



Evaluating the solvation properties of functionalized ionic liquids with varied cation/anion composition using the solvation parameter model

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ABSTRACT

Ionic liquids (ILs) are promising gas chromatography (GC) stationary phases due to their high thermal stability, negligible vapor pressure, and ability to solvate a broad range of analytes. The tunability of ILs allows for structure modification in pursuit of enhanced separation selectivity and control of analyte elution order. In this study, the solvation parameter model is used to characterize the solvation interactions of fifteen ILs containing various cationic functional groups (i.e., dimethylamino, hydroxyl, and ether) and cation types paired with various counter anions, namely, tris(pentafluoroethyl)trifluorophosphate (FAP⁻), bis[(trifluoromethyl)sulfonyl]imide (NTf₂⁻), thiocyanate (SCN⁻), tricyanomethide (C(CN)₃⁻), tetracyanoborate (B(CN)₄⁻), and bis[oxalate(2-)]borate (BOB⁻). The presence of functional groups affected the hydrogen bond basicity, hydrogen bond acidity, as well as dispersion interactions of the resulting ILs, while the change of cation type yielded modest influence on the dipolarity. The switch of counter anions in unfunctionalized ILs produced compounds with higher dipolarity and hydrogen bond basicity. The dipolarity and hydrogen bond basicity of ILs possessing cyano-containing anions appeared to be inversely proportional to the cyano content of the anion. The modification of IL structure resulted in a significant effect on the retention behavior as well as separation selectivity for many solutes, including reversed elution orders of some analytes. This study provides one of the most comprehensive examinations up-to-date on the relation between IL structure and the resulting solvation characteristics and gives tremendous insight into choosing suitable ILs as GC stationary phases for solute specific separations.

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1. Introduction

Recently, the use of ionic liquids (ILs) has attracted much academic and industrial interest due to their unique physico-chemical properties. ILs are generally defined as non-molecular ionic solvents with melting points below 100 °C [1]. This unique class of solvents is usually composed of a nitrogen or phosphorus-containing organic cation and various counter anions. Compared to traditional organic solvents, ILs exhibit significant advantages including nearly undetectable vapor pressures under ambient temperature, wide electrochemical windows, and high thermal stability (often higher than 300 °C). In addition, many physical and chemical properties of ILs, such as viscosity and solubility with other molecules, can be custom designed by simply varying the

cation and anion combination or by introducing desired functional groups to either component [2].

One continually emerging application involving ILs is their employment as gas chromatography (GC) stationary phases [3–5]. The success of ILs as GC stationary phases is due to the advantages they possess over traditional materials such as the substituted polysiloxanes and polyethylene glycol stationary phases. For example, ILs typically exhibit extremely low volatility and high thermal stability as well as the capability of remaining in the liquid state over a wide temperature range. They can be designed to exhibit low column bleed, longer lifetimes, as well as extended operation temperature ranges when used as stationary phases. In addition, ILs are capable of undergoing multiple solvation interactions thereby imparting unique selectivities towards a wide range of molecules with different functional groups. Moreover, the tunability of ILs allows for relatively easy chemical modification of the IL structures, resulting not only in enhanced thermal stability, but tuneable solvation properties and separation selectivity. Currently, the reported modifications include the cation and anion

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combination [6,7], introduction of desired functional groups to the IL [8,9], development of dicationic and tricationic ILs [10–12], as well as polymerization [13–16]. Therefore, IL structural modifications result in unique solvation properties that have instigated the evaluation of new classes of functionalized ILs that consist of more exotic cation and anion combinations.

The solvation parameter model [17], developed by Abraham and co-workers, has been successfully employed to evaluate the solvation properties for a wide class of ILs [6–16,18]. The solvation parameter model, shown in Eq. (1), is a linear free-energy relationship that describes the contribution of individual solvation interactions of a solvent by examining solute/solvent interactions.

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

According to Eq. (1), $\log k$ is the solute retention factor and is determined by measuring the retention time of the analyte and dead volume of the chromatographic column. The solute descriptors (E , S , A , B , L) are probe-specific parameters that have been determined for many molecules [17]. They are defined as follows: E , the excess molar refraction calculated from the solute's refractive index; S , the solute dipolarity/polarizability; A , the solute hydrogen bond acidity; B , the solute hydrogen bond basicity; and L , the solute gas hexadecane partition coefficient determined at 298 K. The system constants (e , s , a , b , l) are used to characterize the strength of each solvation interaction and are defined as: e , a measure of the IL to interact with π and nonbonding electrons of the solute; s , the dipolarity/polarizability of the IL; a , a measure of the IL hydrogen bond basicity; b , the hydrogen bond acidity of the IL; and l describes the IL dispersion forces. The system constants are attained through multiple linear regression analysis of the $\log k$ term and the five solute descriptors. The intercept term, c , can be used to determine and verify the phase ratio of the column.

In this study, a total of fifteen ILs containing different functionalized cations (i.e., pyridinium, imidazolium, ammonium, morpholinium, piperidinium, and pyrrolidinium) as well as various counter anions, namely tris(pentafluoroethyl)trifluorophosphate [FAP⁻], bis[(trifluoromethyl)sulfonyl]imide [NTf₂⁻], thiocyanate [SCN⁻], tricyanomethide [C(CN)₃⁻], tetracyanoborate [B(CN)₄⁻], and bis[oxalato(2-)]borate [BOB⁻], were studied for the first time as gas chromatographic stationary phases. It is important to expand the IL-based stationary phase library with ILs containing different cation functional groups, cation types, or counter anions, since a fundamental understanding of the relationship between the IL structures and the resulting solvation properties will allow for the selection of ideal ILs for specific separations. In this study, the solvation parameter model was used to investigate the change of solvation interactions with the IL stationary phase composition. The effect of the cation/anion composition on the system constants, retention factors, and selectivity for selected solute molecules was evaluated and discussed. This report contains one of the most comprehensive examinations to date of IL solvation interactions consisting of a large number of ILs with varied cation/anion composition.

