Journal of Chromatography A, 1218 (2011) 4552–4558

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

The use of silica nanoparticles for gas chromatographic separation

Na Na[a], Xianglan Cui[a], Thomas De Beer[b], Tingting Liu[a], Tingting Tang[a], Muhammad Sajid[a], Jin Ouyang[a,*]

[a] College of Chemistry, Beijing Normal University, 100875 Beijing, China
[b] Department of Pharmaceutical Analysis, Faculty of Pharmaceutical Sciences, Ghent University, Harelbekestraat 72, B-9000 Ghent, Belgium

ARTICLE INFO

Article history:
Received 19 November 2010
Received in revised form 6 May 2011
Accepted 11 May 2011
Available online 18 May 2011

Keywords:
Silica nanoparticles
Ionic liquid
Stationary phase
Gas chromatography
Silica networks

ABSTRACT

A new IL-dispersed silica nanoparticles (IL-SNs) capillary column, combining properties of silica nanoparticles and ionic liquid (IL), was used for gas chromatographic separation. By dispersing silica nanoparticles in a conventional IL of 1-butyl-3-methylimidazolium hexafluorophosphate ([BuMIm][BF6]), a layer of homogeneous interconnected particulate silica networks (thickness: 0.4–0.6 μm) was formed on the inner surface of a capillary column. This coating integrates advantages of silica nanoparticles (high surface area, high dispersed behaviour) and IL (extended liquid-state temperature range, chemical stability), hence increasing interactions between stationary phase and analytes. It was demonstrated that mixtures of a wide range of organic compounds including alcohols, esters, alkanes, aromatic compounds, as well as isomers and non-polar compounds can be well separated using an IL-SNs capillary column. Comparing to traditional support coated open tubular columns, the IL-SNs capillary column displays retention behaviors of separating both polar and non-polar compounds. The much thinner coating film of IL-SNs capillary column, compared to the coating film of SNs capillary column, decreases the resistance to mass transfer, resulting a good column efficiency of 3030 theoretical plates per meter for n-butanol (which is about 5 times higher than for the SNs capillary column). Furthermore, the IL-SNs capillary column decreases the IL retention selectivity dominated by IL structures, and has a higher coating value than neat IL stationary phase. Moreover, the preparation is simple as no modification of ILs or adoption of additional reagents is needed in pretreatments. This manuscript is the first report on the use of silica nanoparticles for gas chromatography, which would expand the applicability of silica nanoparticles in analytical chemistry.
© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Silicon-based amorphous nanoparticles have a high surface area and a high dispersion behaviour, making them potential sorption reagents [1], substrates [2], carrier systems [3], and large surface area of catalysts [4]. Different types of silicon-based materials have been used for a long time as solid support or stationary bed in chromatographic separations, such as silica gel, celite or silicate bead [5,6]. It has been demonstrated that materials with large surface area, small and uniform size and chemical inertness afford better separation performance, due to the capability of decreasing the Eddy diffusion and the resistance to mass transfer. These advantages provided opportunities of using nanoparticles for chromatographic applications [7–11]. For example, single-walled carbon nanotubes (SWCNTs) with high surface area were reported as a stationary phase for GC [10]. Silica nanoparticles with high surface area and good adsorption ability might make it possible to develop a new stationary phase for chromatographic separations. Moreover, the preparation of support coated open tubular columns (SCOT) using silica nanoparticles is recommended. This could avoid high costs and non-uniform packing generated by the use of nanoparticles for fabricating packed columns. However, it is not easy to develop uniform stationary phases for SCOT using small sized particles. Therefore, more studies on the preparation of new capillary columns using silica nanoparticles are needed to obtain the good separation abilities.

The remarkable properties of the ionic liquid (IL), such as the extended liquid-state temperature range, the negligible vapour pressure, the thermal and chemical stability, and the easily tunable physical and chemical properties [12], have strongly increased applications of ILs in academia and industry [13,14]. The interest of using ILs as stationary phase in gas chromatography (GC) has increased. This kind of IL stationary phase exhibits dual nature retention behaviors of separating both polar and non-polar compounds [13,15]. To overcome shortcomings of common ILs used for GC stationary phases, such as poor film-forming, low thermal stability, unsatisfactory liquid ranges, excessive retention properties for some analytes, and poor peak symmetries [16], special ILs were prepared by polymerization or functionalization in the capillary column [16–20]. However, the impurities of these ILs

* Corresponding author. Tel.: +86 10 58805373; fax: +86 10 62799838.
E-mail address: jinoyang@bnu.edu.cn (J. Ouyang).

0021-9673/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2011.05.043

seriously influenced the separation efficiency, and the retention was selectively dominated by the size of alkyl chains, cation or anion. Furthermore, silane-coupling, acylation reagents or molten salts were used in pretreatment steps to maintain the coating value of the IL in the open-tubular columns [15]. Recently, the first commercially available IL columns were made by Supelco [21,22]. These columns were prepared by the modification of IL components, such as the cation, linkage and anion [23]. In addition, cyclodextrins in IL can also act as chiral stationary phase for GC [24]. However, further studies on IL-based capillary columns are encouraged to obtain good coating values with simple preparation procedures. Hence, common IL applicability in separating various compounds would be enlarged.

