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Novel imidazolium-embedded and imidazolium-spaced octadecyl stationary phases for reversed phase liquid chromatography

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ABSTRACT

Two new stationary phases modified by alkylimidazoliums were prepared for the first time and characterized. One of the new phases was obtained *via* monomeric immobilization of octadecylimidazole to γ-chloropropyltrimethoxysilane modified silica to form polar-embedded phase; the other one was prepared by co-immobilization of two silane coupling agents (γ-chloropropyltrichlorosilane and octadecyltrichlorosilane) to silica, followed by quaternization of methylimidazole to form polar-spaced phase. This study was intended to compare the retention characteristics of these two stationary phases using linear solvation energy relationships model, as well as to examine the difference in selectivity by eluting alkylbenzenes, alkylnaphthalenes, condensed-ring and phenylene polynuclear aromatic hydrocarbons on both phases. Different effects of distributions of polar functional group and octadecyl chain were found to impact the chromatographic properties.

1. Introduction

Ionic liquids (ILs), *i.e.* room temperature ionic liquids (RTILs), can be defined as a class of ionic, nonmolecular substances. The ILs are seen as "tunable" materials which could be purposefully designed and modified to meet various needs.

Due to their unique properties, such as electric conductivity, low volatility, thermostability and tunability, considerable interest has been drawn for their utilizations in many fields [1,2]. Thus far, the utilization of ILs has extended to many fields, such as material chemistry, catalytic chemistry and spectroscopy [3–5]. Applications of ILs, mainly imidazolium salts, in analytical chemistry have been a researching hotspot [6,7]. They are also playing an exceedingly vital role in high performance liquid chromatography (HPLC), where in comparison to aliphatic amines, they have been a better additives to mobile phase (MP) due to their superior capability of participating in multiple interactions with the analytes, as well as shielding the residual silanol groups upon the silica surface. To make better use of ILs, they have been subjected to immobilization upon the surface of silica, resulting in surface-confined IL stationary phase (SCIL SP) [8]. Any of the SCILs is a combination of a cation bearing alkyl subsituents and an anion. The cation part is essentially a close marriage between a charged core, imidazolium or pyridinium, and an alkyl chain, which can be of different length.

Substantial research has been conducted on the synthesis and characterization of alkyl modified silica, since the development of reversed-phase liquid chromatography (RPLC). Among these alkyl chains, C_{18} and C_8 are the most favored choices, constituting the most commonly used separation media in RPLC. The pure alkyl stationary phases still have some disadvantages, *e.g.* low compatibility with highly aqueous eluent and insufficient selectivity towards polar solutes. During the past few years, a series of polar-embedded stationary phases has been developed to address these shortcomings [9–13]. These new phases comprise external hydrophobic segment, like C_{18}, C_{16}, or C_{14}, and incorporated hydrophilic segment near the silica substrate, such as amide, urea and carbamate. These polar-embedded phases are notable for their stability in highly aqueous mobile phase, improved performance in separation of polar compounds, unique selectivity but lower hydrophobicity compared to C_{18} ones. ILs containing long C_{18} chain have been previously synthesized and covalently attached to silica *via* polymeric approach to form "polar-embedded" SPs [14–16], which showed better peak shapes and higher efficiency for polar compounds, particularly for ionizable analytes. Another advantage of the imidazolium-embedded SPs is that they can be used with highly aqueous mobile phases without the phase collapse problem. These polar-embedded phases can provide a mixture of interaction mechanisms, such as hydrophobic, electrostatic, π–π, hydrogen bonding interactions, as well as shape

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and planarity recognition. The advantage of the polar groups in improving the column performance is that they mitigate the deleterious ion-exchange interaction between residual silanols and polar analytes. Alternatively, to facilitate the chromatographic efficiency, the polar group could be anchored on the silica as small molecule spacer, in this way the ligand is not comprised by the polar group and the C_{18} chain, but two different kinds of ligands are co-immobilized on the silica supports, which retain the ion-exchange capability and the water compatibility of polar phase [17].

The linear solvation energy relationships (LSER) model [18], which has extensive utilization in correlating retention with fundamental solute/MP and solute/SP affinities on a diversity of SPs, such as alkyl [19–22], phenyl [20,23,24] phases with little or weak polarity as well as cyano [19,25], diol [25], amine [26,27] and IL-type phases [28–32] with medium or strong polarity. The form of the LSER model is expressed as follows:

$$\log\ k = c + eE + sS + aA + bB + vV \quad (1)$$

where c is a system constant, E the excess molar refraction, S the solute dipolarity/polarizability, A and B the solute overall hydrogen bond donor (HBD) acidity and solute hydrogen bond acceptor (HBA) basicity respectively and V the McGowan characteristic volume. Each parameter represents corresponding intermolecular interaction. The coefficients c, e, s, a, b and v are characteristics of the HPLC system, *i.e.* a particular RP-HPLC SP with a specified composition of MP, they are extracted from multiple linear regression analysis of the retention data set, each of them is a reflection of the difference of a specific interaction of the solutes between SP and MP. A positive value for the system coefficient indicates a more intensive interaction between solute and SP, similarly a negative value signifies a more favorable interaction between solute and MP.

In this study, a new “polar-embedded” SCIL SP was prepared by immobilization of 1-octadecylimidazole on the chloropropylated silica. To better understand the effect of the polar group's positional distribution on the chromatographic behavior of SP, another “polar-spaced” material was prepared by co-immobilization of γ-chloropropyl and octadecyltrichlorosilane and subsequent attachment of 1-methylimidazole to chloropropyl moiety. These two phases have been compared using elemental analysis and contact angle tests in order to construe the merits of preparative pathways. Retention on both of the phases was characterized by LSER model with a set of 20 solutes; hydrophobic and aromatic selectivity of both SPs were illustrated by separations of alkylbenzenes, alkylnaphthalenes, condensed-ring and phenylene polynuclear aromatic hydrocarbons (PAHs). Hopefully, the examination and comparison of the chromatographic evaluations of the SPs will provide insight into the effects upon retention and selectivity of (1) the different distribution of polar cation core and (2) long hydrophobic chain and (3) immobilization of cation/anion pair.