2. Experimental

2.1. Materials

A total of fifteen ILs with varied cation and anion composition were employed in this study. Nine FAP-based ILs, namely *N*-hexylpyridinium FAP, *N*-hexyl-4-(*N,N'*-dimethylamino)pyridinium FAP, *N*-hydroxypropylpyridinium FAP, 1-ethyl-3-methylimidazolium FAP, 1-methoxyethyl-3-methylimidazolium FAP, methoxyethyl-dimethyl-ethylammonium FAP, 1-methoxyethyl-1-methylmorpholinium FAP, 1-methoxyethyl-1-

methylpiperidinium FAP, and 1-methoxypropyl-1-methylpiperidinium FAP, as well as 1-butyl-1-methylpyrrolidinium SCN, 1-butyl-1-methylpyrrolidinium C(CN)₃, 1-butyl-1-methylpyrrolidinium B(CN)₄ and 1-butyl-1-methylpyrrolidinium BOB, were provided by Merck KGaA (Darmstadt, Germany). Hexyltrimethylammonium bis[(trifluoromethyl)sulfonyl]imide (NTf₂) and 1-propyl-1-methylpiperidinium bis[(trifluoromethyl)sulfonyl]imide were prepared according to previous literature precedence [19]. The identity of each IL was confirmed with ¹H-NMR spectroscopy and ESI mass spectrometry. These spectra are included as [Supplementary material](#).

Forty-six probe molecules with varied functional groups were selected for the characterization of the IL-based GC stationary phases using the solvation parameter model. Acetic acid, methyl caproate, naphthalene, and propionic acid were purchased from Supelco (Bellefonte, PA, USA). Bromoethane, butyraldehyde, and 2-nitrophenol were purchased from Acros Organics (Morris Plains, NJ, USA). 1-Butanol, *N,N*-dimethylformamide, ethyl acetate, 2-propanol, and toluene were purchased from Fisher Scientific, and *p*-cresol, *m*-xylene, *o*-xylene, and *p*-xylene were purchased from Fluka (Steinheim, Germany). Cyclohexanol was purchased from J.T. Baker (Phillipsburg, NJ, USA); ethylbenzene was from Eastman Kodak Company (Rochester, NJ, USA); and acetophenone, aniline, benzaldehyde, benzene, benzonitrile, benzyl alcohol, 1-bromohexane, 1-bromooctane, 2-chloroaniline, 1-chlorobutane, 1-chlorohexane, 1-chlorooctane, cyclohexanone, 1,2-dichlorobenzene, 1,4-dioxane, 1-iodobutane, nitrobenzene, 1-nitropropane, 1-octanol, octylaldehyde, 1-pentanol, 2-pentanone, phenetole, phenol, propionitrile, pyridine, pyrrole, and 1-decanol were purchased from Sigma–Aldrich (St. Louis, MO, USA). All probe molecules were used as received. Methylene chloride was purchased from Fisher Scientific. Untreated fused silica capillary tubing (0.25 mm I.D.) was obtained from Supelco.

2.2. Methods

All ionic liquids were placed under vacuum at 50 °C to remove any excess water. Seven meter untreated fused silica capillary columns were coated by the static method at 40 °C. All coating solutions contained 0.45% (w/v) of the studied IL in methylene chloride. All coated columns were conditioned from 30 to 110 °C at 1 °C/min and held for 1 h, using a constant helium flow at a rate of 1.0 mL/min. Column efficiency was determined using naphthalene at 100 °C. All coated columns had efficiencies of at least 2000 plates per meter. Column efficiencies were monitored by recording the retention times of the probe molecules at three temperatures to ensure that the stationary phase did not change throughout the characterization experiment.

The forty-six probe molecules and their corresponding solute descriptors used in this study are provided as [Supplementary material](#). All probe molecules were dissolved in methylene chloride and injected separately at three temperatures, namely 50, 80, and 110 °C. It should be noted that probe molecules that interacted weakly with the IL eluted with the solvent peak, especially at higher temperatures. Meanwhile, other probes that exhibited strong interactions with the stationary phase were retained in the column for 3 h or longer. Therefore, not all 46 probes could be subjected to multiple linear regression analysis at all temperatures examined. All separations were performed using a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector. Helium was used as the carrier gas with a flow rate of 1.0 mL/min. The injector and detector were held at 250 °C. The detector makeup flow of helium was maintained at 23 mL/min, the hydrogen flow at 40 mL/min, and the air flow rate at 450 mL/min. Methane was used to measure the dead volume of each column at the three different temperatures. Multiple linear

regression analysis and statistical calculations were performed using the program Analyze-it (Microsoft, USA).

3. Results and discussion

System constants of the fifteen ILs were determined at three different temperatures (50, 80, 110 °C) using the solvation parameter model. The ILs were carefully chosen to examine the effect of the cation and anion on the resulting system constants. Fig. 1 shows the structures of the ILs evaluated in this study as well as the numbering system used to refer to the ILs throughout this manuscript. Nine of the ILs contain various cations paired with the FAP⁻ anion, while two of the ILs contain an ether functionalized cation paired with the NTf₂⁻ anion. To further examine the effect of the anion on the system constants, four ILs containing the pyrrolidinium cation paired with various anions, namely, C(CN)₃⁻, SCN⁻, BOB⁻, and B(CN)₄⁻, are included in this study.

Table 1 lists the system constants of the fifteen ILs evaluated in this study. For most of the examined ILs, nearly all of the system constants decrease smoothly with increasing temperature. In the case of the *e* system constant, the values tend to drop for most ILs with increasing temperature but do not always appear to follow a consistent trend. All generated models were statistically reliable according to the acceptable standard deviation value for each system constant, high correlation coefficients of the regression line, and satisfactory Fischer coefficients.

3.1. Effect of cation functional group on system constants

In general, the hydrogen bond acidity of unfunctionalized ILs largely depends on the nature of cation and can be regulated by the anion [6,20]. It was reported previously that unique solvation interactions, most importantly, the significantly enhanced hydrogen bond basicity, were observed when sulfone and sulfoxide functionalities were introduced into the cationic moiety of imidazolium-based ILs [21]. In another example, a study of

four functionalized FAP-based ILs revealed that the hydrogen bond basicity, hydrogen bond acidity, and dipolarity of ILs can be modified by introducing alkyl, amino, ester, and hydroxyl functional groups to the ILs [9]. In this study, the system constants of five FAP-based pyridinium and imidazolium ILs (1, 2, 3, 4, and 5 in Fig. 1) were determined and compared in order to further evaluate the effect of the cation functional group on the system constants of the resulting ILs.

