

# Fullerene-impregnated ionic liquid stationary phases for gas chromatography

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A new method has been developed to facilitate the use of fullerenes as stationary phases (SPs) in gas chromatography (GC). In this method, ionic liquids (ILs) are used as solvents to coat fullerenes (C<sub>60</sub>, amino-C<sub>60</sub> and hydroxy-C<sub>60</sub>) onto GC columns. However, the ILs serve not just as coating solvents but also act synergistically with fullerenes to provide unique properties as stationary phases, namely dual modal characteristics. They act as non-polar SPs when separating non-polar analytes (aromatic hydrocarbon mixtures and alkane mixtures), and as polar SPs for polar analytes (*e.g.*, alcohol mixtures). The polarity of the stationary phase can be adjusted by changing either the type of the IL and/or by adding either C<sub>60</sub> (or its amino or hydroxy derivatives) to the IL. It was found that C<sub>60</sub> and its derivatives produce not only a change in the polarity of the SP but also substantial enhancement in separation efficiencies for both non-polar and polar analytes. More importantly, when added to the IL SP, C<sub>60</sub> improves separation efficiencies not just for non-polar analytes (aromatic hydrocarbon mixtures and alkane mixtures) but also for polar analytes (mixtures of *ortho*-, *meta*- and *para*-xylene and alcohol mixtures) as well. Moreover, C<sub>60</sub> SP provides higher efficiencies than amino-C<sub>60</sub> and hydroxy-C<sub>60</sub> for separation of polar analytes. This is rather surprising considering that not only are amino-C<sub>60</sub> and hydroxy-C<sub>60</sub> more polar than C<sub>60</sub>, but that the IL used to coat the amino- and hydroxy-C<sub>60</sub> (*i.e.*, *N*-ethylpyridinium trifluoroacetate, [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>]) is more polar than the IL used to coat the C<sub>60</sub> (*i.e.*, octylmethylimidazolium bis(trifluoromethyl)sulfonyl)amide, [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>]). Moreover, compared to its amino and hydroxy derivatives, the concentration of C<sub>60</sub> in the column was 10 times lower.

## Introduction

Fullerenes have been the subject of wide and intense study in many disciplines including chemistry, physics, and materials science.<sup>1–5</sup> Their popularity stems from their unique structure as well as their unusual and interesting properties.<sup>3,4</sup> For example, they are known to be very non-polar, and can only be dissolved in a few strongly non-polar solvents. Such a property makes it desirable to use fullerenes as a stationary phase (SP) in chromatography. Unfortunately, in spite of intense efforts made by various research groups, only limited success has been achieved to date.<sup>6–12</sup> It has been found that fullerenes, when used as SPs, exhibit, as expected, unique chromatographic properties,<sup>6–12</sup> namely a C<sub>60</sub> SP can be successfully used to separate various compounds including polycyclic aromatic hydrocarbons (PAHs) and calixarenes.<sup>6–12</sup> Unfortunately, in these studies, it was necessary to employ rather elaborate and complicated synthetic schemes to covalently attach C<sub>60</sub> molecules onto either polysiloxane (for GC) or silica particles (for HPLC).<sup>6–12</sup> Because such procedures are not only time-consuming but also require expertise in organic synthesis, they are not particularly easy to implement. It is, therefore, of particular importance that a new

and simple method that does not require elaborate organic synthesis to immobilize fullerenes onto the SP of GC, but which can coat fullerenes directly without any chemical derivatization onto a GC column is developed. Room temperature ionic liquids, with their unique properties, may provide the answer to this problem.

Ionic liquids (ILs) are a group of organic salts that are liquid at room temperature. They have unique chemical and physical properties, including being air- and moisture-stable, having high solubility power, and virtually no vapor pressure.<sup>13–19</sup> Because of these properties, they can serve as a “green” recyclable alternative to the volatile organic compounds that are traditionally used as industrial solvents.<sup>13–19</sup> ILs have, in fact, been successfully used in many applications, including replacing traditional organic solvents in (1) organic and inorganic syntheses, (2) solvent extractions, (3) liquid–liquid extractions, (4) electrochemical reactions and (5) as a medium for enzymatic reactions.<sup>13–25</sup> Of particular interest are applications of ILs in analytical chemistry. Specifically, ILs have been successfully used as solvents to enhance the sensitivity of thermal lens measurements,<sup>26</sup> as both solvent and chiral selectors for determination of enantiomeric compositions of pharmaceutical products,<sup>24,25</sup> as matrixes for MALDI-MS,<sup>27</sup> as buffers for CE and as SPs in GC.<sup>26,28–40</sup> The last application is significant, because it is based on the synergistic exploitation of many advantages of ILs, namely their low vapor pressure, extremely

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high boiling point and high solubility power. For example, Poole *et al.* have shown that ILs based on tetraalkylammonium salts (such as tetraethylammonium 4-toluenesulfonate), when used as a SP in GC, enables the determination of benzene and toluene in gasoline.<sup>36–40</sup> Armstrong *et al.* have shown that SPs based on ILs with a butylmethylimidazolium cation exhibit separation properties that are strongly dependent on the anion.<sup>26,28–30</sup> However, to date, neither SPs based on ILs with a pyridinium cation (*e.g.*, *N*-ethylpyridinium trifluoroacetate) or an imidazolium cation with long alkyl chain (*e.g.*, octylmethylimidazolium bis(trifluoromethylsulfonyl)amide), or SPs that contain both IL and fullerene, have been explored. This is rather unfortunate, considering a recent report which shows that by increasing the length of the alkyl group on the imidazolium to C<sub>8</sub> to increase the hydrophobicity, ILs such as octylmethylimidazolium bis(trifluoromethylsulfonyl)amide can dissolve fullerenes.<sup>41</sup>

The information presented above is indeed indicates that it should be possible to dissolve fullerenes in ILs and to use the C<sub>60</sub>-IL solution as a SP in GC. Such considerations prompted us to initiate this study, which aims to explore these possibilities by initially dissolving fullerene and its derivatives in ILs and coating the GC capillary column with fullerene-IL solutions. Effects of fullerenes on GC separations will be determined by comparing the results obtained with a fullerene-IL column to those found with a column coated with only IL. Additionally, different fullerene derivatives, including hydroxy-C<sub>60</sub> and amino-C<sub>60</sub>, will be used to determine polarity effect of fullerenes on the separation efficiency.

## Experimental

### Chemicals

Octylmethylimidazolium trifluoroacetate or octylmethylimidazolium bis((trifluoromethylsulfonyl)amide) were synthesized from octylmethylimidazolium chloride based on method used in our previous studies.<sup>23,42</sup> Initially, OMIm<sup>+</sup> Cl<sup>-</sup> was prepared by refluxing a 1 : 1 molar ratio mixture of 1-methylimidazole and octyl chloride under nitrogen atmosphere at 60 °C for two days. Initially, there were two layers in the mixture. As the reaction proceeded, it became homogeneous. The product was washed twice with ethyl acetate. The chloride salt was then converted into Tf<sub>2</sub>N<sup>-</sup> salt by metathesis reaction using a procedure reported in our earlier studies.<sup>23</sup> Essentially, 1 : 1 molar amounts of octylmethylimidazolium chloride and LiTf<sub>2</sub>N were separately dissolved in cold water. The solutions was then mixed and stirred for 2 hours at room temperature. As the reaction proceeded, the homogeneous solution separated into two layers with the aqueous layer on top and the [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] layer below. The upper layer was discarded, the IL was further washed with water three times, and dried under vacuum at 60 °C overnight. The ionic liquid [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] obtained was characterized by <sup>1</sup>H NMR and IR.