Some functional materials have been produced combining characteristics of IL and nanoparticles [25–27], such as IL templated mesoporous silica [28] and the room-temperature-conducting solid microsilica spheres dispersed by IL [29,30]. Nano-composite ion gels were formed based on the interconnected particulate silica networks generated from the interaction between silica nanoparticles and IL [31]. The gel can modify phase transitions, while still allowing some molecular mobility [32]. These developments provide good opportunities to develop high performance separation techniques, utilizing nanoscale interactions of silica nanoparticles dispersed by IL. Because of their high surface area, high dispersed behaviors, and nanoscale interactions, silica nanoparticles could be used as stationary phases for GC. Forming silica networks by the dispersion of silica nanoparticles in ILs, a new stationary phase possessing high separation efficiency and high stability would be prepared. To our best knowledge, no research on the applicability of silica nanoparticles for high-resolution capillary GC separation has been reported.

In this study, a new IL-SNs capillary column was developed for GC. A homogeneous layer of interconnected particulate silica networks was formed on the inner surface of a capillary column (10.0 m × 0.25 mm), which sought to establish the synergy of silica nanoparticles with a common IL. This coating layer had a thickness of 0.4–0.6 μm and integrated the advantages of IL and silica nanoparticles, hence increasing the interaction between stationary phase and analytes. Good separation performances for different kinds of compounds were obtained. This has been further confirmed by comparing to a silica nanoparticles (SNs) capillary column, an IL capillary column, and an IL-dispersed SWCNTs (IL-SWCNTs) capillary column. The proposed stationary phase is simply fabricated using silica nanoparticles and a common IL, which offers a high separation efficiency for both polar and nonpolar compounds. The present work affords a new application of silica nanoparticles for chromatographic separation.

2. Experimental

2.1. Materials

Silica nanoparticles (HTSi-01, >99%) were obtained from Nanjing High Technology Nano Material Co. (Nanjing, China). The diameter of the silica nanoparticles was about 20 nm, and the specific surface area was larger than 600 m^2/g. The single-walled carbon nanotubes (SWCNTs, >60%) were supplied by Shenzhen Nanotech Port Co. Ltd. (Shenzhen, P.R. China). The outer diameter of the SWCNTs was lower than 2 nm, with a length of 5–15 μm. The specific surface area of the SWCNTs was about 500 m^2/g. The IL of 1-butyl-3-methylimidazolium hexafluorophosphate ([BuMIm][BF_6], >98%) was purchased from Alfa Aesar (Ward Hill, MA).

In the present study, all reagents were of analytical reagent grade. Dimethylformamide (DMF), sodium hydroxide, hydrochloric acid, methanol, ethanol, n-propanol, isopropanol, n-butanol, n-pentanol, n-hexanol, acetone, butanone, hexane, cyclohexane, dichloromethane, trichloromethane, benzene, toluene, *m*-xylene, *o*-xylene, phenol, naphthalene, α-naphthol, β-naphthol, ethyl acetate, butyl acetate, butyl propionate, isoamyl acetate, dichloromethane and trichloromethane were obtained from Beijing Reagents Co. (Beijing, China). Water was deionized and further purified using a Milli-Q water purification system (Millipore, Milford, MA). Nitrogen (99.99%) was supplied by Huayuan Gas (Beijing, China).

All untreated fused silica capillary tubing (0.25 mm i.d. × 0.37 mm o.d.) with a polyimide outer coating was obtained from Yongnian Optical Fiber Factory (Hebei Province, China).

2.2. Pretreatment of capillary

The untreated fused silica capillary was filled with 1.0 M sodium hydroxide and heated at 100 °C for 6 h. Then, the capillary was washed successively with 0.1 M hydrochloric acid for 15 min, water for 50 min, methanol for 30 min, and purged with dry nitrogen for 30 min.

2.3. Silica nanoparticles capillary column

The coating solution of the silica nanoparticles (SNs) capillary column was prepared by dispersing 50 mg of silica nanoparticles in 5.0 mL of ethanol, followed by ultrasonication for 5 min. The fused-silica capillary tubing, 0.25 mm i.d. with a 10 m length, was coated with the dispersed silica nanoparticles solution by a static method. The prepared silica nanoparticles solution of ethanol was injected into the capillary column, after which the capillary was sealed at both ends and heated at 120 °C for 12 h. The heated capillary was washed for 30 min with DMF, for 30 min with ethanol, and then purged with dry nitrogen for 15 min. Finally, the obtained uniform column was conditioned from 30 to 160 °C with increments of 20 °C, kept at each temperature for 2 h, and finally kept at 160 °C for 6 h.

2.4. IL capillary column

The static coating method was also applied for the preparation of a 10 m IL capillary column (0.25 mm i.d.). The capillary was filled with a [BuMIm][BF_6] IL solution of 0.45% (w/v) in dichloromethane at 35 °C. Then, one end of the capillary was sealed, while the other end was connected to a vacuum system for slow volatilization of the solvent, at a temperature of 10–15 °C lower than the boiling point of the solvent. Afterwards, the IL-coated capillary was flushed with nitrogen for 60 min. Finally, the capillary was conditioned from 30 to 120 °C with increments of 20 °C, kept at each temperature for 2 h, and finally kept at 120 °C for 6 h.

