Examination of Ionic Liquids and Their Interaction with Molecules, When Used as Stationary Phases in Gas Chromatography

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Stable room-temperature ionic liquids (RTILs) have been used as novel reaction solvents. They can solubilize complex polar molecules such as cyclodextrins and glycopeptides. Their wetting ability and viscosity allow them to be coated onto fused silica capillaries. Thus, 1-butyl-3-methylimidazolium hexafluorophosphate and the analogous chloride salt can be used as stationary phases for gas chromatography (GC). Using inverse GC, one can examine the nature of these ionic liquids via their interactions with a variety of compounds. The Rohrschneider-McReynolds constants were determined for both ionic liquids and a popular commercial polysiloxane stationary phase. Ionic liquid stationary phases seem to have a dual nature. They appear to act as a low-polarity stationary phase to nonpolar compounds. However, molecules with strong proton donor groups, in particular, are tenaciously retained. The nature of the anion can have a significant effect on both the solubilizing ability and the selectivity of ionic liquid stationary phases. It appears that the unusual properties of ionic liquids could make them beneficial in many areas of separation science.

Room-temperature ionic liquids that are air and moisture stable have been subject to an increasing number of scientific investigations.^{1–10} Their use as novel solvent systems for organic synthesis has received a good deal of attention.^{2–9} Most recently, polyether-based ionic liquids were shown to be viable solvents for electrochemical studies.¹⁰ Room-temperature ionic liquids (RTILs) resemble ionic melts of metallic salts in that, essentially, every entity in the solution is an ion. RTILs have several properties that could make them useful in a variety of chemical processes. For example, they are good solvents for many organic, inorganic,

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and polymeric substances. Many RTILs are immiscible with water and nonpolar organic solvents. They have a liquid range of 300 °C and good thermal stability. The viscosity of RTILs can vary considerably, but they have no effective vapor pressure. Finally, they are very accessible, given their ease of preparation from relatively inexpensive materials.^{3,5,11}

Given their properties, room-temperature ionic liquids could be used to advantage in a variety of separation methods. Recently they were considered as a water-immiscible phase in liquid—liquid extraction.¹¹ Because of environmental concerns with volatile organic carbon (VOC), the RTILs were considered attractive alternatives (given their lack of vapor pressure). The distribution ratios for a variety of analytes between RTIL and water were approximately an order of magnitude less than the corresponding octanol/water partition coefficients.¹¹ Although there was a rough correlation between these systems, there was a clear polarity difference.¹¹

Our interest in RTILs initially was aroused by their unusual combination of properties (i.e., volatility, viscosity, solubility, and polarity). Our interest was further enhanced when it was found that RTILs could solubilize a number of complex organic molecules of interest to the separation community. For example, the solubility of some cyclodextrins and macrocyclic antibiotics is summarized in Table 1. Also, we believed that gas—liquid chromatography (GLC) could be an attractive way to evaluate differences in various RTILs as well as their interactions with a variety of molecules. In this initial work we examine two ionic liquids by using them as stationary phases in gas—liquid chromatography. Also, they are evaluated as unusual stationary phases.

EXPERIMENTAL SECTION

Materials. 1-Methylimidazole, chlorobutane, hexafluorophosphoric acid, sodium tetrafluoroborate, squalane, anhydrous ethyl ether, anhydrous dichloromethane, and all test solutes were purchased from Aldrich (Milwaukee, WI) or Fluka Chemical Co. (Ronkonkoma, NY). HPLC grade ethyl acetate was purchased from Fisher (St. Louis, MO). Hexafluorophosphonic acid is a corrosive, toxic solution and must be handled with care.

All untreated fused silica capillary tubing (0.25-mm i.d.) was obtained from Supelco (Bellefonte, PA). DB-5 column (30 m \times 0.25-mm i.d., film thickness 0.25 μ m), obtained from J & W Scientific (Folson, CA), was cut into two pieces, each one of 15-m length.