*N*-Ethylpyridinium trifluoroacetate (EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>) was prepared using a reported procedure.<sup>43</sup> Initially, silver(I) oxide (11.59 g, 0.05 mol) was mixed in 50 mL of distilled water and stirred to make a slurry in a flask covered with aluminium foil to avoid the photo-degradation of the silver(I) oxide.

Trifluoroacetic acid (11.4 g, 0.1 mol) was slowly added to this slurry and the mixture was stirred continuously until the solution became clear (about 2 h). *N*-Ethylpyridinium bromide (18.81 g, 0.1 mol) was then added to the above solution. As reaction took place and ionic liquid formed, silver(I) bromide precipitated as yellow crystals. The mixture was stirred for another five hours. The precipitate of silver(I) bromide was filtered off, and the solvent was removed by rotary evaporation under vacuum at about 65 °C. The resulting ionic liquid was dried under vacuum at 60 °C overnight and characterized using <sup>1</sup>H NMR and IR.

Fullerene (C<sub>60</sub>) (99.5%) and poly(hydroxy)fullerene (C<sub>60</sub>(OH)<sub>n</sub>, where *n* = 24) were purchased from MER Corp., Tucson, AZ, and used as received. Poly(*N*-ethylamino)fullerene (C<sub>60</sub>(NHC<sub>2</sub>H<sub>5</sub>)<sub>n</sub>, where *n* = 18–20) was obtained from Bucky USA (Houston, TX). Fig. 1 shows the structures of fullerenes and ILs used in this work. All other chemicals were obtained from Aldrich Chemicals and used as received.

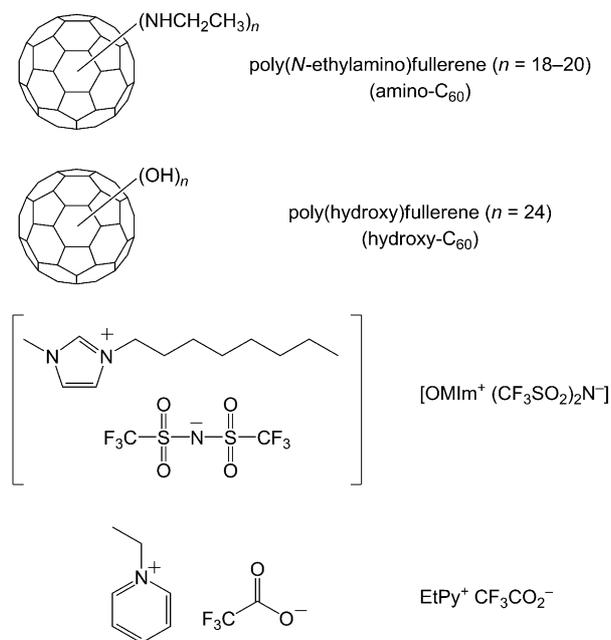


Fig. 1 Structures of fullerenes and ionic liquids used in this study.

### Dissolving C<sub>60</sub> in [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] ionic liquid

C<sub>60</sub> was dissolved in [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] using a reported procedure.<sup>41</sup> Specifically, 2.20 mg of C<sub>60</sub> was added to 11.0 mL of dichloromethane, and the mixture stirred for 12 h in the dark. 0.10 mL of this solution was added to 0.5 mL of [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] ionic liquid. The mixture was stirred for a further 5 h. Subsequently, dichloromethane was removed from the mixture by rotary evaporation. The solution obtained was then centrifuged for 1 h at room temperature at 8000 rpm. The upper part of the centrifuged ionic liquid solution was separated and used to coat the capillary column. A UV-visible absorption spectrum was taken to confirm the presence of C<sub>60</sub> in the ionic liquid solution.<sup>44</sup>

It was found that the hydroxy-C<sub>60</sub> and amino-C<sub>60</sub> are insoluble in [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>]. In fact, they are not soluble in any ILs based on imidazolium ions. They can, however, be dissolved

in EtPy<sup>+</sup> CF<sub>2</sub>COO<sup>-</sup> ionic liquid, and this was therefore carried out using the procedure described above.

### Coating the GC capillary column

25.0 mg of a solution of C<sub>60</sub> (or its hydroxy/amino derivatives) in [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] (or in EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>) ionic liquid prepared using the method described above was dissolved in 10.0 mL of dichloromethane. The solution was then used to coat a silica capillary tubing (10 m long × 0.25 mm ID) (Supelco Corporation) at 40 °C using reported a static coating method.<sup>33</sup> A similar procedure was used to coat another 10 m capillary column with [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] (or EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>) ionic liquid. Coated columns were flushed with dry nitrogen gas for 60 min, and then conditioned in a GC instrument from 30 to 100 °C at 1 °C min<sup>-1</sup> increment overnight.

All separations were carried out, in triplicate, on a Hewlett-Packard model 6890 gas chromatograph with nitrogen as the carrier gas, split injection, and flame ionization detection.

### Results and discussion

Five 10 m columns were coated with either IL alone or IL + fullerenes as the SP. They were [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>], [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] + C<sub>60</sub>, [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>], [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] + amino-C<sub>60</sub> and [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] + hydroxy-C<sub>60</sub>. The thickness of the coating can be calculated using the following equation:<sup>45</sup>