2.5. IL-dispersed silica nanoparticles capillary column

The IL-dispersed silica nanoparticles (IL-SNs) capillary column was also prepared using the static coating method. The prepared silica nanoparticles capillary column was filled with a [BuMIm][BF_6] IL solution of 0.45% (w/v) in dichloromethane at 35 °C. Then, the capillary was flushed with nitrogen for 60 min, and finally conditioned using the same procedure as for the IL capillary column.

2.6. IL-dispersed SWCNTs capillary column

The IL-dispersed SWCNTs (IL-SWCNTs) capillary column was prepared by the static coating method. First, the SWCNTs were pretreated to obtain SWCNTs-COCl, followed by the dispersion in DMF [10]. Secondly, the SWCNTs-COCl solution of DMF was injected into the capillary column, after which the capillary column was sealed at both ends and heated at 95 °C for 96 h. Then the capillary

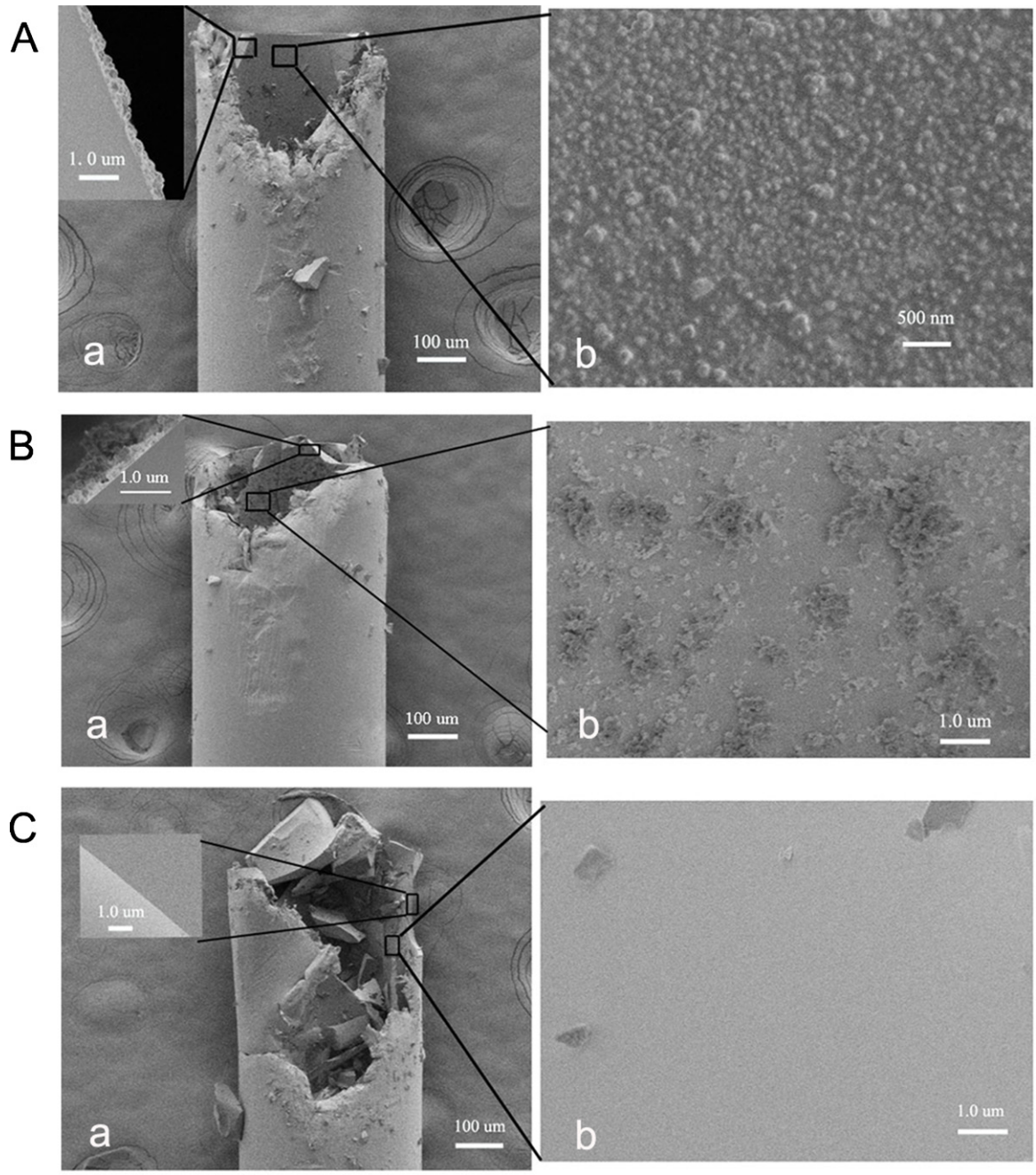

Fig. 1. SEM images of IL-SNs (A), SNs (B) and IL (C) capillary columns. (a) The overview and cross section of the cut capillary columns (the insert). (b) The coated inner surface of the capillary columns.

was washed for 2 h with DMF, for 1.5 h with methanol, for 1.5 h with dichloromethane, and purged with dry nitrogen for 15 min. The produced SWCNTs capillary column was then filled with a [BuMIm][BF_6] IL solution of 0.45% (w/v) in dichloromethane at 35 °C. Finally, the capillary was flushed with nitrogen for 60 min and the obtained capillary was conditioned using the same procedure as for the IL capillary column.