2. Experimental

2.1. Reagents and materials

1-Bromo octadecane (99%) and γ-chloropropyl trimethoxysilane (CPTMS) (99%) were purchased from Sun Chemical Technology Co., Ltd (Shanghai, China); 1-methyl imidazole (MIm) (98%) and imidazole (99%) were obtained from Sinopharm Chemical Reagents Co., Ltd (Shanghai, China); octadecyl trichlorosilane (ODS) (95%, containing 5–10% branched isomers) and γ-chloropropyl trichlorosilane (CPTCS) (97%) were obtained from Alfa Aesar (Tianjin, China); naphthacene and *n*-alkyl benzenes (hexyl benzene (C_6Ph), octyl benzene (C_8Ph), decyl benzene ($C_{10}Ph$) and dodecyl benzene ($C_{12}Ph$)) of analytical standard were supplied by J&K Chemical (Beijing, China); *p*-terphenyl and *p*-quaterphenyl were purchased from Aladdin Industrial Inc. (Shanghai, China). Doubly distilled water, acetonitrile (MeCN), methanol (MeOH) and tetrahydrofuran (THF) of HPLC grade were used; solutes for LSER analysis and other solvents of analytical grade or better were obtained from different origins and were dried by molecular sieve (3 Å) prior to use. 1-*n*-Alkyl naphthalene (1-hexyl naphthalene (C_6Np), 1-octyl naphthalene (C_8Np), 1-decyl naphthalene ($C_{10}Np$) and 1-dodecyl naphthalene ($C_{12}Np$)) [33] and spherical porous silica (diameter: 5 μm, pore size: 90 Å, surface area: 400 $m^2\ g^{-1}$), were synthesized in house.

2.2. Preparation of stationary phases

2.2.1. Preparation of polar-embedded phase

Synthesis of 1-octadecyl imidazole: to an ethanolic solution (100 mL) of sodium (1.28 g, 56 mmol) was added imidazole (3.74 g, 55 mmol) in one portion, the solution was stirred for 3 h at room temperature to deprotonate imidazole. Then 1-bromo octadecane (16.67 g, 50 mmol) was added, the resultant solution was refluxed for 24 h, during which time copious white precipitate (NaBr) appeared. Afterwards the mixture was filtered, ethanol removed. The residue was dissolved in THF (80 mL) to remove insoluble NaBr. Then THF was evaporated, the residue was extracted by *n*-hexane (100 mL) and water (50 mL × 3), the organic layer was dried by magnesium sulfate and concentrated to approximately 40 mL, which after standing in a refrigerator overnight, filtration and washing by cold *n*-hexane afforded a white sparkling powder (10.57 g, 67%), namely pure 1-octadecyl imidazole ($C_{18}Im$). ^1H NMR ($CDCl_3$, 400 MHz) δ ppm: 0.86 (*t*, 3 H, $-CH_3$), 1.23 (m, 30 H, $-(CH_2)_{15}-CH_3$), 1.74 (m, 2 H, $-CH_2-(CH_2)_{15}-CH_3$), 3.90 (*t*, 2 H, $-CH_2-CH_2-(CH_2)_{15}-CH_3$), 6.88–7.031 (d, 2 H, imidazole N–CH=CH–N), 7.44 (s, 1 H, imidazole N–CH=N).

Silica (5 g) was silylated by CPTMS (4 mL) in refluxing dry toluene (50 mL) for 24 h under mechanical stirring to yield chloropropylated silica (CPS). CPS (4 g) and $C_{18}Im$ (4 g) were placed in 50 mL of toluene, and heated to reflux for 48 h in a nitrogen atmosphere. The resulting slurry was centrifuged, the IL-immobilized silica, Sil-Embeded-ImC_{18} (Sil-E-ImC_{18}) was washed by THF, the centrifugation and washing procedure was repeated for three times. The product was dried under vacuum at 80 °C for 12 h before column packing.

2.2.2. Preparation of polar-spaced phase

This phase was synthesized following the reported procedure [13] with slight modification. Briefly, silica (8 g) was dispersed in 50 mL of anhydrous toluene, to which ODS (6.4 mL) together with CPTCS (1.2 mL) dissolved in 30 mL of toluene was added dropwise under mechanical stirring under the protection of nitrogen. After the addition was finished, the slurry was heated at 110 °C for 24 h, with continuous bubbling of nitrogen to remove the gaseous HCl. Then the slurry was treated by repeated centrifugation and washing as foregoing and the modified silica (CPS – ODS) dried under vacuum at 80 °C overnight. This silica intermediate (4 g) was further treated by MIm (8 mL) in refluxing toluene (40 mL) for 48 h, subsequent washings and drying afforded polar-spaced phase, Sil-Spaced-ImC_{18} (Sil-S-ImC_{18}). A schematic illustration is given in Fig. 1.

2.3. Apparatus

The ^1H NMR spectrum of $C_{18}Im$ was recorded on a Varian INOVA-400M instrument (Varian, USA) at 400 MHz using tetramethylsilane reference. The carbon, hydrogen and nitrogen contents of the SPs were determined by elemental analyses using a

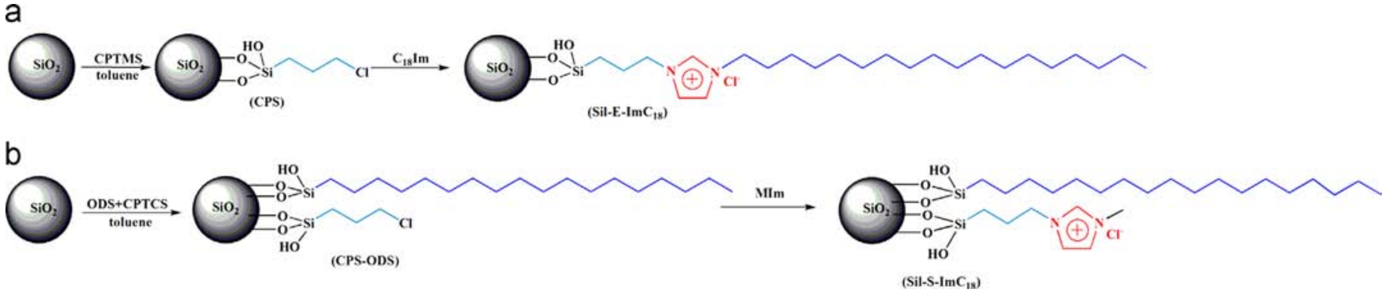

Fig. 1. Synthetic strategy for imidazolium-functionalized polar-embedded (a) and polar-spaced (b) stationary phases.