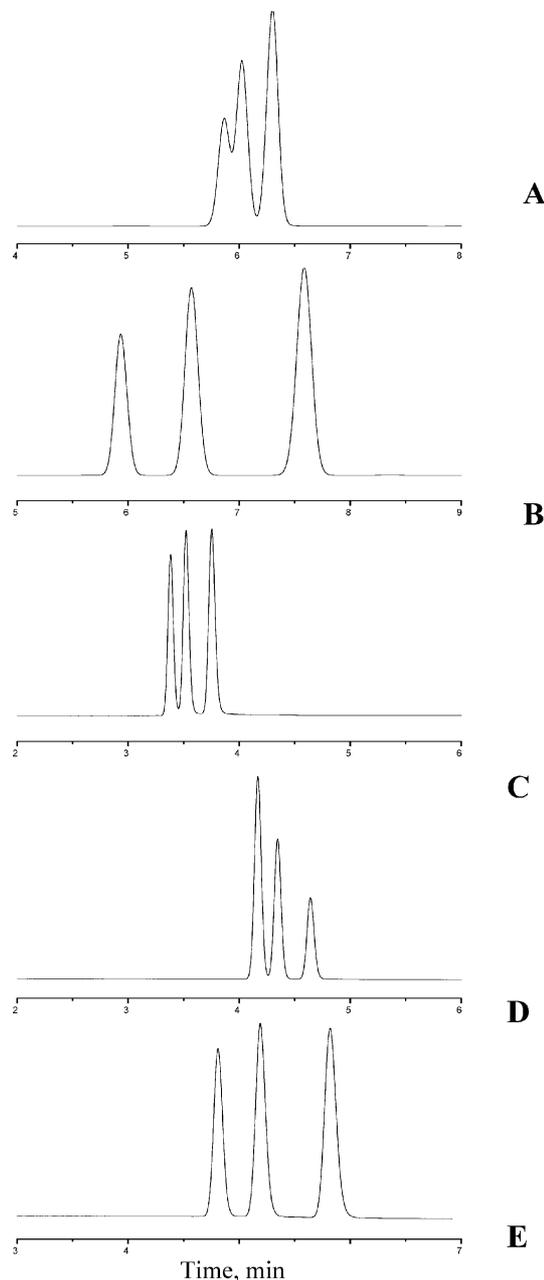
$$d_f = \frac{dc}{400}$$

where  $d_f$  is the film thickness in μm,  $d$  is the ID of the column in μm, and  $c$  is the concentration of IL in the coating solvent (*i.e.*, dichloromethane) in %v/v which in this work, was set at 25 mg of IL in 10 mL of dichloromethane. 25 mg is the total weight of IL or IL + fullerene. Since the solubility of C<sub>60</sub> and its hydroxy and amino derivatives in IL are different (40 μg mL<sup>-1</sup> of C<sub>60</sub> in OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup> and 2.8 mg mL<sup>-1</sup> and 3.8 mg mL<sup>-1</sup>, for hydroxy-C<sub>60</sub> and amino-C<sub>60</sub> in EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup> respectively) the total amounts of fullerene are different for each column (*i.e.*, 0.748 μg of C<sub>60</sub> in the [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] + C<sub>60</sub> column, 53.7 μg of hydroxy-C<sub>60</sub> in the [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] + hydroxy-C<sub>60</sub> column, and 73 μg of amino-C<sub>60</sub> in the [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] + amino-C<sub>60</sub> column).

It was found that all five columns have a similar coating thickness, *i.e.*, 0.116 μm, 0.116 μm, 0.120 μm, 0.120 μm and 0.120 μm for [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>], [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] + C<sub>60</sub>, [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>], [EtPy<sup>+</sup>CF<sub>3</sub>COO<sup>-</sup>] + amino-C<sub>60</sub> and [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] + hydroxy-C<sub>60</sub> column, respectively. Theoretical plate numbers of the columns were determined with naphthalene as solute at 100 °C and calculated using  $W = 5.54(t_R/W_{1/2})^2$ , where  $t_R$  is the retention time of naphthalene and  $W_{1/2}$  is the full-width at half maximum of the naphthalene band. All five columns were found to have efficiencies larger than 20 000 plates. Interestingly, it seems that adding either fullerene or its amino/hydroxy derivatives into the ILs increases the efficiency of the columns. Specifically, efficiencies of columns coated with only ILs ([OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] and [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>]) are 24 000 plates and 21 000 plates, respectively, whereas those coated with IL–fullerene mixtures are 28 000 plates, 35 000 plates and 29 000 plates (for [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] + C<sub>60</sub>, [EtPy<sup>+</sup>

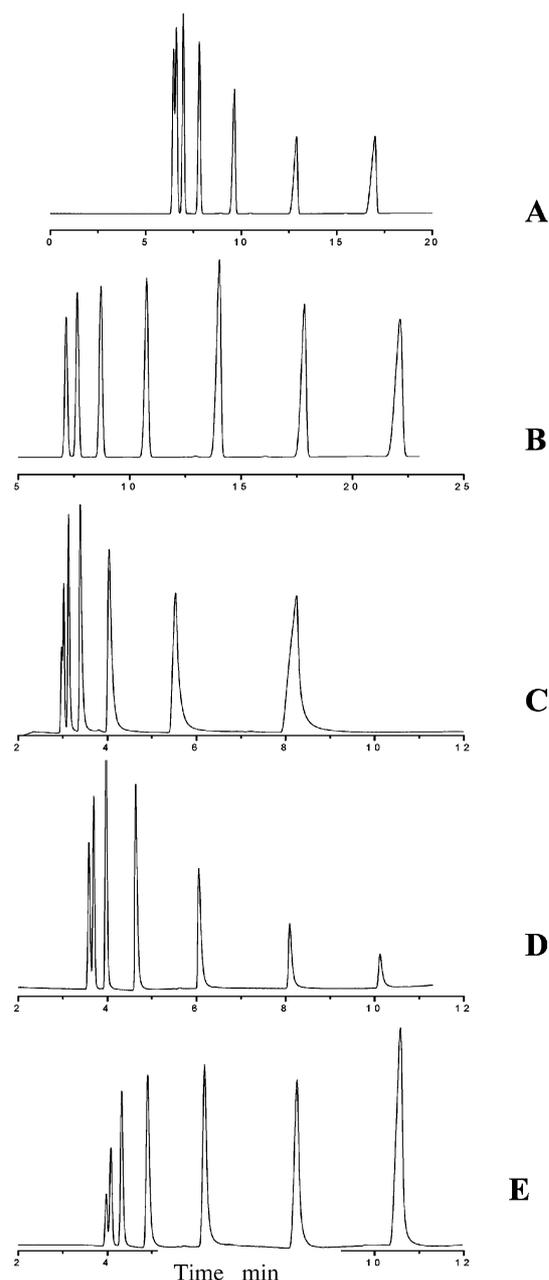
CF<sub>3</sub>COO<sup>-</sup>] + amino-C<sub>60</sub> and [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] + hydroxy-C<sub>60</sub>, respectively). These results clearly indicate that the ILs should serve effectively as SPs in GC, and that adding C<sub>60</sub> or its derivatives to the ILs further increases the efficiency of the SP.

Five different sets of solutes having different properties and polarities were then used to determine properties of these five SPs. They were (1) a mixture of benzene and its derivatives (benzene, toluene and *p*-xylene) (see Fig. 2); (2) a mixture

