



High temperature and highly selective stationary phases of ionic liquid bonded polysiloxanes for gas chromatography

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ABSTRACT

Due to the special performance of “dual nature” and synthetic flexibility, ionic liquids (ILs) have been an attractive research subject of stationary phases for gas chromatography (GC). In this work, a novel ionic liquid (IL) bonded polysiloxane ([PSOMIM][NTf₂]) with anion of bis-trifluoromethanesulfonylimide (NTf₂⁻) was synthesized, and another one with chloride anion ([PSOMIM][Cl]) was also prepared for the purpose of comparison. The thermo-stability of the product was evaluated by thermogravimetric (TG) test and the result indicated that [PSOMIM][NTf₂] did not decompose slightly until 380 °C. Then the solvation behaviors of the ILs were characterized using solvation parameter model. Subsequently, [PSOMIM][NTf₂] and [PSOMIM][Cl] were used as stationary phases to prepare capillary columns for GC, respectively. The column efficiency of [PSOMIM][NTf₂] column was 4776 plates/m ($k = 3.64 \pm 0.08$, naphthalene), and that of the other one was 3170 plates/m ($k = 2.84 \pm 0.11$, naphthalene). The selectivity of the novel stationary phases for analytes, including Grob reagent, aromatic positional isomers was further evaluated. Furthermore, the chromatograms of n-alkanes and polycyclic aromatic hydrocarbons (PAHs) on [PSOMIM][NTf₂] column were compared with that on [PSOMIM][Cl] column. [PSOMIM][NTf₂] stationary phase also exerted good selectivity for fatty acid methyl esters (FAMES), polychlorinated biphenyls (PCBs) and aromatic amines.

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1. Introduction

Gas chromatography (GC) has been a widely employed analytical approach in past decades. For an instrument of GC, one of the most important components is the chromatographic column with specific stationary phase and the selectivity of a chromatographic separation is largely attributed to the stationary phase used. Up to now, a large number of stationary phases with specific selectivity have been developed to meet a wide range of analytical demands in GC. Derivatives of polysiloxane [1] cover a majority of the commercially available and lab-made stationary phases due to their good film-forming ability, chemical stability and thermal resistance. Since a complex sample is usually composed of various polar and nonpolar components, a given stationary phase cannot offer good separation for both polar and nonpolar components in one time. Fortunately, ionic liquid stationary phases provided an unique advantage of “dual nature” [2,3] over traditional stationary phases. It was notable that this special nature may be beneficial to the analysis of

a complex sample comprising of components in wide polarity range.

Ionic liquids frequently refer to the organic salts whose melting points below 100 °C. They are usually composed of asymmetrical organic cations and inorganic anions. Due to their remarkable physicochemical properties, they have been extensively investigated as electrolyte materials, green solvents, catalysts and separation mediums [4–8]. The earliest report on the GC stationary phase of organic molten salts was contributed by Barber et al. in 1950s [9]. Later, Poole and co-workers studied the stationary phase of organic molten salts, such as ethylammonium nitrate and ethylpyridinium bromide [10,11]. These stationary phases exhibited separation ability for a lot of compounds, but their thermal resistances were not satisfying. Hence, little attention was paid to this kind of stationary phase in GC till the publication about IL stationary phase based on imidazolium cations by Armstrong's group [2]. These stationary phases were able to separate a wide range of organic compounds and exhibited a special characteristic of “dual nature”, which stimulated the researches on GC stationary phase.

Since the ionic liquids composed of small molecular could not possess high thermal resistance and good coating stability simultaneously, a method of in-column polymerization was proposed to prepare polymeric stationary phases from the IL monomers

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composed of vinylimidazole [12]. This kind of IL polymer could withstand temperature up to 350 °C, but the reaction was complicated and time consuming [13,14]. Since substituted polysiloxanes have been extensively used as stationary phases for GC owing to its high thermal stability and wide variability in modification [15–20], combining the merits of polysiloxanes with the “dual nature” of ILs was likely to improve the performance of IL stationary phase largely. Therefore, a method of ILs mixing with commercial stationary phases (e.g., OV-1, OV-1701 and FFAP) was proposed [21–23]. Compared with neat IL stationary phases, the mixed stationary phases provided excellent wetting ability on inner wall of capillaries. However, the durability of the physical mixture seemed to be doubted because of the significant difference between ILs and commercial stationary phases. Subsequently, two different synthesis routines of ionic liquid bonded polysiloxanes as stationary phase were reported in format of preliminary communication, respectively [24,25]. The method of Wei et al. [24] was based on hydrosilylation between poly(methylhydrosiloxane) and [VHIm][PF₆]. The column efficiency of it was relatively low (only 2500 plates/m) with the conditioning temperature of 200 °C. Our group [25] proposed an alternative way via the quaterisation of γ -chloropropyl-polysiloxane with methylimidazolium. The content of the imidazolium unit in ionic liquids was about 10%. This kind of IL stationary phase was more stable than the physical mixture and offered better wetting ability on inner wall of capillaries than neat IL stationary phases. Nevertheless, it could not be used over 220 °C. Thus, how to improve the thermal stability of IL bonded polysiloxanes and increase their separation efficiency is still crucial to the development of IL stationary phases.

In this work, a novel ionic liquid bonded polysiloxane ([PSOMIM][NTf₂]) was prepared, employing bis-trifluoromethanesulfonylimide as anion. For the purpose of comparison, another ionic liquid with chloride ([PSOMIM][Cl]) was used. And the content of the imidazolium unit in both ionic liquids was about 30%. Thermogravimetric (TG), based on mass variation with the increase of temperature, was tested to compare the thermal stability of the two kinds of ILs. The result showed that [PSOMIM][NTf₂] was more stable at high temperatures (380 °C). The synthesized polymers were then used as stationary phase for GC and the solvation behavior of the ILs was investigated using the Abraham solvation parameter model. The IL columns were further tested chromatographically through a series of aromatic isomers and congeneric compounds, and the selectivity of theirs was compared to that of DB-1. It suggested that the ionic liquid bonded polysiloxane [PSOMIM][NTf₂] had a great potential in the practical application of stationary phases for high temperature and high selectivity GC.

2. Experimental

2.1. Apparatus and reagents

The apparatus used for column evaluation was an Agilent 6890N gas chromatograph (Agilent Technologies, USA) equipped with split/splitless injection, flame ionization detector (FID) and micro-electron capture detector (μ ECD). Agilent ChemStation software was used for data acquisition. The carrier gas was nitrogen. The make-up flow of nitrogen was at 40 mL min⁻¹, while the hydrogen flow was at 40 mL min⁻¹ and the air flow was at 400 mL min⁻¹. Methane was used as the dead time marker. TG tests were carried out on a SETSYS 16TG thermal analyzer (France). The Microsoft excel program was used to fulfill multiple linear regression analysis (MLRA).