Vario EL III elementat analyzer (Hanau, Germany). Wettability tests of the SPs were carried out on a Dataphysics OCA 20 contact angle measuring and contour anaylsis unit (Filderstadt, Germany), the contact angle of each silica sample was measured twice to give average value.

All the mathematical analyses were performed using Microsoft Office 2003 suites.

All the chromatographic tests were performed on a liquid chromatographic system equipped with a Shimadzu LC-10AT VP pump (Kyoto, Japan), a Perkin Elmer 785A UV/Vis detector (Waltham, MA, USA) and a Rheodyne 7725i injector with 15 μL sample loop (Cotati, CA, USA). A Shimadzu Shim-pack VP-ODS column (diameter: 5 μm, pore size: 120 Å, surface area: 410 m^2 g^{-1}, carbon loading: 20%, end-capped, 150 mm × 4.6 mm I.D.) was used as reference in LSER analysis. All the solutes were dissolved either in MeCN or MeOH and analyzed at room temperature at a fixed flow rate of 1.0 mL min^{-1} with UV detection wavelength at 254 nm. MPs were degassed ultrasonically prior to use.

Sil-E-ImC$_{18}$ and Sil-S-ImC$_{18}$ were dispersed in tetrachloromethane and packed into stainless steel tube column (150 mm × 4.6 mm I.D.) using MeOH and *n*-hexane, respectively, as propulsive solvent by slurry packing technique at a constant liquid pressure of 56 MPa.

3. Results and discussion

3.1. *Preparation and surface chemistry of polar-embedded and polar-spaced phases*

Both of the imidazolium-modified phases could be seen as the result of two different distribution patterns of polar groups, they were prepared by a heterogeneous two-step strategy, in which γ-chloropropyl functional group alone in the case of polar-embedding, and with octadecyl chain in the case of polar-spacing, were preemptively immobilized on the silica, subsequent attachment of desired alkyl imidazoles to chloropropyl ligand to constitute corresponding SCIL. To minimize the difference in the numbers of carbon atoms of the starting material, MIm with the shortest carbon chain was selected.

Due to the heterogeneity of the reaction media and the relatively bulkier volume of octadecyl chain, which is akin to benzyl group [31], immobilization was significantly effected by steric hindrance, the elemental analyses of Sil-E-ImC$_{18}$ and CPS revealed a lower bonding amount of polar group, meaning conversion of γ-chloropropyl groups was approximately 15%. Whereas Sil-S-ImC$_{18}$ demonstrated a higher bonding amount of MIm, the maximum conversion of γ-chloropropyl groups was 56%. In consideration of this incomplete conversion, the maximum C$_{18}$ coverage is 1.27 μmol m^2 as listed in Table 1. Nevertheless, the chromatographic behavior of the silica material indeed was remarkably altered by these imidazolium functional groups, as validated by our previous study [16] and other authors' results [31,34,35].

Table 1
Solute descriptors of the compounds studied.

No.	Compounds	*E*	*S*	*A*	*B*	*V*
1	Benzaldehyde	0.820	1.00	0.00	0.39	0.8730
2	Nitrobenzene	0.871	1.11	0.00	0.28	0.8906
3	Naphthalene	1.340	0.92	0.00	0.20	1.0854
4	Biphenyl	1.360	0.99	0.00	0.26	1.3420
5	Aniline	0.955	0.96	0.26	0.41	0.8162
6	Toluene	0.601	0.52	0.00	0.14	0.8573
7	Anisole	0.708	0.75	0.00	0.29	0.9160
8	Bromobenzene	0.882	0.73	0.00	0.09	0.8914
9	Chlorobenzene	0.718	0.65	0.00	0.07	0.8388
10	*o*-Nitroaniline	1.180	1.37	0.30	0.36	0.9904
11	*p*-Nitroaniline	1.220	1.91	0.42	0.38	0.9904
12	Ethylbenzene	0.613	0.50	0.00	0.15	0.9982
13	*iso*-Propylbenzene	0.602	0.49	0.00	0.16	1.1391
14	Acetophenone	0.818	1.01	0.00	0.48	1.0139
15	N,N-dimethylaniline	0.957	0.84	0.00	0.42	1.0980
16	*o*-Xylene	0.663	0.52	0.00	0.16	0.9980
17	*m*-Xylene	0.623	0.52	0.00	0.16	0.9980
18	Benzyl cyanide	0.751	1.15	0.00	0.45	1.0120
19	Methyl benzoate	0.733	0.85	0.00	0.48	1.0726
20	Phenol	0.805	0.89	0.60	0.30	0.7751

Values obtained from Refs. [35,36].

Hydrophilicity of these materials was determined by contact angle (CA) measurement. Derivatized silica to be measured was immobilized on a flat substrate, upon which water droplet of 7 μL was dispensed. In general, a large CA (> 90°) implies a hydrophobic surface, CA beyond 150° represents a superhydrophobic surface. The results revealed that CA for CPS was 108.8°, which became 127.6° after attachment of C$_{18}$Im moiety, indicating that none of CPS and Sil-E-ImC$_{18}$ is hydrophilic; immobilization of C$_{18}$Im had enhanced the hydrophobicity of CPS. CA for CPS – ODS shrank upon immobilization of MIm from 148.3° to 133.8°, indicating the resulted material was less hydrophobic, as the SCIL herein was hydrophilic. In fact, the free-form 1-propyl-3-methyl imidazolium chloride is water-soluble. According to the differences in elemental analyses and wettability tests, Sil-S-ImC$_{18}$ was expected to express more significant RP characteristics than Sil-E-ImC$_{18}$.

