phosphonium PIL film is homogeneously distributed on the capillary inner wall.

In agreement with the formation of a very homogeneous film along the capillary wall, Fig. 8 shows also a good peak tailing compared to the stationary phase based on GO dispersion and the PIL. As a result, the new stationary phase allows the separation of some pesticides that previously, using the columns discussed above, co-eluted and could not be separated.

4. Conclusions

In this study, eight polymeric phosphonium ionic liquid stationary phases were prepared and their chromatographic properties used for gas chromatography analysis have been studied. The thermal stabilities observed for all the stationary phases based on the phosphonium ionic liquids studied are higher than those of stationary phases based on traditional imidazolium monocationic ionic liquids, therefore allowing separations at higher temperatures than imidazolium ionic liquids.

Moreover, the incorporation of graphene oxide sheets through covalent bonds to phosphonium PILs clearly improved their properties and behavior as gas chromatography stationary phases, due to the formation of a more homogeneous film along the capillary. This fact implies an enhancement of the interactions with the analytes and a decrease in non-specific interactions. As a consequence, the new phases allowed separation of several types of organic compounds with good separation efficiencies.

This research should lead to the development of a wide range of chromatographic columns displaying improved selectivities.

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