ILs 1 and 2 contain pyridinium cations and FAP⁻ anions, and are distinguished from each other by the presence of the dimethylamino moiety in the *para* position of the pyridinium cation (IL 2). The introduction of the dimethylamino group yielded a slight increase in the hydrogen bond basicity (*a* term) at 50 °C. This may be due to the availability of the lone electron pair from the tertiary amine group to interact with proton-donating solute molecules. Dipolar (*s* term) and hydrogen bond acidity (*b* term) interactions were higher on IL 1 while IL 2 was slightly more cohesive.

IL 1 contains a hexyl substituent while IL 3 possesses hydroxyl functionality appended to the pyridinium cation. A two-fold increase in hydrogen bond acidity at 50 °C was observed on IL 3 due to the enhanced proton-donating capability resulting from the hydroxyl group. This observation correlated well with a previous study which revealed that hydroxyl-functionalized ILs exhibited increased hydrogen bond acidity compared to their unfunctionalized analogues [9]. The presence of the hydroxyl moiety also yielded a slight increase in the hydrogen bond basicity but provided no significant changes to the overall dipolarity. IL 1 was more cohesive due to the longer alkyl chain substituent.

A comparison between two imidazolium-based ILs, IL 4 and IL 5, revealed that the presence of the ether functionality resulted in a slight increase in the hydrogen bond basicity at 50 °C. This can be explained by the enhanced interaction of the lone pair of electrons from the ether group with proton donating solutes, which results in increased retention of acidic solute molecules including acids and alcohols. All the other system constants remained largely unchanged.

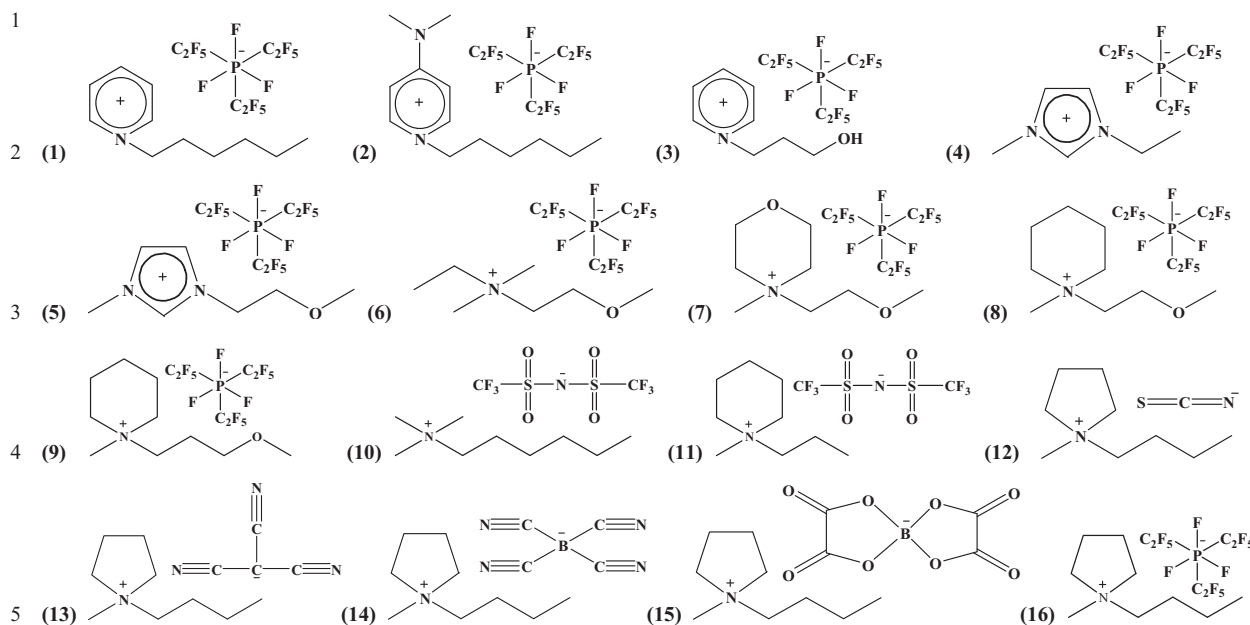


Fig. 1. Structures and numbering system of ILs examined in this study. (1) N-hexylpyridinium FAP, (2) N-hexyl-4-(N,N'-dimethylamino)pyridinium FAP, (3) N-hydroxypropylpyridinium FAP, (4) 1-ethyl-3-methylimidazolium FAP, (5) 1-methoxyethyl-3-methylimidazolium FAP, (6) methoxyethyl-dimethyl-ethylammonium FAP, (7) 1-methoxyethyl-1-methylmorpholinium FAP, (8) 1-methoxyethyl-1-methylpiperidinium FAP, (9) 1-methoxypropyl-1-methylpiperidinium FAP, (10) hexyl-trimethylammonium NTf₂, (11) 1-propyl-1-methylpiperidinium NTf₂, (12) 1-butyl-1-methylpyrrolidinium SCN, (13) 1-butyl-1-methylpyrrolidinium C(CN)₃, (14) 1-butyl-1-methylpyrrolidinium B(CN)₄, (15) 1-butyl-1-methylpyrrolidinium BOB, (16) 1-butyl-1-methylpyrrolidinium FAP.

Table 1
System constants of functionalized IL-based stationary phases examined in this study.