3.2. *LSER study*

3.2.1. *Selection of probe solutes set*

To ensure meaningful results from the LSER analysis, a diversified set of 20 solutes (Table 2) were initially chosen, covering non-polar and polar ones (basic and acidic). The cross-correlation among the descriptors of the solutes should be examined next. Up to this point, the correlation matrix of the descriptors of selected solutes was calculated and listed in Table 3, where it can be seen that a slight correlation has been exhibited by *E* and *S*, which is expected, since they both reflect the polarizability of the solute, and no aliphatic solutes are employed to diminish this correlation [20,32,38]; *S* seems to be weakly coupled to *B*, the

Table 2
Properties of the prepared silica materials.

Materials	Elemental analysis				Contact angle (deg)	Column performance[a]	
	C%	N%	H%	Coverage (μmol m^2)		Pressure (bar)	*N* (plates/m)
CPS	5.09	0.00	1.070	3.530	108.8	/	/
Sil-E-ImC$_{18}$	9.17	0.52	1.720	0.527	127.6	41	28,200 for Tol 26,600 for Nap
CPS–ODS	12.50	0.00	2.349	1.270 for C$_{18}$ 2.440 for CPS	148.3	/	/
Sil-S-ImC$_{18}$	13.66	1.54	2.430	1.270 for C$_{18}$ 1.375 for MIm	133.8	38	32,100 for Tol 31,300 for Nap

[a] Column performance was recorded using toluene (Tol) and naphthalene (Nap) in an elution composed of methanol/water (v/v=80/20) at room temperature.

Table 3
Correlation matrix of the solute descriptors.

	E	*S*	*A*	*B*	*V*
E	1	***0.63***	0.25	0.16	0.38
S		1	***0.53***	***0.57***	0.04
A			1	0.29	−0.36
B				1	0.06
V					1

reason may reside in the fact that they are similarly influenced by the presence of electronegative heteroatoms like oxygen and nitrogen. These atoms can induce higher hydrogen bond basicity and a greater dipolar moment for the solute [38]. The generally low correlation coefficients confirm the suitability of chosen set of solutes for employment with the LSER model.

3.2.2. Evaluation of LSER model and interpretation of the system parameters

The applicability of the LSER model was assessed by comparison of the experimental retention factors (log $k_{(\mathrm{exp})}$) with the calculated values (log $k_{(\mathrm{calc})}$). As displayed in Fig. 2, satisfactory agreements between log $k_{(\mathrm{exp})}$ and log $k_{(\mathrm{calc})}$ was observed for both Sil-E-ImC$_{18}$ and Sil-S-ImC$_{18}$ in two examples of binary MPs (MeCN and MeOH), the correlation coefficients were always larger than 0.98, none of the solutes appeared to be serious outlier. Cross validation of the results has been conducted using “leave-one-out” procedure, which showed that exclusion of any probe has very minimal effect on the system coefficients with the exception of phenol, possibly due to the electron-involving interaction between SP and analyte yet not covered in the LSER model. Therefore, the test set was potent in specifying the interactions either between solute and SP or between solute and MP under RP mode.

To obtain more perceivable information on the interactions involved in the RP chromatographic process, a conventional ODS column was added as reference, which would be useful to depict the differences in the magnitude of the system parameters. The system parameters of this ODS column was acquired using a relatively larger but quite similar probe set in MeCN – water MP [27]. The system parameters were calculated by multiple linear regression analysis of the LSER equation, and summarized in Table 4, where correlation coefficients (R) ranged from 97.4% to 99.1, standard error (SE) varied from 0.025 to 0.053, representing a desirable quality of modeling. The property of the chromatographic system is embodied by these system coefficients. Study of the different SPs could be performed in identical binary MP. Investigation into the variation of a given SP's property could be carried out with gradient variation of MP. For classical ODS columns in RP mode, the *e* and *v* values are always positive, and *s*, *a* and *b* negative [18,19,21].

3.2.2.1. The e coefficient. The *e* parameter emphasizes the capability of the chromatographic system to interact with the solute containing π and/or *n* electrons, *i.e.* the π–π interaction. According to the literature [39–41], polarizability and π–π stacking are connected; the *e* parameter reflects the combinational contribution of polarizability and excess molar refraction (refractive index). All the imidazolium-modified SPs possess a positive *e* value larger than that of ODS (close to zero), which indicates that π–π interaction between SP and solute is stronger than that between MP and solute. This observation is consistent with the result obtained with a butyl imidazolium-modified SP by Stalcup *etc.* [28,29], consolidating their conclusion that SCIL SP behaves like phenyl SP in this aspect. This stronger π–π interaction may be the result of the polarizability of imidazolium core and residual γ-chloropropyl chain.

The high polarizability of imidazolium is well-established, while polarizability of the chloro propyl chain was assumed to be higher than its alkane analog due to the attachment of halogen atom, like the case involving γ-bromo octyl chain [31]. Individually, *e* value for Sil-E-ImC$_{18}$ (e_{SE}), increases with the uplift of MeOH content because of the diminishing polarizability of MP, where its magnitude is larger than that in MeCN, due to the higher polarizability and higher solvent strength of MeCN than those of MeOH. However, it is insensitive to the change of MeCN content. For Sil-S-ImC$_{18}$ (e_{SS}), this value elevates with the increase of MeOH content, but maintains smaller than e_{SE}, attributing to more residual chloro propyl ligands on Sil-E-ImC$_{18}$. As mentioned earlier, refractive index could be considered [31]. The refractive index of 1-chloropropane (1.388) does not differ too much from that of MIm (1.495) and C$_{18}$Im (1.475), so it is not unacceptable to assume that the effect of residual chloropropyl ligands in a large number upon the *e* value is more significant than that of alkyl imidazolium. Thus, Sil-S-ImC$_{18}$ is less capable of π–π interaction. Unexpectedly, e_{SS} irregularly fluctuates with the variation of MeCN – water MP, but it is smaller in 50% MeCN than in 50% MeOH. This unique fluctuation of *e* values limits an explicit interpretation.