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Table 1. Approximate Solubility of Some Compounds in [BuMIm][CI], $[BuMIm][PF_6]$, and $[BuMIm][BF_4]^a$

		solubility (%, w/w)		
compounds	[BuMIm]- [Cl]	[BuMIm]- [PF ₆]	[BuMIm]- [BF4]	
α-cyclodextrin	30	<1	<1	
β -cyclodextrin	21	<1	<1	
γ-cyclodextrin	30	<1	<1	
2,3-dimethyl-β-CD	12	<1	10	
2,6-di- <i>O</i> -methyl-β-CD	3	28	5	
permethyl-β-ČD	34	16	<1	
avoparcin	8	<1	<1	
rifamycin B	3	<1	5	
teicoplanine	${\sim}10$	<1	<1	
vancomycin	${\sim}15$	<1	<1	

 a [BuMIm][Cl] is 1-butyl-3-methylimidazolium chloride. [BuMIm][PF₆] is 1-butyl-3-methylimidazolium hexafluorophosphate and [BuMIm][BF₄] is 1-butyl-3- methylimidazolium tetrafluoroborate.

Methods. The synthesis of 1-butyl-3-methylimidazolium chloride ([BuMIm][Cl]), 1-butyl-3-methylimidazolium hexafluorophosphate ([BuMIm][PF₆]), and 1-butyl-3-methylimidazolium tetrafluoroborate ([BuMIm][BF₄]) were reported elsewhere.^{3,5,11} Briefly, [BuMIm][Cl] was prepared by adding equal amounts (0.5 mol) of 1-methylimidazole and chlorobutane to a round-bottomed flask fitted with a reflux condenser and reacting them for 48-72 h at 70 °C. The resulting viscous liquid was allowed to cool to room temperature and then was washed three times with 50-mL portions of ethyl acetate. After the last washing, the remaining ethyl acetate was removed by heating the liquid to 70 °C under vacuum. [BuMIm][PF₆] was prepared from [BuMIm][Cl] by slowly adding hexafluorophosphoric acid (0.13 mol) to a solution of [BuMIm]-[Cl] (0.1 mol) in 100 mL of water. After stirring for 12 h, the lower liquid portion was washed with water until the washings were no longer acidic. The ionic liquid was heated under vacuum at 70 °C to remove any excess water. The yield was >80%.

Before coating, 15-m fused silica capillary tubing was subjected to a sodium chloride pretreatment as reported by Huang et al.¹² The capillary then was coated by the static method using a solution of 0.15% (w/v) of the stationary phase materials in dichloromethane at 40 °C. Coated columns were flushed with dry Helium gas for 60 min, then conditioned from 30–100 °C at 0.5 °C/min. After conditioning for 8–10 h, column efficiency was tested with naphthalene at 100 °C. The [BuMIm][PF₆] column had 1900 plates/m, while the [BuMIm][Cl] column had 1700 plates/m.

All test solutes were dissolved in ethyl ether. A Hewlett-Packard model 5890 series II was used for all separations. Split injection and flame ionization detection were utilized. The injector and detector were held at 222 °C, and He was used as the carrier gas. The Kováts retention indices and the Rohrschneider-McReynolds constants were determined for these capillary columns as reported previously.¹³

RESULTS AND DISCUSSION

Table 2 lists the Kováts retention indexes of the first five McReynolds solutes on a squalane reference column, a com-

Table 2. Kovátes Indices of the Five First Test Solutes at 100 $^\circ\text{C}$

benzene	butanol	2-pen- tanone	nitro- propane	pyri- dine
656	600	629	655	700
682	666	700	748	763
730	1037	742	900	912
763	851	807	963	944
	benzene 656 682 730 763	benzene butanol 656 600 682 666 730 1037 763 851	benzene butanol 2-pen-tanone 656 600 629 682 666 700 730 1037 742 763 851 807	benzenebutanol2-pen- tanonenitro- propane6566006296556826667007487301037742900763851807963

^a The DB-5 column has a stationary phase of (5%-phenyl)-methylpolysiloxane. [BuMIm][Cl] is 1-butyl-3-methylimidazolium chloride. [BuMIm][PF₆] is 1-butyl-3-methylimidazolium hexafluorophosphate.