1-Methylimidazole and lithium bis-trifluoromethanesulfonylimide (LiNTf₂) were LC grade. They were purchased

from Fluka Corp. (USA) and Acros Corp. (Belgium), respectively. PCBs 16 (2,2',3-trichlorodiphenyl), 40 (2,2',3,3'-tetrachlorodiphenyl), 83 (2,2',3,3',5-pentachlorodiphenyl), 136 (2,2',3,3',6,6'-hexachlorodiphenyl), 178 (2,2',3,3',5,5',6-heptachlorodiphenyl), 194 (2,2',3,3',4,4',5,5'-octachlorodiphenyl) and 208 (2,2',3,3',4,5,5',6,6'-nonachlorodiphenyl) were purchased from AccuStandard Corp. (USA). All probe compounds and other testing compounds used in this study were analytical grade (SCRC, China). The probe solutes for solvation interaction parameters were dissolved in dichloromethane or methanol solvents. Fused-silica capillary tube (0.25 mm inner diameter) was purchased from Yongnian Optical Fiber Factory (Hebei, China). The DB-1 column (8 m \times 0.32 mm i.d., film thickness 0.25 μ m) was cut from a commercial column purchased from Agilent Technologies, the column efficiency was 3635 plates/m (for naphthalene $k=2.91$, 110 °C). The OV-1701 column (8 m \times 0.25 mm i.d., film thickness 0.30 μ m) was homemade using the commercial available stationary phase of OV-1701 and the column efficiency of it was 3378 plates/m (for naphthalene $k=3.22$, 120 °C).

2.2. Synthesis of ionic liquid bonded polysiloxane stationary phase

The IL bonded polysiloxane was prepared as shown in Fig. 1. Firstly, γ -chloropropyl-polysiloxane was synthesized according to Ref. [26]. Then [PSOMIM][Cl] (A) was synthesized through a reaction between γ -chloropropyl-polysiloxane and methylimidazolium, which was similar to Ref. [25]. Lastly, the chloride anion was exchanged for the bis-trifluoromethanesulfonylimide anion (NTf₂⁻).

The general procedures for the synthesis of [PSOMIM][Cl] (A) were as follows: Firstly, γ -chloropropylmethyl-diethoxysilane (0.056 mol, 11.80 g), dimethyldiethoxysilane (0.112 mol, 16.61 g) and hexamethyldisiloxane (0.008 mol, 1.30 g) were added to 150 mL H₂O for hydrolyzation using 15 mL HCl (20%) as catalyst. The mixture was refluxed for 4 h to fulfill hydrolysis and condensation, and γ -chloropropyl-polysiloxane was obtained. The resultant was dissolved in dichloromethane and washed with deionized water till neutral pH. Secondly, 1-methylimidazole (0.056 mol, 4.60 g) was added dropwise to a solution of γ -chloropropyl-polysiloxane (0.008 mol, 17.25 g in 25 mL toluene). The solution was then refluxed for 72 h under N₂ atmosphere. The resultant was washed with deionized water to remove the residue of reactants. After the solvent was removed by evaporating under vacuum, the light-yellow viscous compound [PSOMIM][Cl] (A) was obtained and yield was about 90%. [PSOMIM][Cl] was confirmed by FT-IR and ¹H NMR spectroscopy. FT-IR (KBr, ν /cm⁻¹): 3136 and 3062 [ν (Ar-H)], 2961 [ν (C-H)], 1570, 1454 and 1411 [ν (C=C)], ν (C=N)], 1265 [ν (Si-C)], 1090 and 1021 [ν (Si-O)], 803 [ν (Si-C)]; ¹H NMR (CD₃OD; 300 MHz; δ ppm): 9.06 (s, 1H), 7.63 (t, 2H), 4.23 (t, 2H), 3.95 (s, 3H), 1.91 (m, 2H), 0.56 (t, 2H). The peak at 0.083 ppm was attributed to C-H on Si atoms in the skeleton of the polysiloxane.

Then the ionic liquid [PSOMIM][NTf₂] (B) was prepared through anion-exchange reactions. The process was as follows: the compound (A) was dissolved in methanol, and then 1 molar equiv. of LiNTf₂ in methanol was added dropwise. After stirring for 24 h at room temperature, the light-yellow viscous product appeared. Then it was dissolved in dichloromethane and washed with deionized water. The silver nitrate test was used to confirm that chloride was absence. Finally, the product was evaporated under vacuum to remove the solvent. Furthermore, [PSOMIM][NTf₂] was confirmed by FT-IR and ¹H NMR spectroscopy. FT-IR (KBr, ν /cm⁻¹): 3153 and 3116 [ν (Ar-H)], 2960 [ν (C-H)], 1570, 1466 and 1414 [ν (C=C), ν (C=N)], 1355 [ν (S-C)], 1265 [ν (Si-C)], 1199 [ν (C-F)], 1139 [ν (S-O)], 1057 [ν (Si-O)], 805 [ν (Si-C)], 619 and 515 [ν (C-F)]; ¹H NMR (CD₃OD; 300 MHz; δ ppm): 8.82 (s, 1H), 7.56 (t, 2H), 4.19 (t,

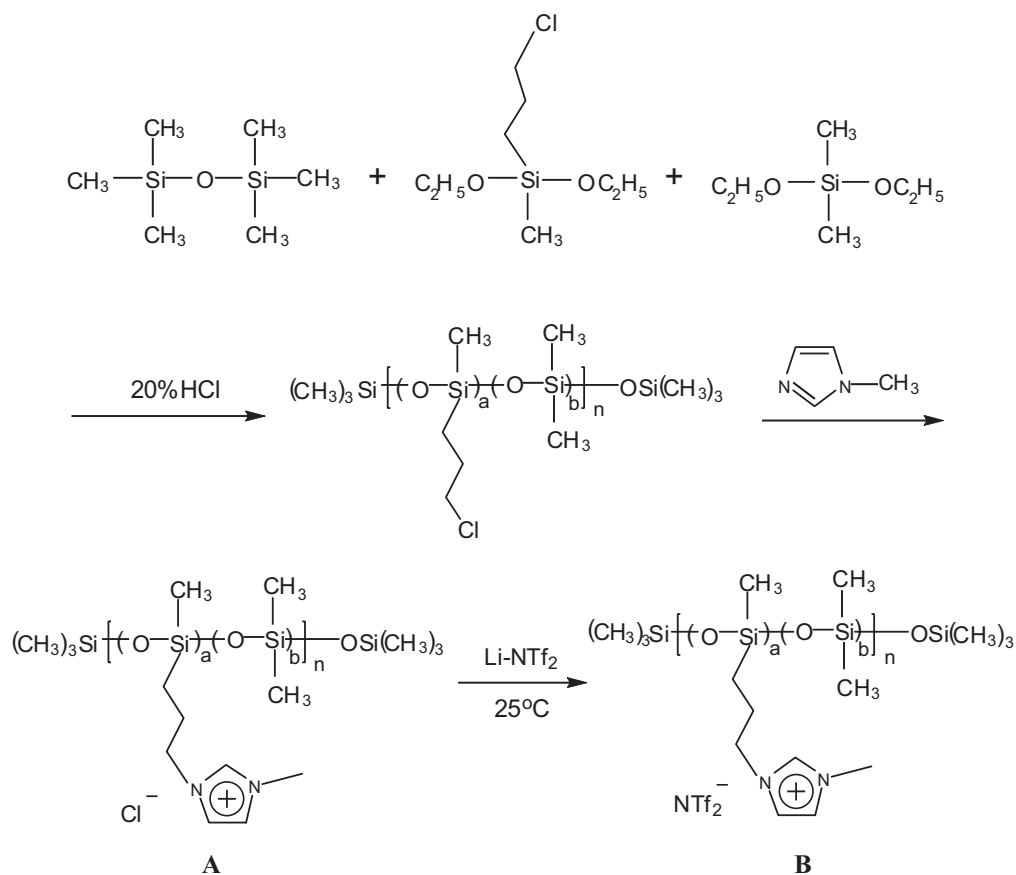


Fig. 1. Synthetic routes of compound (A) [PSOMIM][Cl] and (B) [PSOMIM][NTf₂].