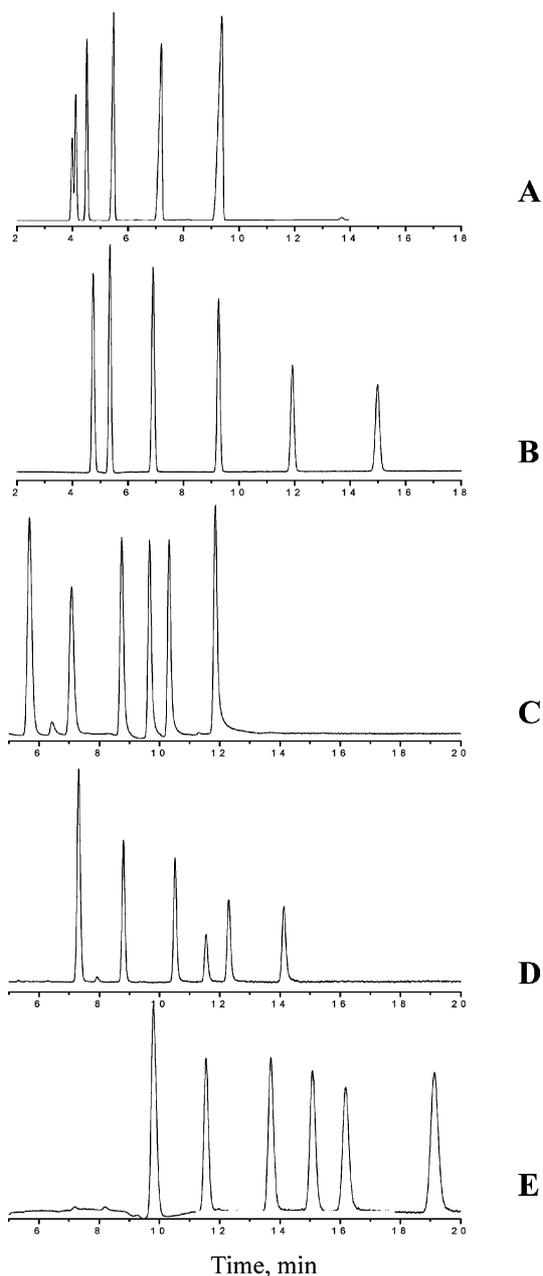


**Fig. 2** GC chromatograms of aromatic mixtures, elution order is as follows: (1) benzene, (2) toluene and (3) *p*-xylene separated on (A) a [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] column; (B) a [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] + C<sub>60</sub> column; (C) a [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] column; (D) a [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] + amino-C<sub>60</sub> column and (E) a [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] + hydroxy-C<sub>60</sub> column. Experimental conditions: 100 °C isotherm for (A) and (B) and 75 °C isotherm for (C)–(E), nitrogen carrier gas, 1.0 mL min<sup>-1</sup> flow rate.

of alkanes (hexane, heptane, octane, nonane, decane, undecane and dodecane) (see Fig. 3); (3) a mixture of n-alcohols (methanol, ethanol, n-propanol, n-butanol, n-pentanol and n-hexanol) (see Fig. 4); (4) a mixture of pentanols (1-pentanol, 2-pentanol, 3-methyl-1-butanol, 2-methyl-2-butanol and 2,2-dimethyl-1-propanol) (see Fig. 5); and (5) a mixture of isomers of xylene (*o*-, *m*- and *p*-xylene) (see Fig. 6).

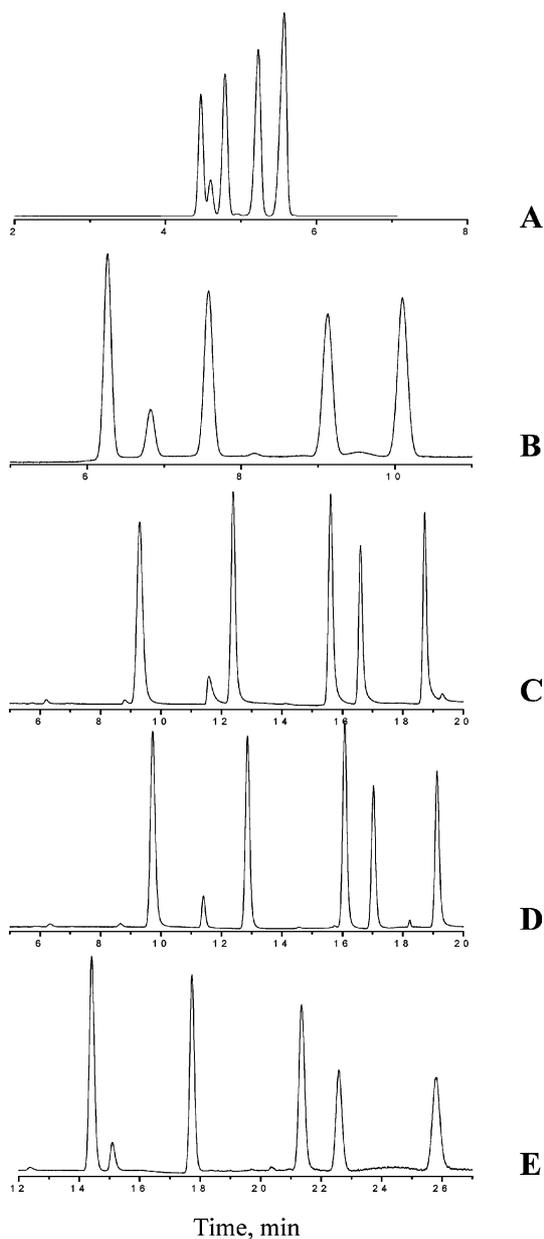


**Fig. 3** GC chromatograms of a mixture of alkanes, elution order is as follows: (1) hexane, (2) heptane, (3) octane, (4) nonane, (5) decane, (6) undecane and (7) dodecane separated on (A) a [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] column; (B) a [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] + C<sub>60</sub> column; (C) a [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] column; (D) a [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] + amino-C<sub>60</sub> column and (E) a [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] + hydroxy-C<sub>60</sub> column. Experimental conditions: gradient elution temperature: 50 °C for 5 min and then at a rate of 10 °C min<sup>-1</sup> to 100 °C for 15 min, nitrogen carrier gas, 1.0 mL min<sup>-1</sup> flow rate.



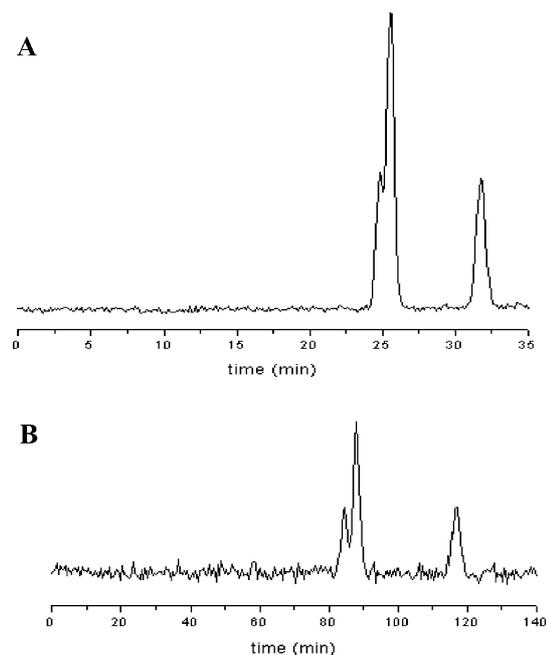
**Fig. 4** Gas chromatograms of a mixture of n-alcohols, elution order is as follows: (1) methanol, (2) ethanol, (3) propanol, (4) butanol, (5) pentanol and (6) hexanol separated on (A) a [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] column; (B) a [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] + C<sub>60</sub> column; (C) a [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] column; (D) a [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] + amino-C<sub>60</sub> column and (E) a [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] + hydroxy-C<sub>60</sub> column. Experimental conditions: gradient elution temperature: (A and B): 70 °C for 5 min and then at a rate of 30 °C min<sup>-1</sup> to 100 °C; (C)–(E): 30 °C for 5 min and then at a rate of 5 °C min<sup>-1</sup> to 100 °C, nitrogen carrier gas, 1.0 mL min<sup>-1</sup> flow rate.