IL No	IL stationary phase/temperature (°C)	System constants ^a								R ²	F
		c	e	s	a	b	l	n			
1	N-Hexylpyridinium tris(pentafluoroethyl)trifluorophosphate										
	50	-2.69	0.12 (0.09)	1.71 (0.11)	0.73 (0.09)	0.82 (0.14)	0.60 (0.02)	38	0.98	401	
	80	-2.76	0.24 (0.07)	1.47 (0.09)	0.55 (0.08)	0.79 (0.12)	0.50 (0.02)	39	0.99	513	
	110	-2.85	0.21 (0.06)	1.39 (0.08)	0.47 (0.06)	0.66 (0.11)	0.42 (0.02)	37	0.99	464	
2	N-Hexyl-4-(N',N'-dimethylamino)pyridinium tris(pentafluoroethyl)trifluorophosphate										
	50	-2.62	0.24 (0.09)	1.61 (0.11)	0.86 (0.09)	0.57 (0.13)	0.63 (0.02)	40	0.98	406	
	80	-2.77	0.30 (0.08)	1.44 (0.09)	0.65 (0.08)	0.50 (0.12)	0.54 (0.02)	41	0.99	470	
	110	-2.79	0.26 (0.06)	1.32 (0.08)	0.50 (0.07)	0.41 (0.10)	0.46 (0.02)	40	0.99	455	
3	N-Hydroxypropylpyridinium tris(pentafluoroethyl)trifluorophosphate										
	50	-2.89	0.28 (0.08)	1.76 (0.11)	1.01 (0.11)	1.78 (0.14)	0.50 (0.02)	33	0.99	527	
	80	-3.06	0.23 (0.07)	1.71 (0.09)	0.84 (0.08)	1.44 (0.11)	0.43 (0.02)	34	0.99	591	
	110	-3.16	0.13 (0.07)	1.66 (0.09)	0.66 (0.08)	1.20 (0.12)	0.37 (0.02)	33	0.99	463	
4	1-Ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate										
	50	-2.82	0.17 (0.08)	1.91 (0.10)	0.89 (0.09)	0.89 (0.13)	0.51 (0.02)	39	0.99	469	
	80	-2.85	0.15 (0.06)	1.74 (0.08)	0.70 (0.07)	0.72 (0.10)	0.42 (0.02)	38	0.99	547	
	110	-3.32	0.11 (0.07)	1.74 (0.09)	0.64 (0.07)	0.66 (0.12)	0.41 (0.02)	35	0.99	417	
5	1-Methoxyethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate										
	50	-2.78	0.05 (0.09)	1.96 (0.11)	1.09 (0.10)	0.89 (0.14)	0.53 (0.02)	43	0.98	392	
	80	-2.82	0.06 (0.07)	1.78 (0.09)	0.86 (0.08)	0.73 (0.12)	0.43 (0.02)	42	0.98	401	
	110	-2.87	0.06 (0.07)	1.61 (0.09)	0.68 (0.07)	0.65 (0.11)	0.37 (0.02)	41	0.98	383	
6	Methoxyethyl-dimethyl-ethylammonium tris(pentafluoroethyl)trifluorophosphate										
	50	-2.79	0.09 (0.08)	1.97 (0.10)	0.91 (0.08)	0.85 (0.13)	0.53 (0.02)	38	0.99	458	
	80	-2.80	0.13 (0.07)	1.68 (0.09)	0.67 (0.08)	0.76 (0.12)	0.44 (0.02)	39	0.99	453	
	110	-2.91	0.10 (0.06)	1.62 (0.08)	0.62 (0.07)	0.64 (0.11)	0.37 (0.02)	38	0.98	419	
7	1-Methoxyethyl-1-methylmorpholinium tris(pentafluoroethyl)trifluorophosphate										
	50	-2.83	0.10 (0.09)	2.05 (0.11)	1.02 (0.10)	0.86 (0.14)	0.51 (0.02)	40	0.98	375	
	80	-2.85	0.10 (0.07)	1.87 (0.09)	0.81 (0.08)	0.70 (0.11)	0.42 (0.02)	39	0.98	432	
	110	-2.93	0.10 (0.07)	1.71 (0.08)	0.68 (0.07)	0.63 (0.10)	0.35 (0.02)	38	0.98	408	
8	1-Methoxyethyl-1-methylpiperidinium tris(pentafluoroethyl)trifluorophosphate										
	50	-2.65	0.16 (0.09)	1.82 (0.11)	0.95 (0.10)	0.58 (0.14)	0.56 (0.02)	40	0.98	372	
	80	-2.70	0.16 (0.08)	1.65 (0.10)	0.74 (0.08)	0.46 (0.12)	0.46 (0.02)	38	0.98	356	
	110	-2.81	0.17 (0.06)	1.52 (0.08)	0.58 (0.06)	0.43 (0.10)	0.40 (0.02)	38	0.98	416	
9	1-Methoxypropyl-1-methylpiperidinium tris(pentafluoroethyl)trifluorophosphate										
	50	-2.63	0.28 (0.09)	1.77 (0.11)	1.25 (0.10)	0.73 (0.16)	0.53 (0.02)	38	0.98	392	
	80	-2.80	0.23 (0.08)	1.66 (0.10)	0.93 (0.08)	0.67 (0.14)	0.45 (0.02)	38	0.98	406	
	110	-2.79	0.25 (0.06)	1.46 (0.08)	0.74 (0.06)	0.59 (0.10)	0.37 (0.01)	37	0.99	558	
10	Hexyl-trimethylammonium bis((trifluoromethyl)sulfonyl)imide										
	50	-2.77	0	1.90 (0.10)	2.00 (0.09)	0.45 (0.12)	0.59 (0.02)	42	0.99	503	
	80	-2.78	0	1.73 (0.08)	1.68 (0.07)	0.37 (0.10)	0.48 (0.02)	43	0.99	584	
	110	-2.93	0	1.66 (0.08)	1.49 (0.06)	0.31 (0.10)	0.41 (0.02)	40	0.99	474	
11	1-Propyl-1-methylpiperidinium bis((trifluoromethyl)sulfonyl)imide										
	50	-2.76	0.28 (0.09)	1.87 (0.11)	2.11 (0.10)	0.35 (0.14)	0.55 (0.02)	41	0.98	439	
	80	-2.85	0.30 (0.08)	1.77 (0.10)	1.86 (0.09)	0.26 (0.13)	0.45 (0.02)	42	0.98	411	
	110	-2.92	0.27 (0.07)	1.63 (0.08)	1.60 (0.07)	0.21 (0.10)	0.39 (0.02)	40	0.99	488	
12	1-Butyl-1-methylpyrrolidinium thiocyanate										
	50	-3.03	0.44 (0.10)	2.21 (0.12)	4.40 (0.17)	0.15 (0.16)	0.54 (0.03)	34	0.99	384	
	80	-3.03	0.41 (0.09)	2.14 (0.11)	4.10 (0.11)	0	0.42 (0.02)	36	0.99	538	
	110	-3.05	0.51 (0.08)	1.98 (0.10)	3.60 (0.11)	0.10 (0.13)	0.31 (0.02)	34	0.99	418	
13	1-Butyl-1-methylpyrrolidinium tricyanomethide										
	50	-2.58	0.18 (0.08)	2.07 (0.09)	3.17 (0.09)	0.16 (0.11)	0.56 (0.02)	34	0.99	439	
	80	-2.87	0.28 (0.07)	1.99 (0.09)	2.81 (0.09)	0.24 (0.12)	0.47 (0.01)	43	0.99	656	
	110	-2.86	0.28 (0.07)	1.82 (0.08)	2.43 (0.07)	0.20 (0.10)	0.39 (0.02)	43	0.99	723	
14	1-Butyl-1-methylpyrrolidinium tetracyanoborate										
	50	-2.48	0.11 (0.08)	1.97 (0.09)	2.25 (0.10)	0.29 (0.12)	0.57 (0.02)	36	0.98	385	
	80	-2.62	0.22 (0.08)	1.76 (0.09)	1.95 (0.08)	0.34 (0.12)	0.47 (0.02)	43	0.99	527	
	110	-2.71	0.21 (0.07)	1.67 (0.07)	1.76 (0.07)	0.26 (0.10)	0.40 (0.02)	41	0.99	544	
15	1-Butyl-1-methylpyrrolidinium bis(oxalato(2-))borate										
	50	-3.08	0.11 (0.09)	2.46 (0.12)	2.45 (0.09)	0.16 (0.13)	0.55 (0.02)	37	0.99	491	
	80	-3.06	0.16 (0.07)	2.16 (0.10)	2.04 (0.07)	0.18 (0.11)	0.45 (0.02)	38	0.99	582	
	110	-3.06	0.17 (0.07)	1.97 (0.09)	1.80 (0.06)	0.15 (0.10)	0.38 (0.02)	36	0.99	536	
16	1-Butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate [†]										
	50	-2.86	0.21 (0.08)	1.61 (0.11)	0.85 (0.08)	0.68 (0.14)	0.54 (0.02)	35	0.99	404	
	80	-3.04	0.21 (0.08)	1.49 (0.10)	0.67 (0.07)	0.66 (0.13)	0.47 (0.02)	34	0.99	403	
	110	-3.22	0.18 (0.07)	1.44 (0.09)	0.56 (0.06)	0.58 (0.12)	0.42 (0.02)	34	0.99	436	