Table 3. Rohrschneider-McReynolds Constants of the Five First Test Solutes at 100 $^\circ\text{C}$

\mathbf{X}^{c}	\mathbf{Y}^{c}	\mathbf{Z}^{c}	U ^c	\mathbf{S}^{c}	Avc
0	0	0	0	0	0
27	66	71	93	63	64
74	437	113	245	212	216
107	251	178	308	244	218
160 ^b	188 ^b	191 ^b	283^{b}	253^{b}	215
	X ^c 0 27 74 107 160 ^b	X ^c Y ^c 0 0 27 66 74 437 107 251 160 ^b 188 ^b	$\begin{array}{ccccc} X^c & Y^c & Z^c \\ 0 & 0 & 0 \\ 27 & 66 & 71 \\ 74 & 437 & 113 \\ 107 & 251 & 178 \\ 160^b & 188^b & 191^b \end{array}$	$\begin{array}{cccccccc} X^c & Y^c & Z^c & U^c \\ \hline 0 & 0 & 0 & 0 \\ 27 & 66 & 71 & 93 \\ 74 & 437 & 113 & 245 \\ 107 & 251 & 178 & 308 \\ 160^b & 188^b & 191^b & 283^b \end{array}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

^{*a*} The DB-5 column has a stationary phase of (5%-phenyl)-methylpolysiloxane. [BuMIm][Cl] is 1-butyl-3-methylimidazolium chloride. [BuMIm][PF₆] is 1-butyl-3-methylimidazolium hexafluorophosphate. The OV-22 column has a stationary phase of phenylmethyldiphenylpolysiloxane (65% phenyl). ^{*b*} Obtained from ref 14. ^cX is benzene, Y is butanol, Z is 2-pentanone, U is nitropropane, and S is pyridine. Av is the average of the five values for each stationary phase.

mercial DB-5 bonded-phase column, and two columns containing ionic liquid stationary phases. The largest Kováts index was for butanol on the [BuMIm][Cl] column. The lowest values for all five solutes were obtained on the squalane reference column followed by the commercial DB-5 column (Table 2).

Table 3 gives the Rohrschneider-McReynolds constants of the five reference analytes on five different columns. The data for the first four stationary phases were generated in this study while the values for OV-22 [phenyl methyl diphenylpolysiloxane (65% phenyl)] were taken from the literature for the purpose of comparison.¹⁴ The average of the five Rohrschneider-McReynolds constants is sometimes used as an approximate polarity scale. However, the individual constants must be considered in order to evaluate different contributions to retention. The respective constants (Table 3) are thought to measure: dispersive interactions (X); proton donor and acceptor capabilities plus dipolar interactions (Y); dipolar interactions plus weak proton acceptor, but not proton donor capabilities (Z); dipolar interactions (U); and strong proton acceptor (but not donor) capabilities (S).¹⁴ Unlike many GLC stationary phases which have smaller variations in these constants, the ionic liquids show considerable differences (Table 3). In particular, proton donor and dipolar interactions appear to be very strong, followed by proton acceptor capabilities. Also, simply changing the nature of the anion has a significant effect on the magnitude of the individual interactions but not on the overall "average polarity" (Table 3).