2H), 3.92 (s, 3H), 1.92 (m, 2H), 0.57 (t, 2H). The peak at 0.093 ppm was attributed to C–H on Si atoms in the skeleton of the polysiloxane.

2.3. Preparation of capillary column

Two capillary columns were prepared for this study. Before coating, two pieces of fused-silica capillary tubes (8 m × 0.25 mm inner diameter) were rinsed with 10 mL methanol and 10 mL dichloromethane. After that, the capillary tubes were purged with nitrogen gas at 300 °C for 4 h. Then, the column A was statically coated with a solution of 0.40% (w/v) [PSOMIM][NTf₂] in methanol and finally, conditioned from 40 °C to 320 °C at 2 °C min⁻¹, then stayed at 320 °C for 8 h under nitrogen atmosphere. Being similar to the above procedure, the column B was coated with a solution of 0.40% (w/v) [PSOMIM][Cl] in methanol by the static method and finally, conditioned from 40 °C to 210 °C at 2 °C min⁻¹ and stayed at 210 °C for 8 h under nitrogen atmosphere. The film thickness (d_f) of the stationary phases was calculated according to Eq. (1) [12,27], where d_c is the diameter of the capillary (in micrometers), and c is the percentage by weight concentration of the coating solution. The film thickness of the capillary columns used in this work was both calculated to be 0.25 μm. Scanning electron microscopy (SEM) was also used to determine the film thickness of capillary columns. From Fig. 2 (cross-sectional view of columns), it can be known that the film thickness of the two capillary columns was both about 0.30 μm:

$$d_f = \frac{d_c c}{100} \quad (1)$$

3. Result and discussion

3.1. The chemical composition of the ionic liquid bonded polysiloxanes

Based on the datum of ¹H NMR, the content of the imidazolium unit in [PSOMIM][NTf₂] and [PSOMIM][Cl] was both about 30%, which was roughly calculated from the ratio of the integrate value at δ 8.82 ppm (attributed to C–H between two N in the imidazole moiety) to that at about δ 0.093 ppm (attributed to Si–CH₃) for [PSOMIM][NTf₂] and δ 9.06 ppm to that at about δ 0.083 ppm for [PSOMIM][Cl].

3.2. Thermal stability of the ionic liquid bonded polysiloxanes

In order to evaluate the thermal stability of the IL bonded polysiloxanes, thermogravimetric (TG) tests were carried out [28,29]. The sample weight was 10 mg and the operating temperature range was from 100 °C to 550 °C at rate of 10 °C min⁻¹ under condition of dynamic nitrogen atmosphere. As can be seen from Fig. 3, [PSOMIM][Cl] began to show weight-loss at 220 °C, but [PSOMIM][NTf₂] decomposed slightly around 380 °C and significantly after 400 °C. It could be deduced that the thermal stability of IL bonded polysiloxanes was affected by the anions. This conclusion was conformed to the reports in Refs. [3,13].

3.3. The durability of capillary columns

The durability of the IL bonded polysiloxane columns could be roughly demonstrated as follows: In order to demonstrate that

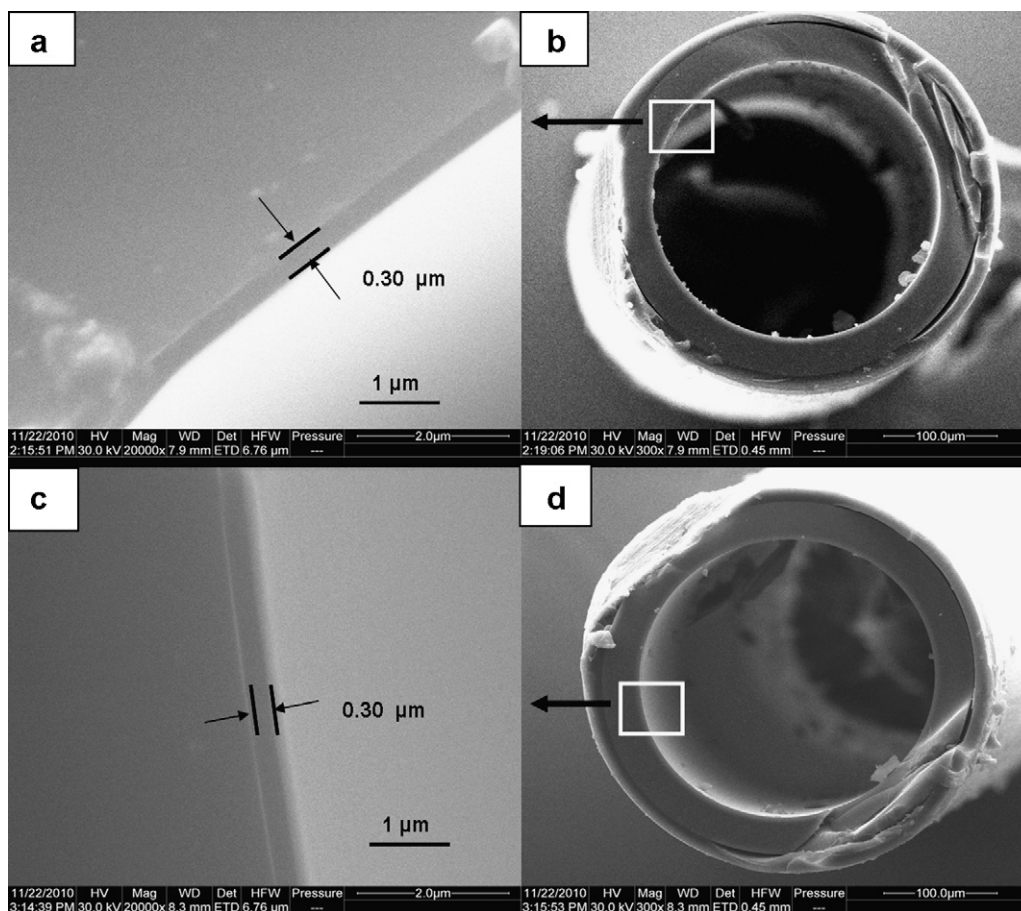


Fig. 2. SEM images (cross-sectional view): (A) 20,000-fold magnification and (B) 300-fold magnification of [PSOMIM][NTf₂] column; (C) 20,000-fold magnification and (d) 300-fold of [PSOMIM][Cl] column.

the films were not altered during the chromatographic separations, the column efficiency and retention factors were monitored after every 100 injections using naphthalene as testing compound under the same experimental conditions. The columns efficiency of [PSOMIM][NTf₂] column and [PSOMIM][Cl] column was 4776 plates/m ($k=3.64 \pm 0.08$, 110 °C) and 3170 plates/m ($k=2.84 \pm 0.11$, 100 °C), respectively. The value of the column efficiencies was distinctly higher than that of normal IL columns [24,30]. The slightly variances of k after hundreds of injections indi-

cated that the films of [PSOMIM][NTf₂] and [PSOMIM][Cl] were very stable, thus the columns could endure long-term use. Therefore, the columns of IL bonded polysiloxane were suitable for further study and practical application.