Fig. 2A and 2B are chromatograms of the benzene mixture separated on the [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] and [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] + C<sub>60</sub> columns, respectively (at 100 °C), and Fig. 2C, 2D and 2E are those for the same mixture separated on [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>], [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] + amino-C<sub>60</sub> and [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] + hydroxy-C<sub>60</sub> columns, respectively (at 75 °C). It is interesting to observe that the two ILs used in this



**Fig. 5** GC chromatograms of a mixture of pentanols, elution order is as follows: (1) 2-methyl-2-butanol, (2) 2,2-dimethyl-1-propanol, (3) 2-pentanol, (4) 3-methyl-1-butanol and (5) 1-pentanol separated on (A) a  $[\text{OMIm}^+(\text{CF}_3\text{SO}_2)_2\text{N}^-]$  column; (B) a  $[\text{OMIm}^+(\text{CF}_3\text{SO}_2)_2\text{N}^-] + \text{C}_{60}$  column; (C) a  $[\text{EtPy}^+\text{CF}_3\text{COO}^-]$  column; (D) a  $[\text{EtPy}^+\text{CF}_3\text{COO}^-] + \text{amino-C}_{60}$  column and (E) a  $[\text{EtPy}^+\text{CF}_3\text{COO}^-] + \text{hydroxy-C}_{60}$  column. Experimental conditions: gradient elution temperature: (A) and (B):  $70^\circ\text{C}$  for 5 min and then at a rate of  $4^\circ\text{C min}^{-1}$  to  $100^\circ\text{C}$ ; (C)–(E):  $30^\circ\text{C}$  for 5 min and then at a rate of  $5^\circ\text{C min}^{-1}$  to  $100^\circ\text{C}$ , nitrogen carrier gas,  $1.0\text{ mL min}^{-1}$  flow rate.

study,  $[\text{OMIm}^+(\text{CF}_3\text{SO}_2)_2\text{N}^-]$  and  $[\text{EtPy}^+\text{CF}_3\text{COO}^-]$ , seem to have different chromatographic properties, *viz.*, the former cannot separate the mixture of these three aromatic compounds (Fig. 2A), while the latter not only can baseline-separate them but did so at a lower temperature ( $75^\circ\text{C}$  compared to  $100^\circ\text{C}$ ) (Fig. 2C). Adding either amino- $\text{C}_{60}$  or hydroxy- $\text{C}_{60}$  to  $[\text{EtPy}^+\text{CF}_3\text{COO}^-]$  not only substantially improved the separation efficiency but also shortened the retention times (compare



**Fig. 6** GC chromatograms of mixtures of xylenes, elution order is as follows: (1) *p*-xylene, (2) *m*-xylene and (3) *o*-xylene separated on (A) a  $[\text{OMIm}^+(\text{CF}_3\text{SO}_2)_2\text{N}^-]$  column and (B) a  $[\text{OMIm}^+(\text{CF}_3\text{SO}_2)_2\text{N}^-] + \text{C}_{60}$  column. Experimental conditions:  $30^\circ\text{C}$  isotherm, nitrogen carrier gas,  $0.5\text{ mL min}^{-1}$  flow rate.

Fig. 2D and 2E with Fig. 2C). While the improved efficiency can be visibly observed in the chromatograms, it is more pronounced when they are compared in terms of resolution ( $R_s$  values) as listed in Table 1. The increase in the resolution is larger for the hydroxy- $\text{C}_{60}$  column than for the amino- $\text{C}_{60}$  column ( $R_s$  values of 1.30 and 2.11 for  $[\text{EtPy}^+\text{CF}_3\text{COO}^-]$  were increased by up to 73% and 54% when hydroxy- $\text{C}_{60}$  was added, and only by 9% and 11% when amino- $\text{C}_{60}$  was added). Of particular interest is the effect of  $\text{C}_{60}$ . As stated above, a column coated with only  $[\text{OMIm}^+(\text{CF}_3\text{SO}_2)_2\text{N}^-]$  cannot separate this aromatic mixture. Adding  $\text{C}_{60}$  into the IL not only can baseline-separate this mixture but also substantially improve the resolution, and the increase in the resolution is higher than for hydroxy- $\text{C}_{60}$  and amino- $\text{C}_{60}$  ( $R_s$  values were increased by 250% and 208% when  $\text{C}_{60}$  was added). Additional information can be obtained from retention factors  $k'$ , which are listed in Table 2. The aromatic compounds were retained longer on the  $[\text{OMIm}^+(\text{CF}_3\text{SO}_2)_2\text{N}^-]$  column compared to columns coated with  $[\text{EtPy}^+\text{CF}_3\text{COO}^-]$  with or without either amino- $\text{C}_{60}$  or hydroxy- $\text{C}_{60}$ . As expected, adding  $\text{C}_{60}$  to  $[\text{OMIm}^+(\text{CF}_3\text{SO}_2)_2\text{N}^-]$  results in an increase in retention time for these compounds. For information, standard deviations associated with  $k'$  values are also listed in Table 2. As can be seen, relative errors associated with  $k'$  values are relatively low (ranging from 0.01% to 2%).

Fig. 3 shows chromatograms of a mixture of alkanes. In contrast to the benzene mixture, columns coated with IL alone ( $[\text{OMIm}^+(\text{CF}_3\text{SO}_2)_2\text{N}^-]$  and  $[\text{EtPy}^+\text{CF}_3\text{COO}^-]$ ) can separate some but not all of compounds in this mixture (Fig. 3A and 3C). Adding either hydroxy- $\text{C}_{60}$  or amino- $\text{C}_{60}$  into the  $[\text{EtPy}^+\text{CF}_3\text{COO}^-]$  IL does not seem to provide any improvement in the separation efficiency either (Fig. 3D and 3E). Conversely,

**Table 1** Resolution ( $R_s$ ) values<sup>a</sup> for columns coated with ionic liquids with or without fullerene and its amino and hydroxy derivatives

Compound	OMIm <sup>+</sup> (CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N <sup>-</sup> column	[OMIm <sup>+</sup> (CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N <sup>-</sup> ] + C <sub>60</sub> column	EtPy <sup>+</sup> CF <sub>3</sub> COO <sup>-</sup> column	[EtPy <sup>+</sup> CF <sub>3</sub> COO <sup>-</sup> ] + amino-C <sub>60</sub> column	[EtPy <sup>+</sup> CF <sub>3</sub> COO <sup>-</sup> ] + hydroxy-C <sub>60</sub> column
<b>Mixtures of benzene, toluene and <i>p</i>-xylene</b>					
Benzene and toluene	0.77	2.69	1.30	1.42	2.26
Toluene and <i>p</i> -xylene	1.26	3.88	2.11	2.34	3.25
<b>Mixtures of <i>o</i>-, <i>m</i>-, and <i>p</i>-xylene</b>					
<i>p</i> -Xylene and <i>m</i> -xylene	0.76	0.84	No separation	No separation	No separation
<i>m</i> -Xylene and <i>o</i> -xylene	4.77	6.05	No separation	No separation	No separation
<b>Mixtures of alkanes</b>					
Hexane and heptane	0.77	1.98	0.27	1.19	0.80
Heptane and octane	1.72	4.02	1.56	3.13	1.96
Octane and nonane	4.29	6.79	3.21	6.77	3.82
Nonane and decane	6.94	8.65	4.68	11.63	6.13
Decane and undecane	7.05	8.40	6.62	13.28	8.84
Undecane and dodecane	7.77	8.90	7.03	12.04	7.69
<b>Mixtures of n-alcohols</b>					
Methanol and ethanol	0.75	3.33	4.89	7.37	5.50
Ethanol and propanol	3.05	8.24	6.21	8.04	7.00
Propanol and butanol	6.40	11.45	3.98	5.90	4.65
Butanol and pentanol	8.60	12.22	2.68	3.31	2.88
Pentanol and hexanol	7.39	11.74	6.61	5.36	6.64
<b>Mixtures of pentanols</b>					
2-Methyl-2-butanol and 2,2-dimethyl-1-propanol	1.00	2.73	8.34	10.11	10.4
2,2-Dimethyl-1-propanol and 2-pentanol	1.47	6.51	8.45	11.25	10.76
2-Pentanol and 3-methyl-1-butanol	3.00	6.56	2.96	3.42	3.25
3-Methyl-1-butanol and 1-pentanol	2.04	3.80	6.25	7.74	7.12