Another interesting facet of the ionic liquids, when used as GLC stationary phases, is that they appear to have a dual nature. This is illustrated in Figure 1. Analytes that are relatively nonpolar

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Table 4. Comparison of Retention Factors (k) of Solutes Eluted from GLC Columns Containing Ionic Liqui	d,
Squalane, and (5%-Phenyl)-methylphenylsiloxane (DB-5) Stationary Phases ^a	

compounds	squalane	DB-5	[BuMIm]- [Cl]	[BuMIm]- [PF6]	compounds	squalane	DB-5	[BuMIm]- [Cl]	[BuMIm] [PF ₆]
-	(A) Paraffins	(100 °C)			(F) Alcohols (2	5-80 °C at 1	°C/min)	/Diols (80 º	C)
<i>n</i> -heptane	0.2	0.1	0.08	0.1	methanol	-0.17	-0.17	6.7	0.8
<i>n</i> -octane	0.5	0.3	0.2	0.3	ethanol	0.0	-0.08	6.7	1.1
<i>n</i> -nonane	1.0	0.6	0.4	0.6	<i>n</i> -propanol	0.04	0.21	10.4	2.3
<i>n</i> -decane	2.2	1.3	0.8	1.2	<i>n</i> -butanol	0.6	1.0	15.1	4.7
<i>n</i> -undecane	4.7	2.5	1.7	2.5	<i>n</i> -pentanol	2.1	2.6	16.0	8.1
<i>n</i> -dodecane	8.4	4.8	3.6	4.4	2-hexanol	3.5	3.3	19.1	8.4
<i>n</i> -dodecane	8.4	4.8	3.6	4.4	3-heptanol	8.2	5.7	20.0	12.1
					<i>n</i> -heptanol	12.0	8.2	24.1	18.1
(B) Substitute	ed Alkanes (2	5-80 °C	at 1 °C/min)	3-octanol	15.3	8.9	29.5	18.9
acetonitrile	-0.1	0.08	1.1	2.7	glycol	0.08	0.3		26.2
propionitrile	0.2	0.3	6.7	3.3	1,3-butanediol	0.6	1.2		39.2
1-chlorobutane	0.9	0.7	0.5	0.7	1,2-pentanediol	1.1	2.0		42.5
1-chloropentane	2.8	2.1	1.7	2.2					
1-chlorohexane	6.3	4.5	4.5	5.5		(F)Amines (100 °C)		
1-chlorooctane	16.5	10.9	16.7	18.1	<i>N</i> -butylamine	0.08	0.09	0.2	0.1
					1,5-dimethylhexylamine	1.3	1.0	5.1	1.1
(C) Aron	natics (Nonio	nizable)	(100 °C)		<i>n</i> -octylamine	1.8	2.0		6.3
benzene	0.8	0.7	0.7	1.2	<i>n</i> -decylamine	11.9	3.1		15.2
<i>p</i> -dichlorobenzene	2.1	1.6	1.6	2.2	aniline	1.1	1.3	37.8	12.6
<i>m</i> -dichlorobenzene	2.4	1.8	1.9	2.7	benzylmethylamine	1.7	1.6		6.5
toluene	2.8	1.7	2.0	3.0	benzylethylamine	3.4	2.0		12.7
<i>p</i> -xylene	7.3	3.2	4.9	7.2	benzylpropylamine	4.5	2.8		11.0
<i>m</i> -xylene	7.4	3.2	4.9	7.2	<i>m</i> -chloroaniline	3.3	3.3	46.8	17.5
o-xylene	8.5	3.5	6.1	8.8	<i>p</i> -chloroaniline	4.5	5.4	122.4	56.3
nitrobenzene	2.4	2.5	5.3	9.6	1-ethylpropylamine	0.2	0.04	3.1	0.6
<i>m</i> -dimethylbenzene	20.0	6.3	15.2	16.6	diethyl amine	0.6	0.5	2.0	1.0
3-chloronitrobenzene	7.0	6.1	11.2	17.3	N,N-ethyldimethylamine	1.5	1.4	13.2	8.5
4-chloronitrobenzene	7.3	6.5	15.4	21.2					
naphthalene	30.3	8.8	33.1	35.0		(G) Phenols	(100 °C)		
1,7-dimethylnaphthalene	37.2	18.5	23.2	41.3	<i>m</i> -nitrophenol	3.7	3.3		14.1
1,3-dimethylnaphthalene	39.2	18.5	24.4	43.0	2,6-dimethylphenol	3.0	2.9		18.6
1,6-dimethylnaphthalene	39.2	18.8	24.4	43.0	o-cresol	1.5	2.1		39.3
1,4-dimethylnaphthalene	43.5	20.6	27.1	47.6	phenol	0.7	1.3		45.8
1,5-dimethylnaphthalene	44.2	20.9	27.7	48.5	2,5-dimethylphenol	3.2	3.9		54.2
1,2-dimethylnaphthalene	46.3	22.4	30.2	54.1	<i>p</i> -cresol	1.6	2.5		61.0
1,8-dimethylnaphthalene	53.7	25.2	37.0	63.6	<i>m</i> -cresol	1.6	2.5		64.3
					2,3-dimethylphenol	3.5	4.8		65.8
(D) Aldehyde	es (25 °C)/An	nides (10	0 °C)/Esters	5	3,5-dimethylphenol	3.8	4.6		89.1
(30–60 °C at 0.5 °C	C/min)/Ketoi	nes (25–	60 °C at 1 °C	/min)	3,4-dimethylphenol	4.0	5.4		114.0
2-methylbutyraldehyde	0.7	1.0	0.8	1.9	<i>m</i> -chlorophenol	3.2	6.2		241.9
valeraldehyde	1.1	1.5	1.3	3.1	<i>p</i> -chlorophenol	3.2	6.2		254.5
formamide	0.0	0.2		19.7					
<i>N</i> -methylformamide	0.1	0.3	27.3	12.3	(H) (Carboxylic A	cids (100	°C)	
<i>N</i> , <i>N</i> -dimethylformamide	0.2	0.3	1.0	4.3	acetic acid	0.0	0.04		3.1
methyl acetate	0.0	0.08	0.1	0.5	propionic acid	0.07	0.13		3.8
ethyl acetate	0.2	0.4	0.3	0.9	2-chloropropionic acid	0.3	0.9		
isopropyl acetate	0.5	0.8	0.4	1.1	dichloroacetic acid		9.0		
<i>n</i> -propyl acetate	1.0	1.4	0.9	2.0	benzoic acid				
<i>n</i> -butyl acetate	3.4	3.8	2.4	4.6					
acetone	-0.1	0.0	0.2	0.9					
2-butanone	0.2	0.4	0.5	1.7					
2-pentanone	0.9	1.1	1.1	3.0					
3-chloro-2-Butanone	1.1	1.6	3.2	5.4					
4-methyl-2-Pentanone	1.7	1.9	1.7	3.9					