2.7. Equipments

A CP-3800 GC (Varian, Walton-on Thames, UK) fitted with a splitter injection port, and a flame ionization detector with Star Chromatography Workstation Ver6.0 (Varian, Walton-on Thames, UK) was used for all GC analyses. The injector was kept at 200 °C, and the carrier gas was nitrogen with a linear velocity of 35–70 cm/s. The injection split was 50:1. The scanning electron microscope (SEM) images were obtained by a HITACHI S4800-II FESEM (Blackwood, NJ USA).

3. Results and discussion

3.1. Characterization of the capillary columns

Visual inspection showed that the IL-SNs and SNs capillary columns were much lighter in color than the IL one. The scanning electron microscopy (SEM) images of the cross sections and the coated films on the inner surface of the IL-SNs capillary column, the SNs capillary column, and the IL capillary column are shown in Fig. 1. The capillary columns were cut to evaluate the inner surfaces and the inner films. From the SEM images, a coating with thickness

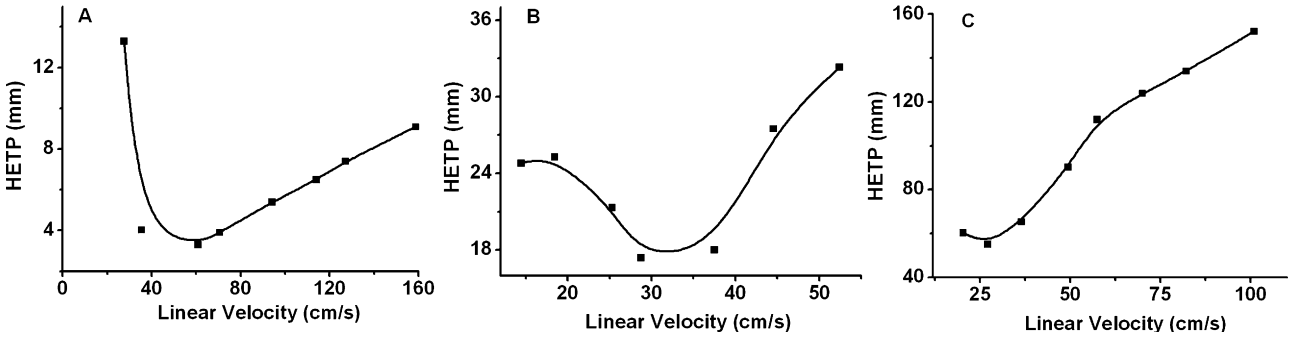

Fig. 2. Van Deemter plots of the capillary columns. (A) IL-SNs capillary column; (B) SNs capillary column; (C) IL capillary column.

of approximately 0.4–0.6 μm was observed on the inner surface of the IL-SNs capillary column (Fig. 1A-a). The microstructure of this nanoparticles coating was uniform, which confirmed the formation of interconnected particulate silica networks (Fig. 1A-b). As demonstrated, the present IL-SNs film thickness was close to the 0.4 μm film of the metal-organic framework MIL-101 coated column [11], but thicker than the coating of gold nanoparticles GC stationary phase (10–75 μm) [7,9,33]. Without IL, the coating film of silica nanoparticles was non-uniform and much thicker (0.9–2.0 μm), and some nanoparticles aggregation was observed for the SNs capillary column (Fig. 1B). No remarkable film was observed for the IL capillary column (Fig. 1C). Thus, the different microstructures were observed on the inner surface of different capillary columns, which might lead to different separation performances.

The chromatographic characteristics of the IL-SNs, SNs and IL capillary columns (10.0 m × 0.25 mm) are shown in Table 1. It was demonstrated that the IL-SNs capillary column possessed the highest column efficiency compared to the other two capillary columns. In addition, Van Deemter plots of the three capillary columns were determined (Fig. 2). As indicated, the IL-SNs capillary column gave a good HETP change with increasing flow rate. The optimal linear velocity order was ranked as: IL-SNs capillary column > SNs capillary column > IL capillary column. Therefore, the IL-SNs capillary column afforded the better separation ability compared to the other two columns.

3.2. Separation of alcohols and esters

In order to evaluate the separation performance of the IL-SNs capillary column, a comparison to the other two capillary columns was carried out. Mixtures of a wide range of organic compounds were separated, including alcohols, esters, alkanes, and some aromatic compounds. The same column temperature and linear velocity of carried gas were used.

For polar functional compounds, a mixture of five alcohols, including ethanol, n-propanol, n-butanol, n-pentanol and n-hexanol, was separated using the three capillary columns. As shown in Fig. 3A-a, separated by the IL-SNs capillary column, the baseline separation for all compounds was achieved within 10 min. However, only four peaks were recorded by the SNs capillary column. The first three peaks were converged into a huge one, making the second and the third peaks shoulder peaks of the first one (Fig. 3A-b). Although five peaks were recorded by the IL capillary column, there was still no baseline separation for any adjacent compounds (Fig. 3A-c). Thus, the IL-SNs capillary column can be well used for the separation of alcohols.