n: Number of probe analytes subjected to multiple linear regression; R²: Correlation coefficient; F: Fischer coefficient.

^a System constants: e = non-bonding and π -electron interactions, s = dipolarity, a = hydrogen bond basicity, b = hydrogen bond acidity, l = dispersion forces.

[†] Data obtained from Ref. [9].

3.2. Effect of cation type on system constants

ILs **5**, **6**, **7**, **8**, and **9** possess FAP⁻ anions and contain an ether functional group appended to imidazolium, ammonium, mor-

pholinium, and piperidinium cations, respectively. A comparison between these ILs allows for an elucidation into the effect of the cation type on the system constants for the corresponding ILs. The two piperidinium-based ILs, IL **8** and IL **9**, showed stronger

non-bonding and π -electron interactions than the other three studied ILs at 50 °C. IL **7** exhibited the highest dipolarity while the lowest values were produced by the two piperidinium-based ILs. The hydrogen bond basicities for most of the ILs did not change significantly except for IL **9** which exhibited a hydrogen bond basicity of 1.25 at 50 °C. The hydrogen bond acidities of ILs containing imidazolium, ammonium, and morpholinium cations were similar to each other and higher than those of the piperidinium-based ILs. Dispersion interactions did not appear to be significantly influenced by the cation type.

In another comparison, the difference between the system constants of ammonium and piperidinium-based ILs can be examined by comparing the system constants of ILs **10** and **11**, which both possess the NTf_2^- anion. When the cation was switched from ammonium to piperidinium, IL **11** exhibited enhanced non-bonding and π -electron interactions in addition to slightly higher hydrogen bond basicity at 50 °C, while a small drop of the hydrogen bond acidity was observed. IL **10** exhibited higher dispersive interactions due to its longer alkyl chain substituent. The dipolarities of these two ILs were nearly identical.

3.3. Effect of anion on system constants

It is widely recognized that the dipolarity and hydrogen bond basicity of unfunctionalized ILs are largely determined by the nature of the counter anion [6]. In this study, a pyrrolidinium-based cation was paired with different counter anions, namely SCN^- , $\text{C}(\text{CN})_3^-$, $\text{B}(\text{CN})_4^-$, and BOB^- , to form ILs **12**, **13**, **14**, and **15**, respectively. The system constants of the ILs were examined and compared with that of a corresponding FAP-containing IL (IL **16** in Fig. 1, data obtained from [9]). ILs consisting of cyano-containing anions (i.e. ILs **12**, **13**, and **14**) all exhibited significantly increased dipolarity and hydrogen bond basicity when compared to IL **16**. Interestingly, the dipolarity and hydrogen bond basicity appears to be correlated with the number of cyano-moieties contained in the anion. For example, compared to IL **16**, the hydrogen bond basicity was 2.6-fold higher on IL **14** (containing the $\text{B}(\text{CN})_4^-$ anion), 4.4-fold higher on IL **13** (paired with the $\text{C}(\text{CN})_3^-$ anion), and 5.2-fold higher on IL **12** (possessing the SCN^- anion) at 50 °C. Correspondingly, IL **16** exhibited higher hydrogen bond acidity than the three comparative ILs. The presence of the SCN^- anion resulted in the strongest non-bonding and π -electron interactions at 50 °C, followed by ILs **16** and **13**. No significant differences in cohesive forces were observed when comparing these three cyano-containing ILs to each other or to IL **16**.