<sup>a</sup>  $R_s = 2[(t_R)_B - (t_R)_A]/(W_A + W_B)$ , where  $(t_R)_A$  and  $(t_R)_B$  are the retention times of compound A and B, and  $W_A$  and  $W_B$  are the widths of the corresponding peaks at the baseline.

C<sub>60</sub> seems to have strong and positive effect when added into the IL. As evident from Fig. 2B and Table 1, adding C<sub>60</sub> into the IL not only provides baseline separation for all compounds but also led to substantial improvements in the resolution values. Furthermore, based on the retention factors  $k'$  listed in Table 2, it is interesting to observe that increased retention time does not translate into better separation efficiency. Specifically, alkane cannot all be separated by the [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] column in spite of the fact that their retention times on this column are at least two to three times longer than those on the [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>], [EtPy<sup>+</sup> CF<sub>3</sub>COO] + amino-C<sub>60</sub> and [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] + hydroxy-C<sub>60</sub> columns.

Fig. 4A–E show chromatograms of mixtures of n-alcohols separated on these five columns. Again, columns coated with [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] can separate some but not all compounds in this mixture (Fig. 4A). As expected, more polar columns, *i.e.*, columns coated with either [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] alone or [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] with either amino-C<sub>60</sub> or hydroxy-C<sub>60</sub>, did in fact provide baseline separation of this more polar mixture of alcohols (Fig. 4C, 4D and 4E). Also, the retention factors of these alcohols on these three columns are, as expected, much longer than those on the [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] column (Table 2). Of particular interest is the fact that the [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] + C<sub>60</sub> column can also baseline-separate this alcohol mixture (Fig. 4B). More significant is the fact that the retention factors for this column are comparable with

those for the [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] column, and are generally shorter than those found for the [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>], [EtPy<sup>+</sup> CF<sub>3</sub>COO] + amino-C<sub>60</sub> and [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] + hydroxy-C<sub>60</sub> columns. Carefully inspecting  $R_s$  values listed in Table 1 reveals that adding either hydroxy-C<sub>60</sub> or amino-C<sub>60</sub> to the [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] column increased the resolution, and that the amino-C<sub>60</sub> column provides relatively better resolution than the hydroxy-C<sub>60</sub> column. The C<sub>60</sub> column not only has a smaller retention factors but also provided the highest resolution. This is rather interesting considering the fact that the alcohols in these mixtures are more polar than those in the benzene and alkane mixtures.

Chromatograms of a mixture of pentanols separated on these five columns are shown in Fig. 5A–E. Similar to the case with the n-alcohol mixture (Fig. 4), the [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] column (Fig. 5A) can separate only 3 out of 5 compounds of the mixture while the other four columns baseline-separated all of the compounds (Fig. 5B–E). Also similar to the case of n-alcohols, the retention factors on the [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] + C<sub>60</sub> column are smaller than those for the [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>], [EtPy<sup>+</sup> CF<sub>3</sub>COO] + amino-C<sub>60</sub> and [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] + hydroxy-C<sub>60</sub> columns. However, in this case, both amino-C<sub>60</sub> and hydroxy-C<sub>60</sub> columns provide better resolution than the C<sub>60</sub> column.

Of particular significance are the results on the separation of a mixture of the three isomers of xylene. As shown in Fig. 6A, the [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] column separated *o*-xylene from *p*- and

**Table 2** Retention factors ( $k'$ ),<sup>a</sup> for columns coated with ionic liquids with or without fullerene and its amino and hydroxy derivatives

Compound	[OMIm <sup>+</sup> (CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N <sup>-</sup> ] column	[OMIm <sup>+</sup> (CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N <sup>-</sup> ] + C <sub>60</sub> column	EtPy <sup>+</sup> CF <sub>3</sub> COO <sup>-</sup> column	[EtPy <sup>+</sup> CF <sub>3</sub> COO <sup>-</sup> ] + amino-C <sub>60</sub> column	[EtPy <sup>+</sup> CF <sub>3</sub> COO <sup>-</sup> ] + hydroxy-C <sub>60</sub> column
<b>Benzene, toluene and <i>p</i>-xylene</b>					
Benzene	10.98	11.10	5.8 ± 0.1	7.59 ± 0.08	8.82 ± 0.01
Toluene	11.30	12.40	6.24 ± 0.06	7.89 ± 0.03	9.55 ± 0.08
<i>p</i> -Xylene	11.86	14.47	6.76 ± 0.09	8.49 ± 0.04	10.88 ± 0.01
<b>Alkanes</b>					
Hexane	12.16	13.59	4.94 ± 0.09	6.30 ± 0.06	7.14 ± 0.06
Heptane	12.49	14.60	5.22 ± 0.06	6.5 ± 0.1	7.33 ± 0.03
Octane	13.20	16.78	5.43 ± 0.04	6.9 ± 0.2	7.79 ± 0.03
Nonane	14.94	20.96	5.92 ± 0.07	8.3 ± 0.2	8.9 ± 0.2
Decane	18.67	27.60	7.31 ± 0.06	11.1 ± 0.3	11.60 ± 0.05
Undecane	25.33	35.41	10.27 ± 0.09	15.4 ± 0.2	15.82 ± 0.02
Dodecane	33.59	44.20	15.84 ± 0.04	18.6 ± 0.9	20.41 ± 0.07
<b>n-Alcohols</b>					
Methanol	7.14	8.69	10.60 ± 0.05	13.94 ± 0.06	19.10 ± 0.05
Ethanol	7.40	9.92	13.50 ± 0.08	16.98 ± 0.02	22.5 ± 0.1
Propanol	8.20	12.98	16.8 ± 0.1	20.45 ± 0.06	26.70 ± 0.08
Butanol	10.18	17.88	18.70 ± 0.05	22.59 ± 0.07	29.8 ± 0.1
Pentanol	13.69	23.28	20.20 ± 0.07	24.16 ± 0.05	32.1 ± 0.1
Hexanol	18.14	29.60	23.20 ± 0.07	27.65 ± 0.02	38.0 ± 0.1
<b>Pentanol</b>					
2-Methyl-2-butanol	8.12	11.86	17.49	17.50	28.33
2,2-Dimethyl-1-propanol	8.39	12.98	23.96	24.60	35.24
2-Propanol	8.77	14.50	30.43	31.73	42.45
3-Methyl-1-butanol	9.67	17.67	32.20	33.80	45.10
1-Pentanol	10.37	19.60	36.37	37.92	51.56