Another mixture of four esters (ethyl acetate, butyl acetate, butyl propionate and isoamyl acetate), whose polarities were lower than alcohols, was separated. As indicated in Fig. 3B, all esters were completely separated within 3 min by the IL-SNs capillary column (Fig. 3B-a). However, peak tailing was recorded when using the SNs capillary column, whose retention time was longer than 30 min (Fig. 3B-b). Although the separation can be finished in 8 min by the IL capillary column, the peaks were broad and not completely separated (Fig. 3B-c). This proves the better separation performance of the IL-SNs capillary column for esters.

3.3. Separation of aromatic compounds

Both volatile and non-volatile aromatic compounds were analyzed using the three capillary columns. As shown in Fig. 4A, four volatile aromatic compounds, benzene, toluene, *o*-xylene and *m*-xylene, were well separated in 5 min by the IL-SNs capillary column, showing narrow and symmetrical peaks. A good relative retention

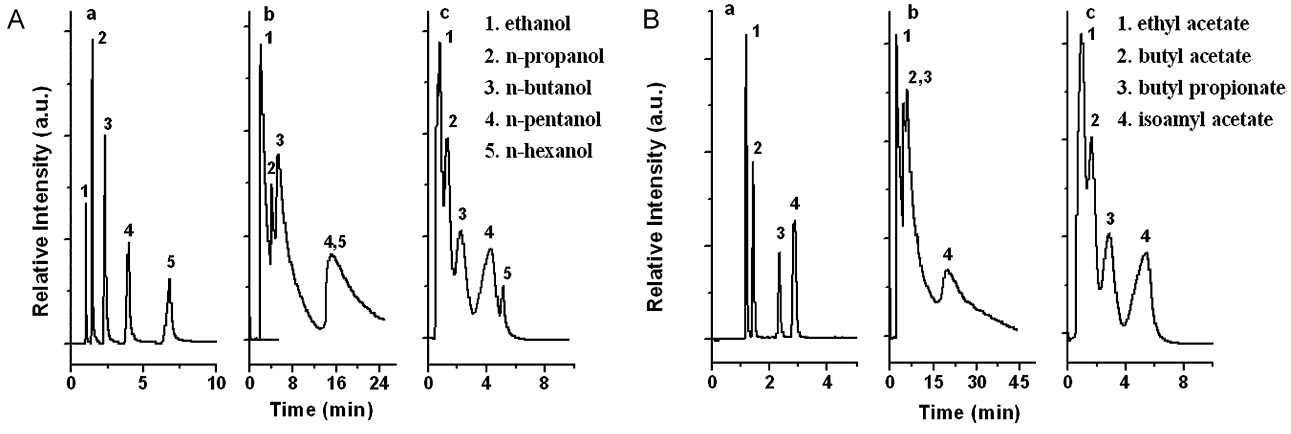

Fig. 3. Chromatograms of mixtures of alcohols (A) and esters (B) by three capillary columns. (a) IL-SNs capillary column, (b) SNs capillary column, (c) IL capillary column. Column temperature was 50 °C.

Table 1
Characteristics for three capillary columns in GC.

Column	Column dimension (m × mm)	Capacity factor (k')	Opt linear velocity (cm/s)	Column efficiency (plates/m)	Compound tested
IL-SNs	10.0 × 0.25	7.999	60.83	3030	n-Butanol
Silica	10.0 × 0.25	16.19	28.74	588	n-Butanol
IL	10.0 × 0.25	3.327	27.14	666	n-Butanol

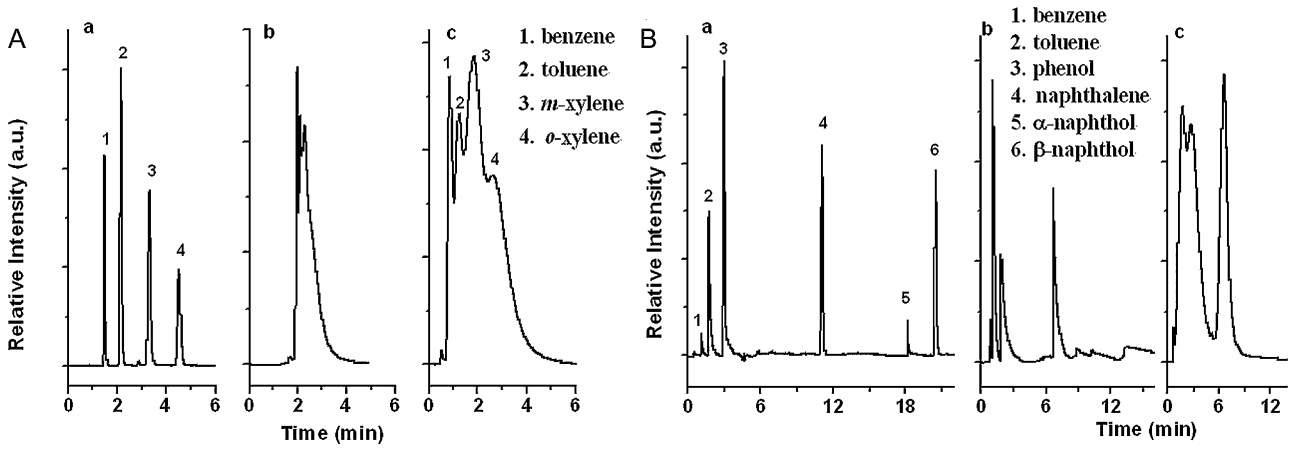

Fig. 4. Chromatograms of mixtures of volatile (A) and non-volatile (B) aromatic compounds by three capillary columns. (a) IL-SNs capillary column, (b) SNs capillary column, (c) IL capillary column. Column temperature was 50 °C for (A), and 50 °C (5 min)–100 °C (20 min) for (B).