ILs **14** and **15** contain the $\text{B}(\text{CN})_4^-$ and BOB^- anions, respectively. Compared to IL **16**, ILs **14** and **15** yielded increased dipolar and hydrogen bond basicity interactions. For example, a 1.5-fold increase in dipolarity and a 2.9-fold increase in hydrogen bond basicity were observed for IL **15** relative to IL **16**. Non-bonding and π -electron interactions and hydrogen bond acidity were higher on IL **16** compared to the borate-containing ILs. Dispersion interactions were largely unchanged.

3.4. Effect of IL stationary phase composition on solute molecule retention behavior

Structural tunability is an interesting and unique property exhibited by IL-based stationary phases which allows for the modulation of solute retention. Table 2 shows the retention factors for selected solute molecules on three FAP-based IL stationary phases containing pyridinium cations at 80 °C. A wide variety of analytes, including alcohols, aromatics, and haloalkanes, exhibited increased retention on IL **2**. This is presumably due to the presence of the lone pair electrons from the tertiary amine group as well as the enhanced cohesive interactions of IL **2**. Due to the presence of the hydroxyl

Table 2

Comparison of retention factors for selected solute molecules on stationary phases composed of ILs containing functionalized pyridinium cations and FAP^- anion at 80 °C.

Cation functionality Probe molecule	Alkyl IL 1	Tertiary amine IL 2	Hydroxyl IL 3
Benzyl alcohol	27.6	32.7	36.9
<i>p</i> -Cresol	26.6	41.1	29.0
1-Decanol	22.3	31.6	14.5
Benzonitrile	17.8	22.2	14.3
Benzaldehyde	12.7	15.8	10.6
Ethyl phenyl ether	6.7	10.0	3.7
2-Chloroaniline	41.0	66.8	28.1
Octylaldehyde	6.3	7.4	3.6
1-Bromooctane	3.0	5.0	1.3
Pyridine	2.3	3.1	4.6
Toluene	0.9	1.3	0.4
Ethyl benzene	1.5	2.1	0.7
<i>o</i> -Xylene	2.2	3.2	1.1
Naphthalene	48.6	89.5	23.4

group, analytes such as benzyl alcohol and pyridine retained longer on IL **3**, which can be rationalized by the enhanced hydrogen bond acidity and basicity of IL **3**. Table 3 compares the retention factors of selected solutes on ILs **4** and **5** which contain imidazolium cations with the FAP^- anion. A comparison of retention factors for solute molecules on ILs **4** and **5** revealed that the switch of the alkyl substituent with an ether functionality produced higher retention of proton donating solute molecules. For example, compared to IL **4**, the retention factor of propionic acid was enhanced 60% when the separation was performed on IL **5** stationary phase. This is due to the slightly higher hydrogen bond basicity of IL **5** resulting from the presence of the lone pair of electrons from the ether group.

Compared to the cation functional group, the cation type was found to have only a moderate effect on the retention behavior of many solute molecules. As shown in Table 4, different analytes, including acids, alcohols, aldehydes, and substituted aromatic compounds, exhibited varied retention factors when subjected to separation on ILs containing different types of cations. Proton donating solutes such as *p*-cresol and phenol retained longer on IL **9**, due to its stronger hydrogen bond basicity. Basic solute molecules, such as *N,N*-DMF, exhibited higher retention factors on ILs **5**, **6**, and **7**, due to the fact that the imidazolium, ammonium, and morpholinium-based ILs possess higher hydrogen bond acidity than the ILs containing the piperidinium cation. The retention factors for selected solute molecules on ILs **10** and **11** are shown as Supplementary data in Table S-2. Similarly, it was observed that basic solutes exhibited higher retention on IL **10** due to its slightly enhanced hydrogen bond acidity, while IL **11** exhibited longer retention for acidic molecules due to its moderately improved

Table 3

Comparison of retention factors for selected solute molecules on stationary phases composed of ILs containing functionalized imidazolium cations and FAP^- anion at 80 °C.

Cation functionality Probe molecule	Alkyl IL 4	Ether IL 5
1-Bromooctane	1.2	1.6
Ethyl phenyl ether	3.5	4.3
Cyclohexanol	1.7	2.3
1-Decanol	8.7	12.7
Benzyl alcohol	18.7	24.2
Propionic acid	1.0	1.6
Octylaldehyde	3.0	4.0
Methyl caproate	1.7	2.3
<i>N,N</i> -DMF	19.6	24.5
Pyridine	1.5	2.0
2-Chloroaniline	21.1	26.5
Benzonitrile	10.9	13.8

Table 4
Comparison of retention factors for selected solute molecules on stationary phases composed of ILs containing various cation types with FAP⁻ anion at 80 °C.

Cation Probe molecule	Imidazolium IL 5	Ammonium IL 6	Morpholinium IL 7	Piperidinium IL 8	Piperidinium IL 9
1-Bromohexane	0.5	0.5	0.4	0.7	0.7
Propionic acid	1.6	1.3	1.6	1.4	2.2
<i>p</i> -Cresol	22.9	18.9	19.1	26.3	32.5
Phenol	13.0	10.8	11.0	14.5	18.8
Benzyl alcohol	24.2	21.6	24.8	26.3	27.7
1-Octanol	4.4	4.2	3.5	4.9	5.2
Octylaldehyde	4.1	3.9	3.4	4.6	4.3
<i>p</i> -Xylene	0.9	1.0	0.8	1.4	1.3
Ethyl phenyl ether	4.3	4.1	3.6	5.7	5.3
Benzonitrile	13.8	13.0	12.9	15.0	13.6
2-Chloroaniline	24.5	24.7	26.8	36.1	35.0
N,N-DMF	24.5	22.9	26.9	19.4	21.8

hydrogen bond basicity. The exception occurs for aniline, which exhibited increased retention on IL 11, presumably due to the significantly enhanced non-bonding and π -electron interactions of IL 11.