3.4. Columns polarity

The sum of the five Rohrschneider–McReynolds constants was commonly used to characterize the polarity scale of a stationary phase for chromatography. Each probe molecule interacted with the stationary phase in a particular way: X'—dispersive interactions; Y'—proton donor and acceptor capabilities plus dipolar interactions; Z'—dipolar interactions plus weak proton acceptor, but not proton donor capabilities; U'—dipolar interactions; and S'—strong proton acceptor capabilities [31]. Table 1 lists the Rohrschneider–McReynolds constants on four different columns at 120 °C. These comparison showed that the polarity of the IL bonded polysiloxanes column were far higher than DB-1 column (100% polymethylsiloxane), but close to FFAP column (Carbowax 20M-2-nitro-terephthalic acid) [23]. The results indicated that these IL stationary phases were in the range of high polarity, and their polarities were predominated by the ionic liquid moieties of stationary phases. Additionally, changing the anion type of the IL bonded polysiloxanes had a significant effect on the individual interactions, but had little effect on the average polarity. Since the proton donor (Y') and proton acceptor (S') capabilities were very strong, the hydrogen bond interaction may be the primary between analytes and the IL bonded polysiloxane stationary phases.

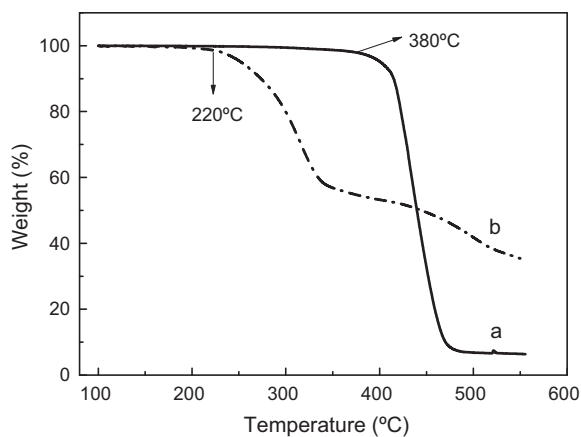


Fig. 3. Thermogravimetric (TG) analysis for the (a) [PSOMIM][NTf₂] and (b) [PSOMIM][Cl]. Temperature programmed from 100 °C to 550 °C at a heating rate of 10 °C min⁻¹.

Table 1
Rohrshneider–McReynolds constants of stationary phases at 120 °C.

Stationary phase	ΔI					Polarity $\sum \Delta I$	Average polarity
	Benzene (X')	n-Butanol (Y')	2-Pentanone (Z')	1-Nitropropane (U')	Pyridine (S')		
[PSOMIM][NTf ₂]	333	557	536	665	716	2807	561
[PSOMIM][Cl]	223	758	328	514	407	2230	446
DB-1 ^{a)}	12	41	42	62	46	203	41
FFAP ^{b)}	340	580	397	602	627	2546	509

The DB-1 column was a stationary phase of 100% methylpolysiloxane. Data obtained from Ref. [23].

3.5. Solvation interaction parameters of the ionic liquid bonded polysiloxanes

In Rohrshneider–McReynolds approach, five selected probe molecules are used to characterize five different types of interaction. However, the approach cannot explain the fact that ILs with identical “polarity parameters” can exhibit completely different solvation behaviors [32]. To address this problem, the solvation parameter model developed by Abraham et al. [33–36] has been used as an alternative to characterize ILs. In principle, this approach is similar to the Rohrshneider–McReynolds method, but it could reveal the differences of various IL stationary phases more distinctly, because much more probe molecules were employed and the interaction between IL stationary phases and probe molecules were investigated statistically. The solvation parameter model has been demonstrated to be more practical than Rohrshneider–McReynolds approach while used to categorize IL stationary phases [30,37].

A linear solvation free energy relationship (LSER) can be obtained from the solvation model of Abraham (Eq. (2)), which describes the solvation process of a solute as occurring in three stages [35]. Each solute molecule will possess some different solute–solvent interactions. Each kind of interactions was represented by a particular solute descriptor: *E*, *S*, *A*, *B*, *L* [33,38]. The descriptors of 33 probe solutes were used in this study and the data was obtained from Ref. [33]. The retention factor *k*, was determined chromatographically. Then the solute descriptors and retention factors were subjected to multiple linear regression analysis (MLRA) to acquire the interaction parameter coefficients (*e*, *s*, *a*, *b*, *l*) [33]: *e* represented the ability of the ionic liquid to interact with π and *n* electrons of the solute; *s* measured the dipolarity/polarizability of the ionic liquid; *a* and *b* defined hydrogen bond basicity and hydrogen bond acidity of the ionic liquid respectively; and *l* described dispersion forces toward solute:

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

The interaction parameters of the IL bonded polysiloxanes were examined at four different temperatures (40 °C, 70 °C, 100 °C, and

120 °C) to illustrate how interactions change with temperature (Table 2). It could be seen that most value of relative coefficients of the IL bonded polysiloxanes decreased with the increased temperature. That may be owing to the decreased interactions between the probe solutes and the stationary phases at higher temperature. It was also found that the most dominant interaction for the IL bonded polysiloxanes was strong hydrogen bond basicity (*a*), and the followed was dipolarity (*s*), which indicated that the IL bonded polysiloxanes stationary phase had strong retention for polar solutes. Perhaps the large *a* and *s* system constants can distinguish the ionic liquid from the non-ionic stationary phases as reported by Abraham et al. [39]. Moreover, in contrast with the large *a* values, the *b* values were small for the IL bonded polysiloxanes. This result was conformed to that in the previous report [14,32]. Meanwhile, the statistical data in Table 2 proved that [PSOMIM][Cl] column was non-hydrogen-bond acidic (*b*=0). The result was also accordant to that of the report about liquid organic chloride salts [39]. In addition, [PSOMIM][NTf₂] column showed obviously lower value of the hydrogen bond basicity in comparison with [PSOMIM][Cl] column at 40 °C, 70 °C, 100 °C, and 120 °C, respectively. It seems that the *a* values of IL bonded polysiloxanes were largely influenced by the anion. Moreover, the dispersion forces (*l*) of IL stationary phases were close to that of OV-11 [29] due to the component of polysiloxane in IL stationary phases. This meant that the IL stationary phases probably had good selectivity for weak or non-polar analytes like OV-11.