3.2.2.2. The s coefficient. The *s* coefficient signifies the tendency of the chromatographic system to participate in dipole – dipole interaction with solute. Table 4 shows negative *s* value for all the SCIL SPs and ODS. A negative value indicated that dipole – dipole interaction is stronger between MP and solute even if imidazolium cation has highly dipolar and polarizable natures. This is understandable, as the system contains bulky eluent. For all the SCIL SPs, the *s* values remains negative and becomes larger with the increase of water content in MP, since water has larger dipole moment and polarizability than any of MeOH and MeCN. On the other hand, *s* values in MeOH – water eluent is less negative than in MeCN – water, on account of the difference between the salvation properties of MeOH and MeCN, the former is able to solvate ions more vigorously than the latter [42,43].

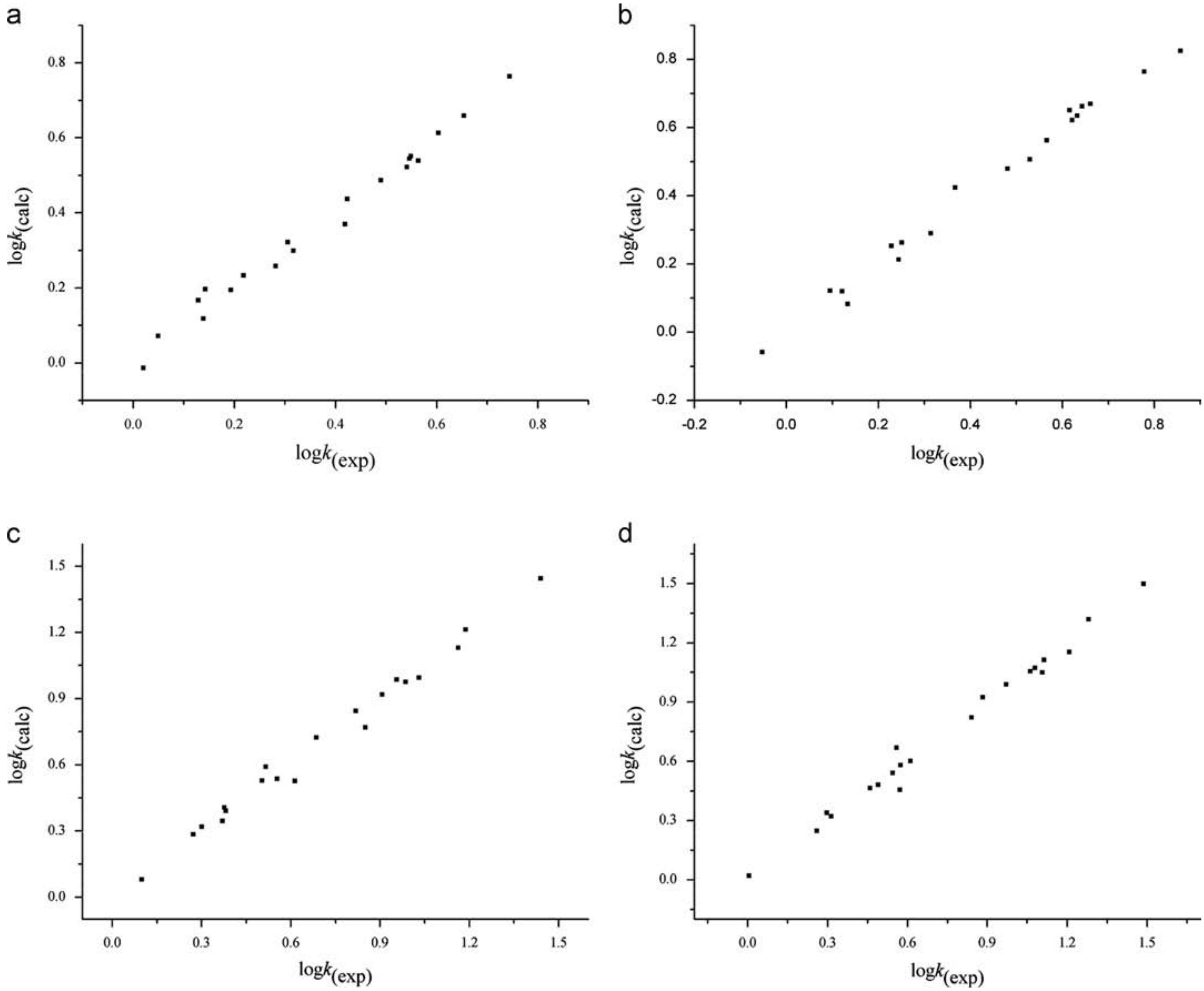

Fig. 2. log $k_{(calc)}$ − log $k_{(exp)}$ plots for Sil-E-ImC$_{18}$ (a, c) and Sil-S-ImC$_{18}$ (b, d) in two types of binary eluents ((a,b) 50% MeCN, (c,d) 50% MeOH).

Table 4
LSER coefficients acquired with different SP–MP systems.