The solvation properties of ILs possessing cyano- and borate-containing anions make them exceptionally interesting stationary phases for GC separations. Table 5 shows the comparison of retention factors for selected solute molecules on ILs 12, 13, 14, and 15 at 80 °C. For comparison purposes, the retention factors for the same analytes on IL 16 are also included. The higher dipolarity and hydrogen bond basicity of ILs 12, 13, 14, and 15 resulted in greater retention of proton-donating molecules (i.e. alcohols and acids). For instance, the retention factor of propionic acid increased from 4.3 on IL 15 to 98.8 on IL 12. The retention behavior of other molecules was also greatly affected by the counter anion. The retention factor of octylaldehyde experienced a 150% increase on IL 14 and a 92% increase on IL 13 but a 37% decrease on IL 12 when compared to IL 15. Compared to IL 16, a wide variety of solute molecules including acids, alcohols, ketones, and substituted aromatics experienced changes in retention behavior when the separation was performed using ILs possessing cyano- and borate-containing anions due to the significantly enhanced dipolarity and hydrogen bond basicity. For example, the retention factor of 2-chloroaniline increased from 14.8 on IL 16 to 246.4 on IL 12.

3.5. Effect of IL stationary phase composition on solute pair separation selectivity

In this study, the separation selectivity of IL-based stationary phases was determined using the ratio of two solute retention factors. Table 6 lists the selectivity for selected molecule pairs on

Table 5
Comparison of retention factors for selected solute molecules on stationary phases composed of 1-butyl-1-methylpyrrolidinium cation and various counter anions at 80 °C.

Anion Probe molecule	[SCN ⁻] IL 12	[C(CN) ₃ ⁻] IL 13	[B(CN) ₄ ⁻] IL 14	[BOB ⁻] IL 15	[FAP ⁻] IL 16
1-Chlorooctane	0.9	1.9	2.4	1.1	0.7
Propionic acid	98.8	23.4	9.1	4.3	0.6
1-Butanol	3.2	2.3	1.7	0.7	0.2
Cyclohexanol	14.5	11.8	8.5	3.3	N/A
2-Pentanone	0.5	1.2	1.4	0.6	0.6
Cyclohexanone	4.2	8.7	10.2	4.2	3.0
Methyl caproate	0.8	2.1	3.0	1.1	1.2
Octylaldehyde	1.9	5.0	6.5	2.6	2.3
Ethyl phenyl ether	4.2	7.7	8.4	3.7	2.6
2-Chloroaniline	246.4	194.7	134.4	80.6	14.8
Nitrobenzene	36.4	58.9	54.3	33.8	10.7
Ethyl benzene	0.8	1.7	1.9	0.7	0.6
<i>o</i> -Xylene	1.3	2.4	2.9	1.1	0.9
Naphthalene	41.7	60.4	60.7	26.9	16.2

Table 6
Comparison of selectivity for selected solute molecules on stationary phases composed of ILs containing functionalized pyridinium cations and FAP⁻ anion at 80 °C.

Cation functionality Solute pair	Alkyl IL 1	Tertiary amine IL 2	Hydroxyl IL 3
1-Octanol/1-bromooctane	1.9	1.6	2.7
Methyl caproate/ <i>o</i> -xylene	1.3	1.1	1.6
Cyclohexanol/1-butanol	2.6	2.4	2.7
1-Decanol/1-butanol	14.9	20.8	9.5
Naphthalene/nitrobenzene	2.4	1.7	1.2
Naphthalene/acetophenone	1.4	2.1	0.73 ^a
Naphthalene/benzaldehyde	1.5	1.4	2.1
Naphthalene/ <i>o</i> -xylene	15.3	21.7	11.7
Benzonitrile/ethyl benzene	7.6	7.6	9.0

^a By definition, the value of the separation factor should be greater than unity. However, some analytes exhibited reversal of elution order making it impossible to report integers greater than unity for all stationary phase compositions.

stationary phases composed of FAP-based ILs containing the pyridinium cation at 80 °C, while Table 7 lists the selectivity for selected molecule pairs on stationary phases composed of FAP-based ILs containing the imidazolium cation at 80 °C. It was observed that the introduction of a functional group to the IL utilized as stationary phase varied the selectivities of some solutes. For example, the selectivity between 1-decanol and 1-butanol increased from 14.9 on IL 1 to 20.8 on IL 2 due to the presence of the tertiary amine group while it dropped to 9.5 on IL 3 because of the introduction of the hydroxyl functionality. A reversed elution order for some solute pairs can be obtained by simply switching the alkyl chain with an ether moiety. For example, acetic acid eluted quicker than ethyl

Table 7
Comparison of selectivity for selected solute molecules on stationary phases composed of ILs containing functionalized imidazolium cations and FAP⁻ anion at 80 °C.

Cation functionality Solute pair	Alkyl IL 4	Ether IL 5
Acetic acid/ethyl benzene	0.95 ^a	1.1
Propionic acid/benzene	1.6	2.0
Naphthalene/ <i>o</i> -xylene	10.4	11.2
Acetophenone/1-decanol	2.3	2.0
N,N-DMF/ <i>o</i> -xylene	9.8	11.2
1-Octanol/1-bromooctane	1.9	2.1
1-Octanol/nitropropane	1.3	1.5
Ethyl phenyl ether/ethyl benzene	2.6	2.8
Benzonitrile/ethyl benzene	6.8	7.9
1-Decanol/2-pentanone	4.9	6.3
Cyclohexanol/benzene	2.1	2.5
Cyclohexanol/1-butanol	2.0	2.2
1-Decanol/1-butanol	7.0	9.4

^a By definition, the value of the separation factor should be greater than unity. However, some analytes exhibited reversal of elution order making it impossible to report integers greater than unity for all stationary phase compositions.

Table 8Comparison of selectivity for selected solute molecules on stationary phases composed of ILs containing various cation types and FAP⁻ anion at 80 °C.