$$^a k' = (t_R - t_0)/t_0.$$

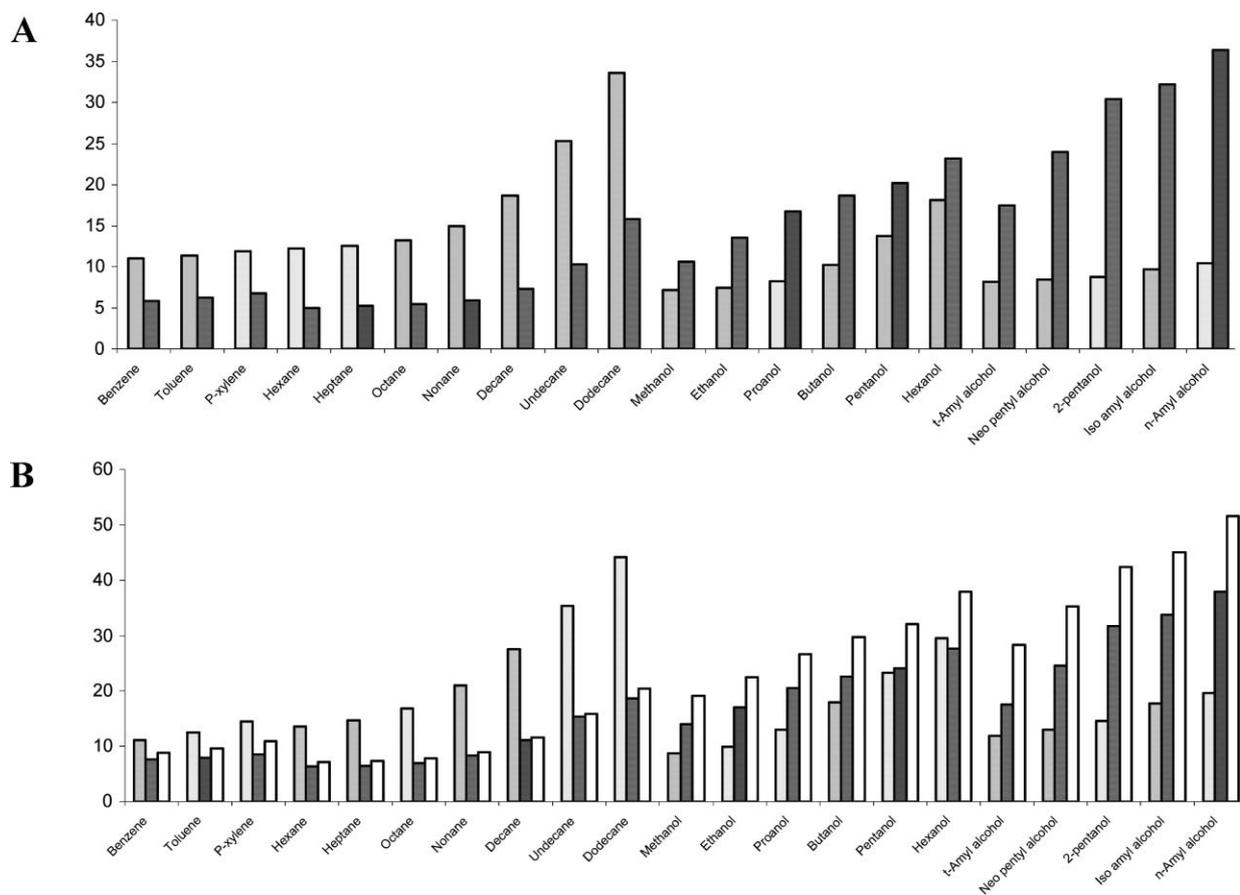
*m*-xylene. However, it cannot separate *p*-xylene from *m*-xylene. Adding C<sub>60</sub> to [OMIm<sup>+</sup> Tf<sub>2</sub>N<sup>-</sup>] led to substantial improvement in the separation efficiency: this [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] + C<sub>60</sub> column (Fig. 6B) not only separated *o*-xylene from *p*- and *m*-xylene, but also *p*-xylene from *m*-xylene (although this was not baseline-separation). As expected, the three more polar columns ([EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>], [EtPy<sup>+</sup> CF<sub>3</sub>COO] + amino-C<sub>60</sub> and [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] + hydroxy-C<sub>60</sub>) cannot separate the three compounds in this mixture.

Careful inspection of the chromatograms reveals that not only do these IL-coated columns provide high separation efficiencies for many different types of polar and non-polar compounds, but that also most of chromatogram peaks exhibited good symmetry. A few peaks were found with asymmetry factor > 1, but only for [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>], [EtPy<sup>+</sup> CF<sub>3</sub>COO] + amino-C<sub>60</sub> and [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] + hydroxy-C<sub>60</sub> columns and also for solutes with relatively long retention times. A variety of reasons may account for this peak-tailing, including the relatively limited solubility of solutes on these stationary phases. Detailed investigations are currently underway in our laboratory to gain insight into this peak-tailing effect.

More insight into the nature of ILs can be gained by examining retention factors. Shown in Fig. 7 are retention factors for columns coated with only ILs ([OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] and [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>]) for compounds in all four groups. Retention factors for non-polar compounds (benzene mixtures and alkane mixtures) are longer on the [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] column

than those on the [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] column. Conversely, the [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] column can retain polar compounds (alcohol mixtures) longer than the [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] column. These results seem to suggest that the [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] SP is more non-polar than the [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] SP. Retention factors for the three columns coated with IL + fullerenes indicate that as SPs, [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] + C<sub>60</sub> is the most non-polar and [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] + hydroxy-C<sub>60</sub> is the most polar. This is hardly surprising considering the fact that not only is the hydroxy group more polar than the secondary amino group, but also that there are more hydroxy groups ( $n = 24$ ) in the hydroxy-C<sub>60</sub> fullerene than amino groups ( $n = 18-20$ ) in the amino-C<sub>60</sub> fullerene.

To determine the effect of fullerenes on the polarity of ILs, we compared the ratios of retention factors for the IL columns with and without fullerenes (Fig. 8A and 8B). Interestingly, as illustrated in Fig. 8A, adding C<sub>60</sub> to the [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] column increases the retention times not only for non-polar compounds (benzenes and alkanes) but also for polar compounds as well. Similar results were also found for the hydroxy-C<sub>60</sub> and amino-C<sub>60</sub> columns: adding fullerene derivatives to the [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] column increases the retention time for non-polar compounds as well as for polar compounds (Fig. 8B). While the effect on the non-polar compounds is similar for amino-C<sub>60</sub> and hydroxy-C<sub>60</sub>, the latter exerts a stronger effect on polar compounds (*i.e.*, larger retention factors).