3.6. Selectivity for Grob test mixtures

Fig. 4 presents the chromatogram of Grob test mixtures on the columns [PSOMIM][NTf₂], [PSOMIM][Cl] and DB-1. It showed that all components were well separated except 2-ethylhexanoic acid in Fig. 4. This result indicated that the IL bonded polysiloxanes had good film-forming ability like DB-1 (100% polydimethylsiloxane). Meanwhile, the reduced peak areas of the 2-ethylhexanoic acid indicated the irreversible acid–base adsorption may occur at relatively low temperature. Compared with Fig. 4(A), dicyclohexylamine was tailing in Fig. 4(B) because of the stronger

Table 2
Comparison of interaction parameters at different temperatures obtained from the solvation parameter model.

Stationary phase	Temperature (°C)	Interaction parameter ^{a)}						<i>n</i>	<i>R</i> ²
		<i>c</i>	<i>e</i>	<i>s</i>	<i>a</i>	<i>b</i>	<i>l</i>		
[PSOMIM][NTf ₂]	40	−3.009 (0.11)	0.034 (0.10)	1.861 (0.11)	2.146 (0.10)	0.497 (0.12)	0.623 (0.03)	25	0.99
	70	−3.098 (0.08)	0.007 (0.07)	1.799 (0.07)	1.845 (0.07)	0.373 (0.09)	0.511 (0.02)	27	0.99
	100	−3.391 (0.08)	0.002 (0.07)	1.766 (0.07)	1.617 (0.06)	0.311 (0.09)	0.459 (0.02)	27	0.99
	120	−3.236 (0.08)	0.051 (0.07)	1.569 (0.07)	1.340 (0.06)	0.267 (0.08)	0.359 (0.02)	25	0.99
[PSOMIM][Cl]	40	−3.699 (0.17)	0.189 (0.13)	1.882 (0.18)	6.306 (0.28)	0	0.709 (0.04)	22	0.99
	70	−3.613 (0.11)	0.074 (0.10)	1.801 (0.13)	4.951 (0.17)	0	0.570 (0.03)	29	0.99
	100	−3.675 (0.09)	0.149 (0.09)	1.563 (0.12)	4.208 (0.14)	0	0.490 (0.03)	29	0.99
	120	−3.668 (0.09)	0.148 (0.09)	1.469 (0.10)	3.549 (0.10)	0	0.402 (0.03)	29	0.99
OV-11 ^{b)}	120	−0.300	0.100	0.540	0.170	−	0.516	39	0.99

^{a)} Parameters: *c*, constant; *e*, ability of stationary phase to interact via nonbonding and π -electrons of solute molecule; *s*, stationary phase dipolarity; *a*, stationary-phase hydrogen bond basicity; *b*, stationary-phase hydrogen bond acidity; *l*, stationary-phase dispersion forces; *n*, number of probe molecules; *R*², statistical correlation coefficient.

^{b)} Data obtained from Ref. [29].

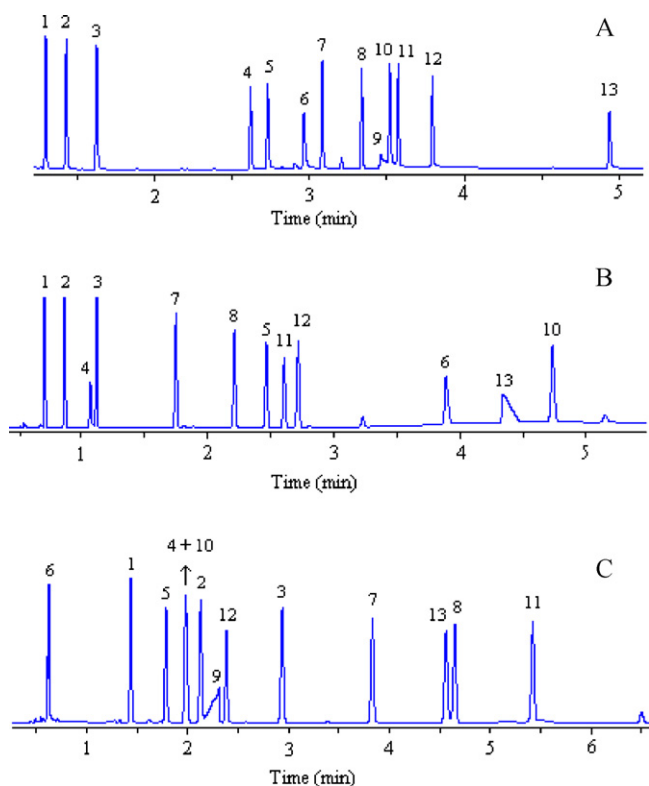


Fig. 4. Chromatograms of Grob reagents on the (A) [PSOMIM][NTf₂], (B) [PSOMIM][Cl] and (C) DB-1 columns. Peaks: 1. n-decane; 2. n-undecane; 3. n-dodecane; 4. nonanal; 5. n-octanol; 6. 2,3-butanediol; 7. methyl decanoate; 8. methyl undecanoate; 9. 2-ethylhexanoic acid; 10. 2,6-dimethylphenol; 11. methyl dodecanoate; 12. 2,6-dimethylaniline; 13. dicyclohexylamine. Conditions: (A) 80 °C for 1 min, 35 °C min⁻¹ to 220 °C. Carrier gas velocity: 15 cm s⁻¹. (B) Temperature programmed from 100 °C to 180 °C at 18 °C min⁻¹. Carrier gas velocity: 27 cm s⁻¹. (C) 80 °C for 1 min, 15 °C min⁻¹ to 160 °C. Carrier gas velocity: 31 cm s⁻¹

hydrogen bond force of [PSOMIM][Cl]. It also could be seen that the resolution of column [PSOMIM][NTf₂] was better than that of column [PSOMIM][Cl] due to the higher column efficiency of [PSOMIM][NTf₂]. Another character in Fig. 4(A) and (B) was that both 2,3-butanediol and n-octanol eluted after n-decane, n-undecane and n-dodecane, contrary to the corresponding elution order in Fig. 4(C). This revealed that the interaction of hydrogen bond between the ionic liquid bonded polysiloxanes and analytes would play important role in chromatographic separation. Moreover, the bonded IL groups were able to dominate the selectivity of the stationary phase in spite of the relatively low content of IL moiety in the stationary phase.

3.7. Selectivity for isomers and congeneric compounds

Table 3 lists the separation factors (α) and capacity factors (k) of the tested aromatic positional isomers on [PSOMIM][NTf₂], [PSOMIM][Cl], DB-1 and OV-1701 columns [poly(cyanopropylphenyldimethylsiloxane)]. Comparing the separation factors of each group of isomers, it could be found that most tested polar isomers such as cresol and toluidine isomers were better separated on the two ionic liquids columns than on DB-1 and OV-1701 columns; on the other hand, the separation factors (α) of the tested weak polar isomers such as methylnaphthalenes and xylenes isomers also showed better or comparative selectivity of the ionic liquid columns than DB-1 and OV-1701 columns. Moreover, for the separation of *m*-, *p*-xylenes, [PSOMIM][NTf₂] exhibited evident advantages over [BuMIm][Cl] and [BuMIm][PF₆] columns [2]. All the results seemed to demonstrate that incorporation IL

moiety into polysiloxane was effective to improve the selectivity of a stationary phase, and the “dual nature” of IL was retained though the content of IL moieties was relatively low. Compared with [PSOMIM][Cl] column, [PSOMIM][NTf₂] column owned higher column efficiency and polarity, and could separate most of isomers much better such as *m*-, *p*-xylenes and *m*-, *p*-chlorotoluenes isomers, whereas had relative weak resolution towards methylnaphthalenes and pinenes isomers. This indicated that the IL bonded polysiloxane with bis-trifluoromethanesulfonylimide anion was more suitable to separate the polar isomers than that with chloride anion due to the higher polarity of [PSOMIM][NTf₂].