Cation Solute pair	Imidazolium IL 5	Ammonium IL 6	Morpholinium IL 7	Piperidinium IL 8	Piperidinium IL 9
Acetic acid/benzene	1.5	1.4	1.6	1.3	1.7
N,N-DMF/ <i>o</i> -xylene	11.2	10.1	12.9	7.1	8.3
N,N-DMF/ <i>p</i> -cresol	1.1	1.2	1.4	0.75 ^a	0.68 ^a
Naphthalene/phenol	1.8	2.3	2.1	2.5	2.0
Naphthalene/benzonitrile	1.7	2.0	1.8	2.4	2.7
Naphthalene/butyraldehyde	17.7	19.3	17.8	27.0	29.4
Phenol/cyclohexanone	1.9	1.6	1.6	2.1	3.3
Acetophenone/1-decanol	2.0	1.9	2.4	1.8	1.6
1-Decanol/1-butanol	9.4	10.2	7.8	11.3	12.2

^a By definition, the value of the separation factor should be greater than unity. However, some analytes exhibited reversal of elution order making it impossible to report integers greater than unity for all stationary phase compositions.

Table 9

Comparison of selectivity for selected solute molecules on stationary phases composed of 1-butyl-1-methylpyrrolidinium cation and various counter anions at 80 °C.

Anion Solute pair	[SCN ⁻] IL 12	[C(CN) ₃ ⁻] IL 13	[B(CN) ₄ ⁻] IL 14	[BOB ⁻] IL 15	[FAP ⁻] IL 16
Acetic acid/ethyl benzene	40.0	5.9	2.2	2.4	0.84 ^a
Propionic acid/ <i>o</i> -xylene	43.2	7.1	2.6	2.5	0.86 ^a
2-Chloroaniline/acetic acid	3.4	12.4	21.3	20.1	11.7
Benzonitrile/acetic acid	0.31 ^a	2.0	5.8	4.8	5.8
Benzaldehyde/pyrrole	0.56 ^a	1.1	1.4	1.3	1.7
2-Chloroaniline/naphthalene	5.8	3.2	2.2	2.9	0.92 ^a
Benzyl alcohol/naphthalene	N/A	4.0	2.3	2.2	0.66 ^a
Naphthalene/1-decanol	0.79 ^a	1.0	1.2	1.6	2.2
Nitrobenzene/cyclohexanol	2.6	5.1	5.8	10.5	5.8
1-Octanol/1-bromooctane	8.0	4.8	3.3	2.2	1.5
1-Decanol/1-butanol	12.9	18.5	18.8	10.2	6.5

^a By definition, the value of the separation factor should be greater than unity. However, some analytes exhibited reversal of elution order making it impossible to report integers greater than unity for all stationary phase compositions.

benzene on IL 4, while it retained longer than ethyl benzene on IL 5.

Table 8 summarizes the selectivities for selected solute pairs on five FAP-based ILs containing different cation types. The piperidinium-based ILs exhibited enhanced separation selectivities for solute pairs such as naphthalene and benzonitrile, naphthalene and butyraldehyde, as well as phenol and cyclohexanone. For certain solute pairs, a reversal of elution order was observed. For example, the selectivity for N,N-DMF and *p*-cresol was 1.1, 1.2, and 1.4 on ILs 5, 6, and 7, respectively. However, when the same separation was performed on ILs 8 and 9, *p*-cresol eluted quicker than N,N-DMF. The comparison of selectivity for selected solute molecules on two NTF₂-based ILs, ILs 10 and 11, is included as Supplementary data in Table S-3. Separation selectivities for solute pairs, for example, N,N-DMF and *o*-xylene, methyl caproate and benzene, as well as naphthalene and nitrobenzene, can be finely tuned by the switch of cation type. An example of reversed elution order can be observed for acetophenone and 1-decanol.

Table 9 shows the selectivity for selected solute molecules on stationary phases composed of the pyrrolidinium cation with various counter anions. ILs possessing the cyano- and borate-containing anions exhibited higher selectivity between proton-donating molecules (i.e. alcohols and acids) and aromatic solutes because of their enhanced dipolarity and hydrogen bond basicity. A comparison of separation selectivity between 1-octanol and 1-bromooctane revealed that the selectivity increased from 1.5 on IL 16 to 2.2 on IL 15, 3.3 on IL 14, 4.8 on IL 13, and further to 8.0 on IL 12. Several reversals of elution order were observed including the separation between acetic acid and ethyl benzene, propionic acid and *o*-xylene, benzonitrile and acetic acid, benzaldehyde and pyrrole, 2-chloroaniline and naphthalene, benzyl alcohol and naphthalene, as well as naphthalene and 1-decanol. These observations clearly demonstrate that a desirable selectivity can be achieved by choosing a specific cation and anion

combination in the make-up and composition of the IL stationary phase.

4. Conclusions

ILs have been shown to be very useful classes of GC stationary phases due to their unique and interesting properties. The chemical tunability of ILs is one of their paramount properties that can be exploited in the development of IL-based GC stationary phases. The presence of functional groups, namely dimethylamino, hydroxyl, and ether appended to the cationic moiety, produced varied system constants dependent on the nature of the employed functional group. The cation type also yielded a moderate effect on the overall solvation characteristics of the ILs. Four different cyano- and borate-containing anions were paired with a pyrrolidinium cation and the obtained system constants were compared with that of their FAP-based analogue. It was observed that the switch of counter anion produced ILs with enhanced dipolarity and hydrogen bond basicity. The 1-butyl-1-methylpyrrolidinium thiocyanate exhibited the highest hydrogen bond basicity, while the strongest dipolarity was demonstrated by the 1-butyl-1-methylpyrrolidinium bis[oxalato(2-)]borate IL. Correspondingly, all four pyrrolidinium-based ILs exhibited lower hydrogen bond acidity when compared to the analogous FAP-based IL. The dipolarity and hydrogen bond basicity of ILs consisting of cyano-containing anions were inversely proportional to the number of cyano moieties within the anion. The modulation of cation and anion combination allowed for control of solute retention as well as separation selectivity. Reversals of elution order were achieved for many solute pairs by simple IL structure modification of the employed stationary phase. This study demonstrates the utility of tailoring ILs using cation appended functional groups and/or [FAP⁻], [SCN⁻], [BOB⁻], [C(CN)₃⁻], [B(CN)₄⁻] anions to produce stationary phases that exhibit unique selectivity often

not easily observed with commercially available GC stationary phases.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2011.05.083.

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