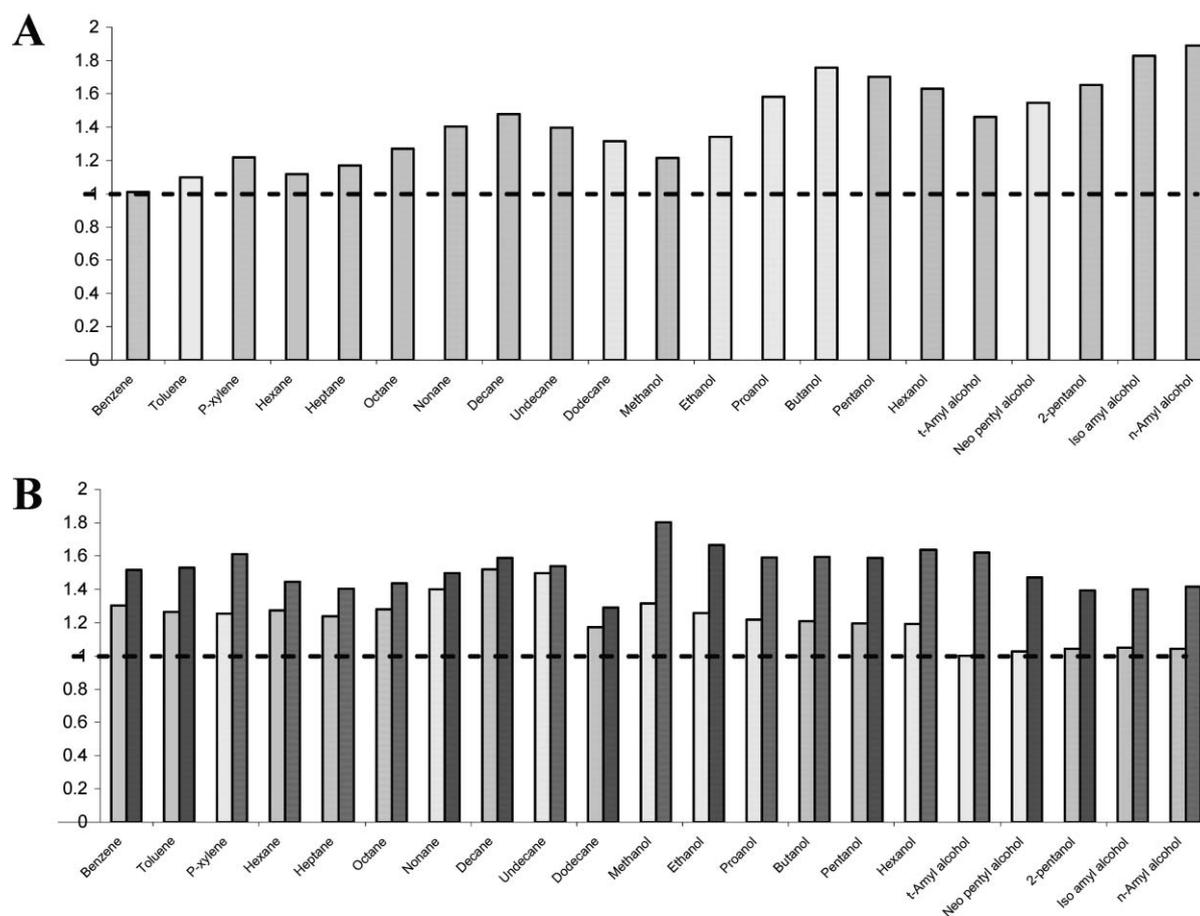
**Fig. 7** Plots of retention factors of (A) a [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] column (pale bars) and a [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] column (dark bars), and (B) a [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] + C<sub>60</sub> column (pale bars), a [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] + amino-C<sub>60</sub> column (dark bars) and a [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] + hydroxy-C<sub>60</sub> column (white bars).

## Conclusion

We have successfully demonstrated for the first time that fullerenes can be successfully used as a stationary phase (SP) in GC by use of ILs as solvents. While the ILs dissolve the fullerenes and facilitate coating of fullerenes onto GC columns, they also act synergistically with fullerenes to provide stationary phases with unique properties. Namely, the ILs exhibit a dual nature when used as SPs, acting as non-polar SPs when separating non-polar analytes, and as polar SPs when separating polar analytes. Because this dual nature was retained when the IL was changed from [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] to [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>], it seems that it is this behaviour that is general. Since [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] is more non-polar than [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] for non-polar analytes and [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>] is more polar than [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] for polar analytes, it is possible to change the polarities of the non-polar and polar SPs by making appropriate changes in the type of IL (or just their cation/anion). However, the polarity of IL stationary phases can also be modified by adding C<sub>60</sub> (or its amino/hydroxy derivatives) to the ILs. More importantly, it is noteworthy that adding either C<sub>60</sub> or its derivatives to the ILs not only produces a change in the polarity of the SP but also substantially improves separation efficiencies, for both non-polar analytes and polar analytes. In fact, C<sub>60</sub> SP provides higher efficiencies than amino-C<sub>60</sub> and

hydroxy-C<sub>60</sub> for separation of polar analytes. This is rather surprising considering the fact that not only are amino-C<sub>60</sub> and hydroxy-C<sub>60</sub> both more polar than C<sub>60</sub>, but that the IL used to coat the amino- and hydroxy-C<sub>60</sub> (*i.e.*, [EtPy<sup>+</sup> CF<sub>3</sub>COO<sup>-</sup>]) is more polar than the IL used to coat the C<sub>60</sub> (*i.e.*, [OMIm<sup>+</sup> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>]). Moreover, compared to its amino and hydroxy derivatives, the concentration of C<sub>60</sub> in the column was 10 times lower.

It is important to add that not only have we successfully developed a novel method to use C<sub>60</sub> and its derivatives as a SP in GC, but that we have also demonstrated, for the first time, that C<sub>60</sub> and its derivatives, when used as SPs, can substantially increase the separation efficiency. As described in the Introduction, previous use of fullerenes (in HPLC rather than GC) required elaborate synthetic steps to covalently bond C<sub>60</sub> to the silica SP, and increased the retention time only for PAHs, which have a somewhat similar structure; moreover, no effect on the separation efficiency was observed.<sup>6-12</sup> A variety of reasons may account for the substantially higher separation efficiencies observed here, including the fact that in this study, C<sub>60</sub> molecules retain their original structure (and hence can exert a strong and cohesive effect), whereas in earlier HPLC studies, the structure of C<sub>60</sub> was modified. The higher separation efficiencies of GC compared to HPLC may also contribute to the enhanced efficiency observed here.



**Fig. 8** (A) Ratios of the retention factors of the  $[\text{OMIm}^+ (\text{CF}_3\text{SO}_2)_2\text{N}^-] + \text{C}_{60}$  column over the  $[\text{OMIm}^+ (\text{CF}_3\text{SO}_2)_2\text{N}^-]$  column. (B) Ratios of the retention factors of the  $[\text{EtPy}^+ \text{CF}_3\text{COO}^-] + \text{amino-C}_{60}$  column over the  $[\text{EtPy}^+ \text{CF}_3\text{COO}^-]$  column (pale bars), and the  $[\text{EtPy}^+ \text{CF}_3\text{COO}^-] + \text{hydroxy-C}_{60}$  column over the  $[\text{EtPy}^+ \text{CF}_3\text{COO}^-]$  column (dark bars).

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