The stationary phases of IL bonded polysiloxanes were then applied to separate the compounds with high boiling point. Fig. 5(A) and (B) shows excellent chromatograms of n-alkanes with symmetrical peaks on [PSOMIM][NTf₂] and [PSOMIM][Cl] columns, respectively. Fig. 5(A) also demonstrated that [PSOMIM][NTf₂] column could be used up to 300 °C with very slight baseline drift, whereas the baseline drifted evidently in Fig. 5(B) when the temperature rising to 180 °C for [PSOMIM][Cl] column. Furthermore, Fig. 5(C) and (D) shows the chromatograms of polycyclic aromatic hydrocarbons (PAHs) on [PSOMIM][NTf₂] and [PSOMIM][Cl] columns. These compounds eluted in the order of their increasing dispersion force and baseline separation could be achieved for most components except β -methylnaphthalene and α -methylnaphthalene. The separation of sixteen compounds was completed under a programmed temperature up to 300 °C without obvious baseline drift (Fig. 5C). The distinction in baselines drift between Fig. 5(A) and (C) and Fig. 5(B) and (D) was owing to the better thermostability of [PSOMIM][NTf₂]. Compared with the MPMIM-TfO column (10m) [3], on which twelve PAHs were separated using about 20 min, [PSOMIM][NTf₂] column could separate sixteen PAHs in less than 7 min (Fig. 5C). The reduced analysis time exhibited higher separation efficiency of [PSOMIM][NTf₂] column for PAHs.

Additionally, some congeneric compounds had also been employed to test the selectivity of [PSOMIM][NTf₂] stationary phase. Fig. 6 illustrates the chromatograms of alcohols, phenols and esters. The fact that baseline separation of all components was achieved within 5 min indicated the high separation efficiency. Meanwhile, it could be found that the peaks of alcohols and esters were nearly symmetrical, while the phenols were tailing in Fig. 6(B), which could be attributed to the hydrogen bond basicity of [PSOMIM][NTf₂] stationary phase. Moreover, the strong hydrogen bond basicity could also account for the result that phenol eluted after *o*-chlorophenol, 2,6-dimethylphenol and *o*-cresol on [PSOMIM][NTf₂] column. This result was accordant to that on [BuMIm][PF₆] column [2], but contrary to that on the commercial HP-5MS column [poly(phenylmethylsiloxane)] [40] and DB-5 column [poly(phenylmethylsiloxane)] [2], respectively. It demonstrated that [PSOMIM][NTf₂] could retain the selectivity of neat IL stationary phases [2] after IL was bonded to polysiloxane.

3.8. Separation of FAMES, PCBs and aromatic amines

Owing to its unique selectivity of “dual nature”, IL bonded polysiloxanes should be suitable for the analysis of samples composed of polar or weak polar compounds. Hence, fatty acid methyl esters (FAMES), polychlorinated biphenyls (PCBs) and aromatic amines would also be tested on [PSOMIM][NTf₂] column (Fig. 7).

The determination of FAMES is of importance for biodiesel obtained through a simultaneous transesterification from biological materials such as vegetable oils and animal fats [41–43]. Fig. 7(A) illustrates the separation of FAMES. It could be seen that ten components were separated with symmetrical peaks within about 3 min. Moreover, due to the extra π - π interaction between imi-

Table 3Retention factors (k) and separation factors (α) of isomers on the columns of [PSOMIM][NTf₂], [PSOMIM][Cl], DB-1 and OV-1701 at their optimized conditions.

Solutes	Isomers	[PSOMIM][NTf ₂]			[PSOMIM][Cl]			DB-1			OV-1701		
		k	α^a	$T(^{\circ}\text{C})$	k	α	$T(^{\circ}\text{C})$	k	α	$T(^{\circ}\text{C})$	k	α	$T(^{\circ}\text{C})$
Dichlorobenzene	<i>o</i> -	0.67	1.34	110	0.81	1.31	110	5.58	1.17	60	5.31	1.26	80
	<i>m</i> -	0.42	0.84		0.54	0.87		4.56	0.96		3.96	0.94	
	<i>p</i> -	0.50	1.00		0.62	1.00		4.75	1.00		4.22	1.00	
Cresol	<i>o</i> -	5.17	0.64	110	7.80	0.67	175	7.11	0.83	60	6.18	0.78	100
	<i>m</i> -	8.43	1.04		12.29	1.05		8.55	1.00		7.94	1.00	
	<i>p</i> -	8.11	1.00		11.66	1.00		8.55	1.00		7.94	1.00	
Chlorotoluene	<i>o</i> -	3.38	0.90	50	1.77	0.92	60	8.52	0.98	35	6.05	0.94	60
	<i>m</i> -	3.74	1.00		1.92	1.00		8.70	1.00		6.47	1.00	
	<i>p</i> -	3.90	1.04		1.92	1.00		8.99	1.03		6.63	1.02	
Toluidine	<i>o</i> -	0.78	0.92	160	0.98	0.93	160	10.89	0.96	50	7.44	0.95	80
	<i>m</i> -	0.93	1.09		1.16	1.10		11.71	1.03		8.09	1.03	
	<i>p</i> -	0.85	1.00		1.05	1.00		11.32	1.00		7.84	1.00	
Xylene	<i>o</i> -	5.33	1.37	35	0.65	1.35	60	2.75	1.21	50	5.66	1.28	50
	<i>m</i> -	3.89	1.00		0.48	1.00		2.28	1.00		4.41	1.00	
	<i>p</i> -	3.79	0.97		0.48	1.00		2.28	1.00		4.41	1.00	
Methylnaphthalene	α -	2.61	1.00	130	1.96	1.00	130	6.13	1.00	100	2.98	1.00	140
	β -	2.46	0.94		1.74	0.89		5.64	0.92		2.72	0.91	
Pinene	α -	0.15	0.60	90	0.20	0.50	70	0.95	0.75	90	0.81	0.70	100
	β -	0.25	1.00		0.40	1.00		1.26	1.00		1.16	1.00	
		2.06	0.65		120	2.10		0.81	140		4.24	0.89	
Quinoline		3.19	1.00		2.58	1.00		4.77	1.00		4.25	1.00	
Diphenylamine	<i>o</i> -	0.66	0.59	230	–	–	–	0.78	0.80	140	1.28	0.78	180
	<i>m</i> -	1.47	1.32		–	–		1.13	1.16		2.04	1.24	
	<i>p</i> -	1.11	1.00		–	–		0.97	1.00		1.64	1.00	
Nitroaniline	<i>o</i> -	0.59	0.56	250	–	–	–	0.25	0.81	200	1.84	0.63	200
	<i>m</i> -	1.06	1.00		–	–		0.31	1.00		2.91	1.00	
	<i>p</i> -	2.79	2.63		–	–		0.45	1.45		5.59	1.92	