SP	MP	*c*	*e*	*s*	*a*	*b*	*v*	*R* (%)	*F*	SE	*n*
Sil-S-ImC$_{18}$	70%MeOH	−0.66	0.05	−0.03	0.26	−1.67	1.23	97.4	114	0.049	20
	60%MeOH	−0.54	0.13	−0.17	0.33	−1.83	1.51	98.8	209	0.043	20
	50%MeOH	−0.51	0.16	−0.23	0.31	−2.12	1.89	98.9	302	0.050	20
	70%MeCN	−0.47	0.12	−0.27	0.17	−0.84	0.72	98.1	136	0.030	20
	60%MeCN	−0.30	0.21	−0.38	0.06	−0.94	0.82	98.8	218	0.030	20
	50%MeCN	−0.25	0.10	−0.27	0.10	−1.25	1.11	98.8	253	0.031	20
Sil-E-ImC$_{18}$	70%MeOH	−0.59	0.17	−0.11	−0.06	−1.08	1.02	99.1	300	0.025	20
	60%MeOH	−0.19	0.15	−0.18	−0.04	−1.36	1.23	97.6	164	0.054	20
	50%MeOH	−0.43	0.26	−0.29	−0.07	−1.59	1.65	98.8	228	0.046	20
	70%MeCN	−0.33	0.12	−0.18	−0.07	−0.43	0.42	94.2	45	0.035	20
	60%MeCN	−0.24	0.14	−0.27	−0.13	−0.76	0.65	98.2	152	0.028	20
	50%MeCN	−0.16	0.14	−0.35	−0.19	−0.97	0.84	98.6	205	0.029	20
Shimadzu VP-ODS	70%MeCN	−0.39	0.06	−0.28	−0.41	−1.21	1.15	97.9	231	0.047	30
	60%MeCN	−0.29	0.08	−0.30	−0.43	−1.40	1.34	97.9	230	0.053	30
	50%MeCN	−0.23	0.02	−0.27	−0.45	−1.82	1.62	99.2	613	0.038	30

Separately, for Sil-S-ImC$_{18}$, its *s* value (s_{SS}) approaches zero at higher MeOH concentration, meaning the dipole – dipole interactions are approximately equally strong between SP and solute and between MP and solute. In both hydro-MeOH and hydro-MeCN eluents, s_{SS} maintains less negative than that for Sil-E-ImC$_{18}$ (s_{SE}), reflecting a stronger dipole – dipole interaction occurs between Sil-S-ImC$_{18}$ and solute than between Sil-E-ImC$_{18}$ and solute in identical MP due to the higher coverage of imidazolium on Sil-S-ImC$_{18}$.

3.2.2.3. The a coefficient. The *a* parameter denotes the hydrogen-bond basicity of the chromatographic system. The *a* values involved in three systems here are quite distinct from each other. For Sil-E-ImC$_{18}$ and ODS, their negative *a* coefficients (a_{SE} and a_{ODS}) indicate the strong hydrogen bonding acceptor property of the MP, whereas the basicity of Sil-E-ImC$_{18}$ is still stronger than alkyl SP. In contrast, for Sil-S-ImC18, its *a* value (a_{SS}) surpasses zero, this behavior is similar to the cases involving diol- and amine-based SPs operated in normal-phase (NP) mode [36], symbolizing the strongest hydrogen bond acceptor ability of Sil-S-ImC$_{18}$ amongst the three SPs. On comparison among a_{SE}, a_{SS} and a_{ODS}, it's intuitive that the SCIL SPs are much more capable hydrogen bond acceptors than ODS due to the attached cation, which is a proven hydrogen bond acceptor [44], and higher bonding amount of imidazolium has remarkably enhanced this characteristic.

Two kinds of organic modifiers employed have different effects upon this parameter. In hydro-MeOH MP, *a* is not very sensitive to the variation of MP compositions, because of the similar hydrogen bond acceptor ability (β in Table 5) of water and MeOH. Meanwhile, *a* is more negative in hydro-MeCN MP, probably due to the presence of chloride anion [45,46], which is highly solvated by water, exiguously less solvated by MeOH and least by MeCN [47], like its congener bromide [29,31]. As a result of these dissimilarities, chloride ion will more actively interact with hydro-MeOH MP *via* hydrogen bonding. Thus a stronger hydrogen bond basicity of SCIL SPs entails.

3.2.2.4. The b coefficient. The *b* coefficient represents the hydrogen bond acidity of the chromatographic system, *vis*. the capability of SP and MP to donate a proton to solute. According to the literature [46], imidazolium ILs show little hydrogen bond acidity, which prevents them from participating in hydrogen bond donation interaction with the solute. In view of this fact, hydrogen donation is essentially the contribution of residual surface silanols. A more negative *b* means either intensified proton donation from MP or weakened donation from SP. For all the SCIL SPs, the *b* values are significantly less negative than that for ODS (endcapped) in all hydro-MeCN MPs, probably due to their lower organic surface coverage than ODS SP's, more uncovered silanols in another word.

For the two SCIL SPs, Sil-S-ImC$_{18}$ demonstrates a more negative *b* value than Sil-E-ImC$_{18}$, this observation is similar to the reported case [31], the reason may lie in that (1) the more residual silanols on Sil-E-ImC$_{18}$, and (2) higher bonding amount of alkylimidazole on Sil-S-ImC$_{18}$, which after quaternization can shield the residual silanols through the interaction with silica surface [31,35], mitigating the silanol activity (SA). To be more precise, we examined the individual case of aniline and phenol, which are test compounds in the following equation of the Galushko test [48]: $SA_G = 1 + 3[(k_{aniline}/k_{phenol}) - 1]$. The results show that SA$_G$ for Sil-E-ImC$_{18}$ and Sil-S-ImC$_{18}$ are -3.266 and -4.566, respectively. Aniline was eluted before phenol on both SCIL SPs, suggesting the residual silanols are well shielded and they cannot interact with the solutes. It is obvious that Sil-E-ImC$_{18}$ shows higher SA$_G$, in line with the results of the *b* values. Under the same conditions, the commercial ODS columns show positive SA$_G$ and usually a reversed elution order [49]. In both hydro-MeOH and hydro-MeCN MPs, *b* value tend to be more negative with the increase of water concentration, owing to the strongest hydrogen bond acidity (α in Table 5) of water among all the solvents. In hydro-MeCN, *b* values are less negative, as the hydrogen bond acidity of MeCN is much weaker than that of MeOH, the overall hydrogen bond acidity of MP will decline when MeOH is substituted by MeCN, so will the hydrogen bond donating ability of the MP.

Table 5
Solvatochromic properties of bulky solvents.

Solvent	π^*	β	α
Water	1.09	0.48	1.19
MeOH	0.60	0.62	0.93
MeCN	0.75	0.31	0.19

Values obtained from Ref. [39].