value (α) for all two adjacent peaks was obtained. For example, α was 1.571 for toluene (Peak 2) and *m*-xylene (Peak 3). Even for the isomers of *m*-xylene (Peak 3) and *o*-xylene (Peak 4), α was 1.378. These four compounds were not separated when using the SNs and IL capillary columns, where broad peaks were observed (Fig. 4A-b and c).

The separation of a mixture of volatile and non-volatile aromatic compounds, including benzene, toluene, phenol, naphthalene, α-naphthol (p.b. 280 °C) and β-naphthol (p.b. 285 °C), was employed. Here, the initial oven temperature was set at 50 °C for 5 min, then increased to 100 °C and held for 20 min. Using the IL-SNs capillary column (Fig. 4B-a), the six compounds were well separated. The peaks were divided into three groups according to the boiling points: benzene, toluene and phenol (Peak 1–3) were the first group, naphthalene (Peak 4) was the second one, and the isomers of α-naphthol and β-naphthol (Peak 5 and 6) were the third one. However, as shown in Fig. 4B-b and c, the good separation efficiency was not obtained when using the other two capillary columns. In addition, demonstrated from the separation of naphthalene (p.b. 218 °C) and phenol (p.b. 182 °C), the thermal stability issues were still well separated at 200 °C using the IL-SNs capillary column. Therefore, the IL-SNs capillary column is effective for the separation of aromatic compounds.

3.4. Separation of isomers and nonpolar compounds

The IL-SNs capillary column can also be used for the separation of isomers and non-polar compounds. Using the IL-SNs capillary column, the isomers of n-propanol and isopropanol were baseline separated in 3 min. Both peaks were narrow and symmetrical possessing an α value of 1.384 (Fig. 5A-a). However, only one peak was obtained for the two isomers when using the SNs and IL capillary columns (Fig. 5A-b and c). Although boiling points of benzene and cyclohexane are close (benzene is 80.1 °C and 80.7 °C for cyclohexane), the baseline separation was still achieved by the IL-SNs capillary column. Here, an α value of 2.090 was obtained (Fig. 5B-a). These two non-polar compounds were not separated when using the SNs and IL capillary columns (Fig. 5B-b and c). Furthermore,

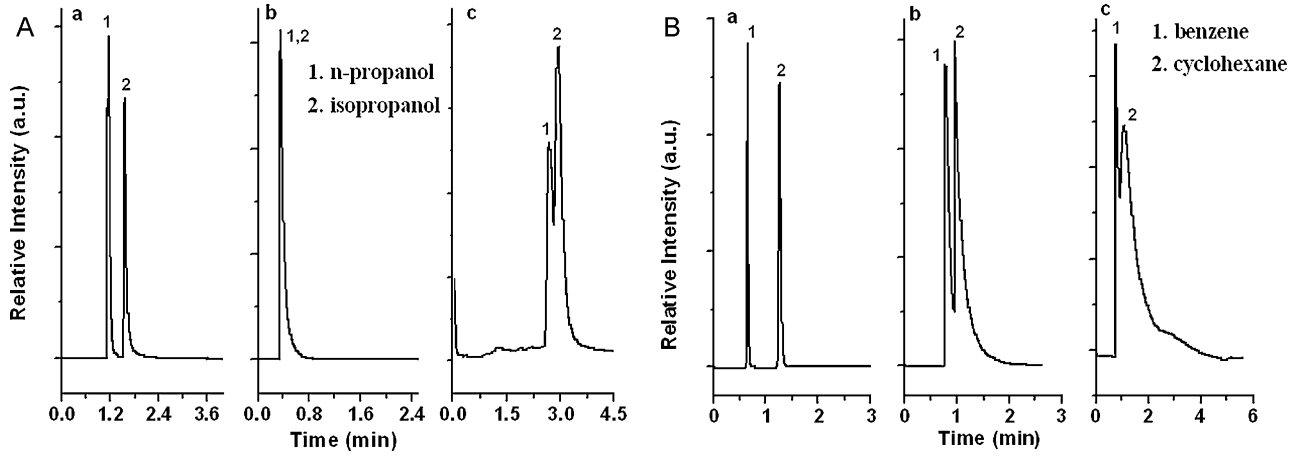

Fig. 5. Chromatograms of mixtures of n-propanol and isopropanol (A), benzene and cyclohexane (B). (a) IL-SNs capillary column, (b) SNs capillary column, (c) IL capillary column. Column temperature was 50 °C.