^a α is the relative retention, which is the ratio of k of each isomer to the second largest k among isomers.

dazole moiety in [PSOMIM][NTf₂] stationary phase and the C=C double bond in unsaturated fatty acid esters, the unsaturated fatty acid esters were eluted after the corresponding saturated one like that on commercial ionic liquid column SLB-IL100 [41]. The elution order of the unsaturated fatty acid esters on [PSOMIM][NTf₂] column was in accordance with that on polar columns such as Rtx-2330 [poly (biscyanopropyl-cyanopropylphenylsiloxane)]

[43], whereas contrary to that on nonpolar column such as DB-1 [44].

Since the PCBs were serious environmental pollutants and could be slowly released into trophic food chains [45,46], more attention had been paid to the developments in chromatographic techniques for the determination of these pollutants in recent years. In this work, the separation ability of [PSOMIM][NTf₂] column for PCBs

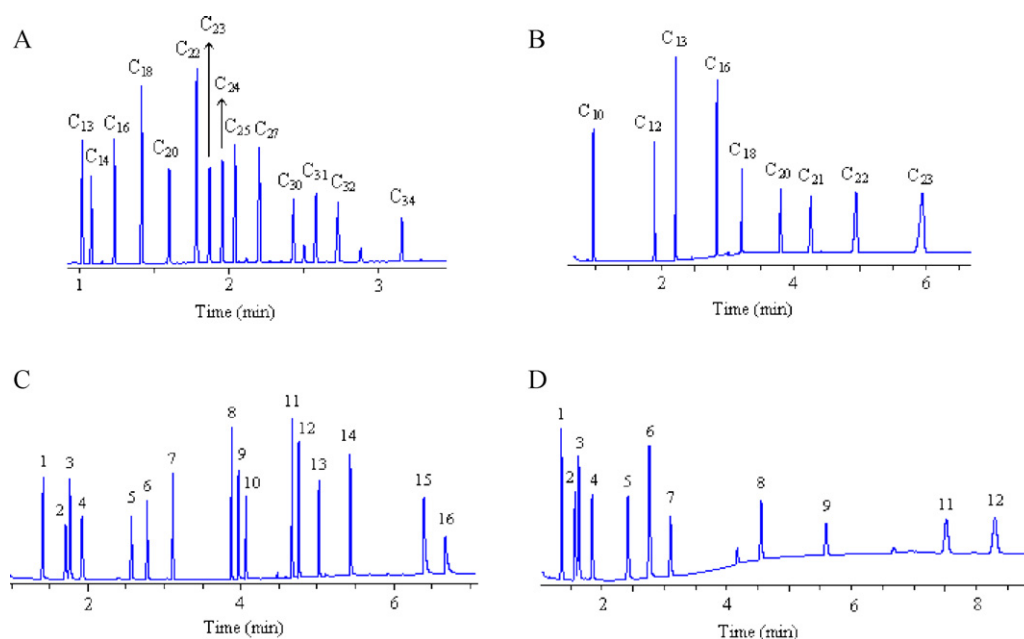


Fig. 5. (A and B) Chromatograms for the separation of n-alkanes on the (A) [PSOMIM][NTf₂] and (B) [PSOMIM][Cl] columns. Conditions: (A) temperature programmed from 85 °C to 300 °C at 70 °C min⁻¹, Carrier gas velocity: 20 cm s⁻¹; (B) 80 °C for 1.5 min, 60 °C min⁻¹ to 180 °C. Carrier gas velocity: 24 cm s⁻¹. (C and D) chromatograms for the separation of polycyclic aromatic hydrocarbons on the (C) [PSOMIM][NTf₂] and (D) [PSOMIM][Cl] columns. Peaks: 1. naphthalene; 2. β -methyl-naphthalene; 3. α -methyl-naphthalene; 4. biphenyl; 5. acenaphthene; 6. dibenzofuran; 7. fluorene; 8. phenanthrene; 9. tritane; 10. 7,8-benzoquinoline; 11. fluoranthene; 12. pyrene; 13. carbazole; 14. chrysene; 15. benzo[fluoranthene]; 16. benzopyrene. Conditions: (C) 150 °C for 2 min, 50 °C min⁻¹ to 300 °C. Carrier gas velocity: 17 cm s⁻¹. (D) 150 °C for 2 min, 18 °C min⁻¹ to 190 °C. Carrier gas velocity: 15 cm s⁻¹

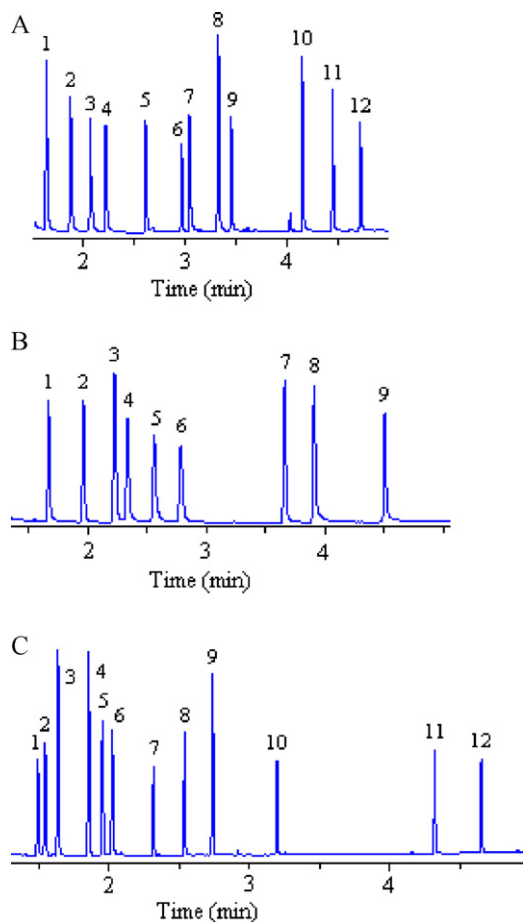


Fig. 6. Separation of congeneric compounds on [PSOMIM][NTf₂] column. (A) Chromatogram for the separation of alcohols: 1. n-propanol; 2. n-butanol; 3. 2-pentanol; 4. n-pentanol; 5. n-hexanol; 6. cyclohexanol; 7. n-heptanol; 8. linalool; 9. n-octanol; 10. n-decanol; 11. undecanol; 12. dodecanol; conditions: 80 °C for 1.5 min, 30 °C min⁻¹ to 180 °C. Carrier gas velocity: 13 cm s⁻¹. (B) Chromatogram for the separation of phenols: 1. *o*-chlorophenol; 2. 2,6-dimethylphenol; 3. *o*-cresol; 4. phenol; 5. 2,4-dimethylphenol; 6. *m*-cresol; 7. *p*-tert-butylphenol; 8. *m*-chlorophenol; 9. *p*-bromophenol; conditions: 155 °C for 3 min, 40 °C min⁻¹ to 220 °C. Carrier gas velocity: 15 cm s⁻¹. (C) Chromatogram for the separation of esters: 1. ethyl butyrate; 2. butyl acetate; 3. isoamyl acetate; 4. ethyl caproate; 5. isoamyl butyrate; 6. amyl butyrate; 7. ethyl caprylate; 8. ethyl nonylate; 9. phenylethyl acetate; 10. ethyl caprate; 11. benzyl benzoate; 12. phenylethyl phenylacetate. Conditions: 90 °C for 1 min, 50 °C min⁻¹ to 270 °C. Carrier gas velocity: 14 cm s⁻¹.