3.2.2.5. The v coefficient. The *v* parameter originates from the unity of cavity formation and dispersive interactions, and is the barometer of the hydrophobicity of the chromatographic system. As shown in Table 4, the *v* values for two SCIL SPs are positive but smaller than those for ODS SP in the same MP composition. This is self-evident, as the ODS SP is well-known for its superior hydrophobic feature. Moreover, the introduction of hydrophilic moieties will bring down the overall hydrophobicity of the SP [21,22]. Despite its possession of more imidazolium moieties, Sil-S-ImC$_{18}$ demonstrates a larger value than Sil-E-ImC$_{18}$, due to more C$_{18}$ ligands the former contains. Both of them exhibit smaller *v* values in hydro-MeCN MPs than in hydro-MeOH MPs of identical organic concentration, for MeCN is more lipophilic than MeOH, and its eluting power is much stronger than MeOH's, its presence will boost the hydropbobicity of the MP.

In conclusion, the SCIL SPs can provide typical RP retention mechanisms with distinctive characteristics, such as their behavior similar to phenyl SP's in π–π stacking and their stronger hydrogen bond basicity than ODS SP's.

3.3. Hydrophobic and aromatic selectivity

In order to better understand the influences of positive parameters (*e*, *v*) in LSER analysis on the chromatographic retention and to know the usefulness of SCIL SPs in differentiating analogs, we have conducted comparative study of the selectivity of both SPs towards a series of aromatic solutes, including alkyl benzene, 1-alkyl naphthalenes, planar condensed-ring PAHs and linear phenylene type PAHs.

Firstly, 1-alkyl naphthalene was selected because of its structural similarity to and stronger π–π stacking over alkyl benzenes with identical carbon chain, by comparison of their retention factors, intuitive information on the chromatographic selectivity can be obtained. 6 alkyl benzenes and 4 alkyl naphthalenes were eluted, their log $k_{(exp)}$ values were plotted against corresponding octanol–water partition coefficient (log *P*). As can be seen in Fig. 3a, log *k* went monotonically up with the increase of alkyl chain length; Sil-S-ImC$_{18}$ demonstrated sharper slopes for alkyl benzenes and 1-alkyl naphthalenes than Sil-E-ImC$_{18}$, indicating the superior methylene selectivity of Sil-S-ImC$_{18}$ to that of Sil-E-ImC$_{18}$, which was in line with the larger *v* value for Sil-S-ImC$_{18}$. For each of the SPs, its selectivity towards 1-alkyl naphthalenes was enhanced compared to that towards alkyl benzenes, this may be the result of the stronger π–π stacking and hydrophobicity of naphthalene.

Then, condensed-ring (naphthalene anthracene, naphthacene) and phenylene PAHs (biphenyl, *p*-terphenyl and *p*-quaterphenyl) were used. For each type of PAHs with each SP, a curve was

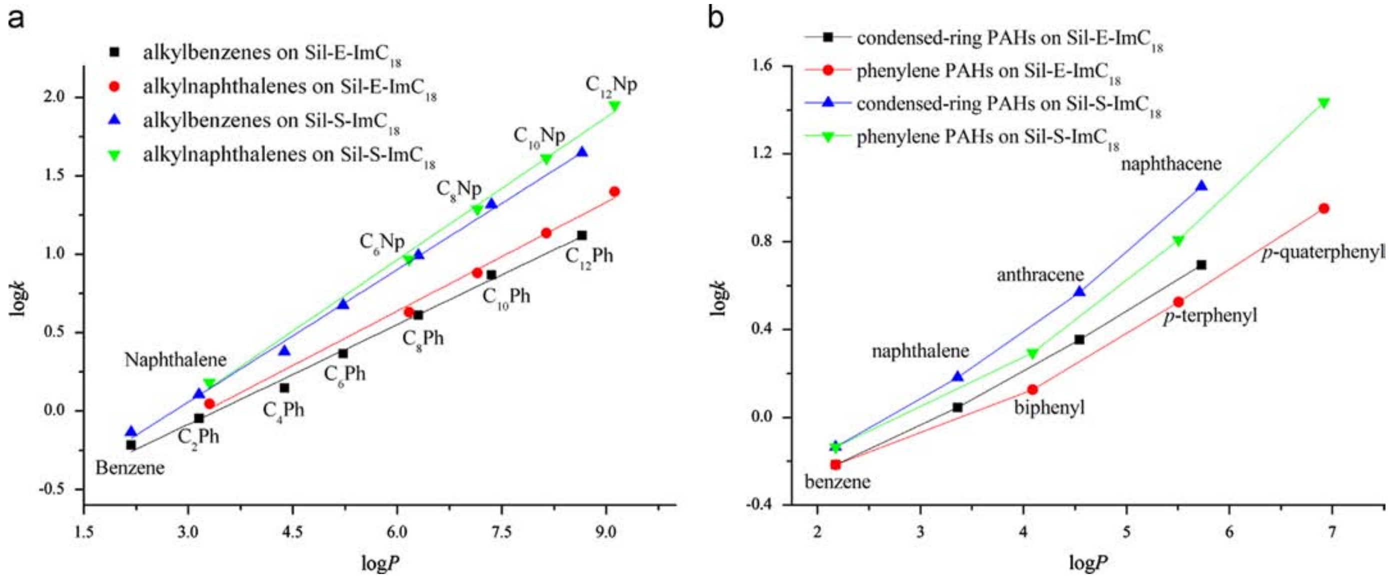

Fig. 3. log $k-\log P$ plots of alkylaroamtics (a) and PAHs (b) for Sil-E-ImC$_{18}$ and Sil-S-ImC$_{18}$ in 80% MeOH.

Table 6
Selectivity factors (α) for aromatic isomers in 70%MeOH.