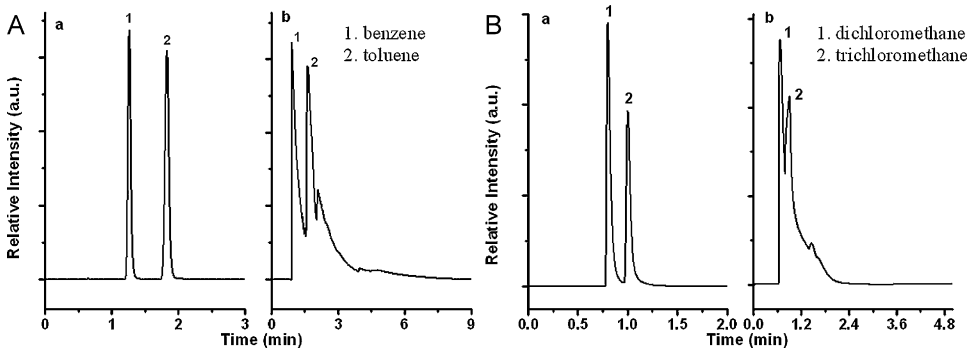

Fig. 6. Chromatograms of mixtures of benzene and toluene (A), dichloromethane and trichloromethane (B). (a) IL-SNs capillary column, (b) IL-SWCNTs capillary column. Column temperature was 50 °C.

no research results on the separation of these mixtures by the IL stationary phase have been reported so far. Thus, the IL-SNs capillary column can be used for the separation of both polar and non-polar compounds, even for isomers and components having similar boiling points.

3.5. Possible separating mechanism of IL-SNs capillary column

The good separation behaviour of the IL-SNs capillary column might be generated from the silica nanoparticles' high special surface area, their high dispersed behaviour [1], and their well synergistic effect with the chemical stable IL [13]. Here, the silica nanoparticles act as the support [2] for the potential liquid phase of IL [17]. Thus, a thin and homogeneous layer of silica nanoparticles supported IL is obtained on the inner surface of the capillary column, forming interconnected particulate silica networks [31,32]. Hence, the interaction between the stationary phase and the analytes is increased, resulting a higher separation efficiency.

To confirm that the high special surface area of silica nanoparticles was important for the separation, a comparison between two capillary columns prepared using two types of nanoparticles with different special surface areas was made. SWCNTs, with a special surface area of 500 m^2/g, were dispersed into ILs to fabricate an IL-SWCNTs capillary column [10]. Then a comparison was done versus the IL-SNs capillary column (the special surface area of silica nanoparticles was higher than 600 m^2/g). Two mixtures (benzene and toluene, dichloromethane and trichloromethane) were separated using the two capillary columns, respectively. As shown in Fig. 6, a better separation efficiency was obtained for both mixtures when using the IL-SNs capillary column. However, the mixtures were not separated by the IL-SWCNTs capillary column fabricated using the same coating procedure as for the IL-SNs column. To further study the effect of high surface area of silica nanoparticles for IL-SNs capillary column, loading capacity of three capillary columns was studied [34,35]. The loading capacity of these columns was ranked as: SNs capillary column > IL-SNs capillary column > IL capillary column (7.7:1.8:1.0). In addition, taking the detection of toluene for example, the linear range of the IL-SNs capillary column was 0.07–1.38 μg in comparison with the linear range of the IL column (0.07–0.28 μg). Thus, silica nanoparticles with high special surface area are suitable for GC separation.

Furthermore, IL can improve the microstructures of the silica nanoparticles coated capillary coating film. As shown in Fig. 1, a thin and homogeneous 0.4–0.6 μm thickness of IL-SNs layer was generated when dispersing nanoparticles in ILs (Fig. 1A). However, aggregation of silica nanoparticles was observed without ILs, giving a heterogeneous layer of silica nanoparticles (Fig. 1B). Thus, by the support of silica nanoparticles with high special surface area and a good dispersed behaviour, ILs can be well coated on the inner surface of the capillary column, forming a thin and homogenous layer of IL-SNs. This plays an important role in the separation process by enhancing the interaction between analytes and stationary phase, which has been proved by the good separation behaviors of the IL-SNs capillary column.

4. Conclusion

In conclusion, the synergy of silica nanoparticles with IL is sought to be developed in the form of a new IL-SNs capillary column for GC separation. The advantages of both silica nanoparticles and IL are integrated, hence enhancing the interaction between stationary phase and analytes, which results a good separation efficiency for different compounds. Comparing to SCOT, the IL-SNs capillary column displays dual nature retention behaviors towards both polar and non-polar compounds, and skips supporter pretreatment processes needed for SCOT. The much thinner coating film compared to the SNs column helps to drastically decrease the resistance to mass transfer, hence increasing the separation efficiency. Comparing with the neat IL stationary phase, the IL-SNs stationary phase exhibits the higher coating value. It can decrease the retention selectivity on ILs structures, which enlarges the applicability of a simple conventional IL. Moreover, the fabrication of an IL-SNs capillary column needs a reduced number of steps required for the capillary column preparation, by skipping modifications or the use of any additional reagents in pretreatments. The present work will not only provide us a new stationary phase for GC separation, but also expand the application of silica nanoparticles in analytical chemistry.

Acknowledgments

The authors gratefully acknowledge the support from the National Nature Science Foundation of China (20975016, 21005007, 91027034), National Grant of Basic Research Program of China (2011CB915504), and the Fundamental Research Funds for the Central Universities (2009SC-1).