was also evaluated by GC with μ ECD detector. Fig. 7(B) indicates that all of PCBs 16, 40, 83, 136, 178, 194 and 208 were separated completely. It seemed to demonstrate that [PSOMIM][NTf₂] had great potential in the analysis of PCBs samples.

Aromatic amines, like toluidines, phenylenediamines and chloroanilines, have been widely used in the dye product. Since they may be absorbed by human beings and converted to carcinogenic aromatic amines [47–51], determining aromatic amines in various samples is very crucial. However, even on weak polar column of DB-5MS [poly (phenylmethylsiloxane)] [51], the peaks of aromatic amines are always tailed seriously due to their high polarity. In order to improve the peak shape, complex and time consuming derivatization [50,51] had to be adopted frequently. In this work, fifteen aromatic amines were directly separated on [PSOMIM][NTf₂] stationary phase with good selectivity (Fig. 7C) and all of the peaks were narrow and symmetrical. It is known that the peak tailing of amines could be largely attributed to poor film formation of a stationary phase and excessive hydrogen-bonding interaction between analytes and stationary phases. For [PSOMIM][NTf₂], polysiloxane was its main

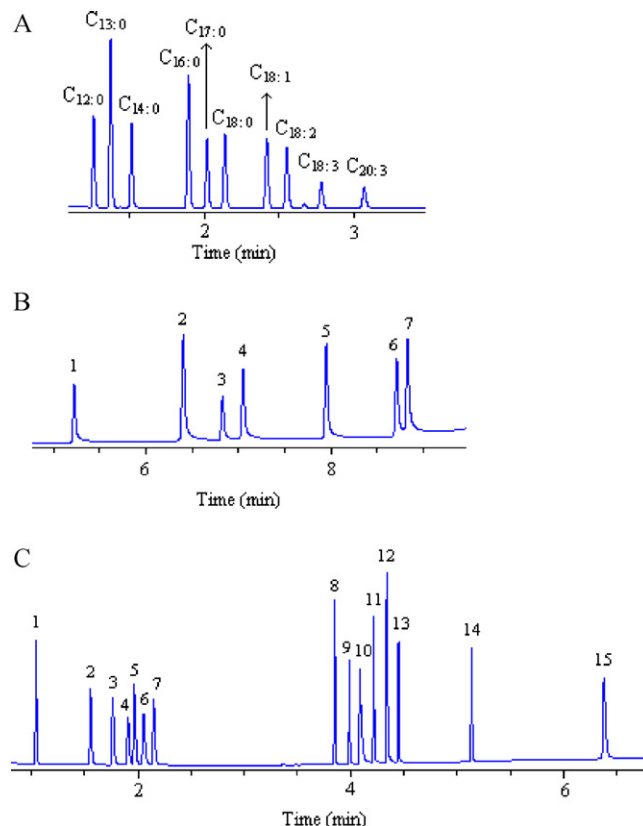


Fig. 7. (A) Chromatogram for the separation of FAMES on [PSOMIM][NTf₂] column. Conditions: temperature programmed from 170 °C to 190 °C at 5 °C min⁻¹. Carrier gas velocity: 20 cm s⁻¹. (B) Chromatogram for the separation of PCBs on [PSOMIM][NTf₂] column. Peaks: 1. PCB 16; 2. PCB 40; 3. PCB 83; 4. PCB 136; 5. PCB 178; 6. PCB 194; 7. PCB 208. Conditions: temperature programmed from 100 °C to 280 °C at 15 °C min⁻¹. Carrier gas velocity: 27 cm s⁻¹. (C) Chromatogram for the separation of aromatic amines on [PSOMIM][NTf₂] column. Peaks: 1. *N,N*-dimethylaniline; 2. aniline; 3. *o*-toluidine; 4. *o*-chloroaniline; 5. 2,6-dimethylaniline; 6. *m*-toluidine; 7. 2,4-dimethylaniline; 8. diphenylamine; 9. *o*-nitroaniline; 10. 1,4-diaminobenzene; 11. 1-naphthylamine; 12. 2,4-diaminotoluene; 13. *m*-nitroaniline; 14. *p*-nitroaniline; 15. benzidine. Conditions: 130 °C for 2 min, 50 °C min⁻¹ to 280 °C. Carrier gas velocity: 30 cm s⁻¹.

skeleton. Therefore, good film was readily obtained and high column efficiency was achieved. On the other hand, the α value in Table 2 revealed that hydrogen-bonding interaction decreased evidently at a higher temperature. Considering that the thermal resistance of [PSOMIM][NTf₂] was better than that of commercially available polar columns, higher oven temperature could be adopted to weaken peak tailing resulting from excessive hydrogen-bonding interaction, and the selectivity of [PSOMIM][NTf₂] for amines was still retained. Therefore, [PSOMIM][NTf₂] column took advantage over common commercial columns for the separation of amines. The chromatogram (Fig. 7C) also showed that the separation of fifteen aromatic amines was achieved within 7 min. All of these indicated the high efficiency, selectivity and thermal resistance of [PSOMIM][NTf₂] column.

4. Conclusions

This work proposed a synthesis method of ionic liquid bonded polysiloxane ([PSOMIM][NTf₂]) with anion of NTf₂⁻. For the purpose of comparison, another ionic liquid [PSOMIM][Cl] was also synthesized. When [PSOMIM][NTf₂] was used as stationary phase to prepare capillary column for GC, it exhibited good coating ability and durability. Moreover, the solvation parameter evaluation showed that hydrogen bond basicity of [PSOMIM][NTf₂]

was obviously lower than that of [PSOMIM][Cl] under the test conditions. In addition, it was found that the anions have significant influences on the thermal stability, polarity and selectivity of the IL bonded polysiloxanes. The results also indicated that [PSOMIM][NTf₂] column possessed higher separation efficiency than [PSOMIM][Cl] column. Furthermore, the good selectivity for analytes in wide range of polarity including aromatic isomers, fatty acid methyl esters (FAMES), polychlorinated biphenyls (PCBs) and aromatic amines suggested the novel IL bonded polysiloxane [PSOMIM][NTf₂] had a great potential in the high temperature and highly selective GC. In our opinion, the synthesis approach of the IL bonded polysiloxanes could also be utilized to prepare other forms of separation material for various purposes.

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