Solute	Sil-E-ImC$_{18}$		Sil-S-ImC$_{18}$	
	k	α	k	α
Phenanthrene	7.27	1.06	7.03	1.10
Anthracene	7.73		7.74	
o-Terphenyl	9.33	1.45	7.34	1.81
m-Terphenyl	13.54	1.05	13.27	1.21
p-Terphenyl	14.28	1.05	16.01	1.14
Triphenylene	14.95	1.04	18.34	1.14
Chrysene	15.58		20.88	

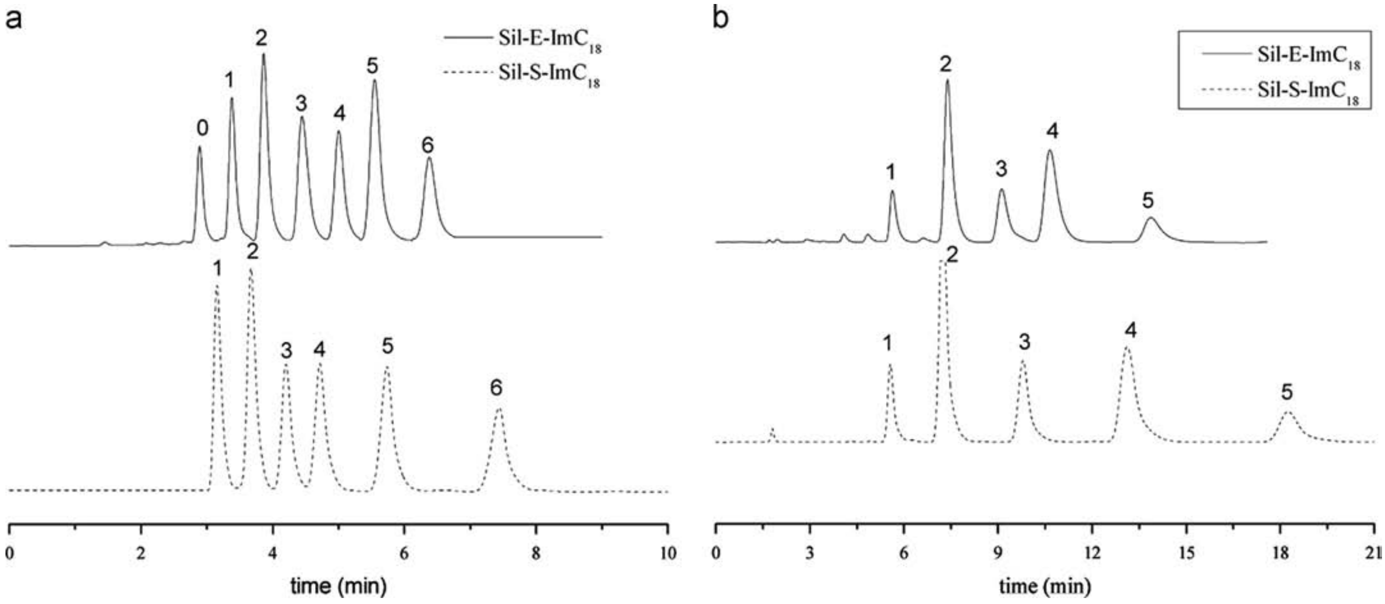

Fig. 4. Chromatograms of alkylbenzenes and PAHs on Sil-E-ImC$_{18}$ and Sil-S-ImC$_{18}$ in 70% MeOH. a: (0) benzene, (1) toluene, (2) ethylbenzne, (3) *iso*-propylbenzene, (4) *tert*-butylbenzene, (5) *n*-butylbenzene, (6) *n*-pentylbenzene; b: (1) naphthalene, (2) biphenyl, (3) fluorene, (4) anthracene, (5) fluoranthene.

obtained in Fig. 3b, rather than a straight line like the case of alkyl aromatics. Nevertheless, it was still noticeable that at a specified value of log P, condensed-ring PAHs exhibited a larger log k, presumably due to their higher aromaticity, *i.e.* condensed-ring selectivity was stronger than phenylene selectivity. Comparison between the two SCIL SPs revealed that Sil-S-ImC$_{18}$ again expressed superior aromatic selectivity. It was not contradictory that Sil-E-ImC$_{18}$ with larger e value possessed an inferior aromatic selectivity, because even though the difference in the magnitude of e was significantly smaller than that of v, resulting in a slightly stronger π–π interaction for Sil-E-ImC$_{18}$, but a pronouncedly stronger hydrophobic interaction for Sil-S-ImC$_{18}$.

Selectivity towards isomers of condensed-ring and phenylene PAHs was also examined; the results were summarized in Table 6. It could be observed that, for each pair of solutes, Sil-S-ImC$_{18}$ showed a larger selectivity factor (α). If all α values were multiplied, a more quantitative measure of selectivity was resulted [50], namely selectivity factor product (α_p), by which the value for Sil-E-ImC$_{18}$ was 1.76, while for Sil-S-ImC$_{18}$ was 3.13, confirming the latter's much better isomer selectivity. This larger α_p could be ascribed to the higher surface concentration of C$_{18}$ ligands on Sil-S-ImC$_{18}$ and the potential of imidazolium cation to reduce the mobility of the C$_{18}$ chain, whereby a more orderly conformation of C$_{18}$ ligands might take place. Due to the lower bonding amount of C$_{18}$Im, Sil-E-ImC$_{18}$ had relatively sparse C$_{18}$ ligands, constituting a more flexible and disorderly conformation, thus reduced isomer selectivity, or shape selectivity was expressed (Fig. 4).

4. Conclusions

Two new SCIL stationary phases bearing C$_{18}$ chain have been prepared *via* different synthetic pathways and chromatographically characterized by LSER model and eluting alkyl benzenes, 1-alkyl naphthalenes and PAHs. Alkyl imidazoles of steric hindrance will lead to a lower surface coverage, the presence and distribution of imidazolium cations will substantially influence the property of the stationary phase and further impact the mobility of the C$_{18}$ ligands. The imidazolium core enhances the aromatic selectivity remarkably and also weakens the hydrophobicity of the alkyl chain. The multiple interactions provided by the combination of polar group and lipophilic moiety, like π–π, hydrogen bonding and hydrophobic interactions, have endowed the SCIL SPs with unique chromatographic performance, such as fine hydrophobic and aromatic selectivity, as well as recommendable isomer selectivity.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.03.057.

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