References

[1] J. Fang, X.Q. Shan, B. Wen, J.M. Lin, X.C. Lu, X.D. Liu, G. Owens, Langmuir 24 (2008) 10929.
[2] H.C. Choi, S. Kundaria, D.W. Wang, A. Javey, Q. Wang, M. Rolandi, H.J. Dai, Nano Lett. 3 (2003) 157.
[3] J.M. Rosenholm, E. Peuhu, J.E. Eriksson, C. Sahlgren, M. Linden, Nano Lett. 9 (2009) 3308.
[4] Y.Y. Wu, S.C. Zhang, N. Na, X. Wang, X.R. Zhang, Sens. Actuat. B – Chem. 126 (2007) 461.
[5] H.M. Mcnair, J.K. Miller, Basic Gas Chromatography, John Wiley & Sons, Inc., New York, 1997.
[6] K.D. Bartle, P. Myers, Trends Anal. Chem. 21 (2002) 547.

[7] Q.S. Qu, F. Shen, M. Shen, X.Y. Hu, G.J. Yang, C.Y. Wang, C. Yan, Y.K. Zhang, Anal. Chim. Acta 609 (2008) 76.
[8] G.M. Gross, J.W. Grate, R.E. Synovec, J. Chromatogr. A 1029 (2004) 185.
[9] G.M. Gross, D.A. Nelson, J.W. Grate, R.E. Synovec, Anal. Chem. 75 (2003) 4558.
[10] L.M. Yuan, C.X. Ren, L. Li, P. Ai, Z.H. Yan, M. Zi, Z.Y. Li, Anal. Chem. 78 (2006) 6384.
[11] Z.Y. Gu, X.P. Yan, Angew. Chem. Int. Ed. 49 (2010) 1477.
[12] T. Torimoto, T. Tsuda, K. Okazaki, S. Kuwabata, Adv. Mater. 22 (2010) 1196.
[13] P. Sun, D.W. Armstrong, Anal. Chim. Acta 661 (2010) 1.
[14] M. Antonietti, D.B. Kuang, B. Smarsly, Z. Yong, Angew. Chem. Int. Ed. 43 (2004) 4988.
[15] C. Yao, J.L. Anderson, J. Chromatogr. A 1216 (2009) 1658.
[16] M.L. Qi, D.W. Armstrong, Anal. Bioanal. Chem. 388 (2007) 889.
[17] D.W. Armstrong, L.F. He, Y.S. Liu, Anal. Chem. 71 (1999) 3873.
[18] J.L. Anderson, D.W. Armstrong, Anal. Chem. 77 (2005) 6453.
[19] T. Payagala, Y. Zhang, E. Wanigasekara, K. Huang, Z.S. Breitbach, P.S. Sharma, L.M. Sidisky, D.W. Armstrong, Anal. Chem. 81 (2009) 160.
[20] J.L. Anderson, D.W. Armstrong, Anal. Chem. 75 (2003) 4851.
[21] C. Villegas, Y. Zhao, J.M. Curtis, J. Chromatogr. A 1217 (2010) 775.
[22] C. Ragonese, P.Q. Tranchida, D. Sciarrone, L. Mondello, J. Chromatogr. A 1216 (2009) 8992.
[23] L.M. Sidisky, M.D. Buchanan, Supelco Reporter 26.2 (2008) 3.
[24] K. Huang, X. Zhang, D.W. Armstrong, J. Chromatogr. A 1217 (2010) 5261.
[25] T.Y. Kim, W.J. Kim, S.H. Hong, J.E. Kim, K.S. Suh, Angew. Chem. Int. Ed. 48 (2009) 3806.
[26] P. Wang, S.M. Zakeeruddin, P. Comte, I. Exnar, M. Gratzel, J. Am. Chem. Soc. 125 (2003) 1166.
[27] B.H. Wu, D. Hu, Y.J. Kuang, B. Liu, X.H. Zhang, J.H. Chen, Angew. Chem. Int. Ed. 48 (2009) 4751.
[28] B.G. Trewyn, C.M. Whitman, V.S.Y. Lin, Nano Lett. 4 (2004) 2139.
[29] D.S. Jacob, A. Joseph, S.P. Mallenahalli, S. Shanmugam, S. Makhluf, J. Calderon-Moreno, Y. Koltypin, A. Gedanken, Angew. Chem. Int. Ed. 44 (2005) 6560.
[30] K. Ueno, S. Imaizumi, K. Hata, M. Watanabe, Langmuir 25 (2009) 825.
[31] K. Ueno, K. Hata, T. Katakabe, M. Kondoh, M. Watanabe, J. Phys. Chem. B 112 (2008) 9013.
[32] M.A. Neouze, J. Le Bideau, P. Gaveau, S. Bellayer, A. Vioux, Chem. Mater. 18 (2006) 3931.
[33] G.M. Gross, J.W. Grate, R.E. Synovec, J. Chromatogr. A 1060 (2004) 225.
[34] G. Liu, Z. Yu, Techniques of Chromatographic Column, Chemical Industry Press, Beijing, 2006.
[35] A. Klinkenberg, Gas Chromatography, Butterworths Scientific Publications, London, 1960.