^a Whenever no value is reported, this indicates that the solute was not eluted under the indicated conditions.

and are not acidic nor basic, tend to separate on ionic liquid stationary phases in much the same manner (and with similar retention) as on relatively nonpolar stationary phases, such as DB-5 (see compounds 1, 2, 3, 6, and 8 in Figure 1A and B). Conversely, highly polar molecules and proton-donor molecules (particularly weak acids) have very different retention behavior (Figure 1B). These types of molecules are strongly retained by the ionic liquid stationary phases (Figure 1) and in some cases are not eluted under these test conditions (see the phenols, carboxylic acids, and diols in Table 4). Some of the larger protonacceptor analytes (i.e., the amines) also show this type of behavior, but not to the same extent as the acids. The strong proton donor and acceptor effects observed for ionic liquids in this work support a previous report by Elaiwi et al.¹⁵

Table 4 lists the retention factors for a variety of compounds on GLC columns containing two different ionic liquid stationary

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Figure 1. Chromatograms comparing the retention and separation of eight compounds on the same size GC columns (15 m \times 0.25-mm i.d.) and under identical conditions (isothermal @ 100 °C and a pressure of 9 psi). Column A is a commercial DB-5 column, and Column B utilizes the ionic liquid [BuMIm][PF₆] as the stationary phase. The test compounds are: 1, butyl acetate; 2, *n*-heptanol, 3, *p*-dichlorobenzene, 4, *o*-cresol, 5, 2,5-dimethylphenol, 6, *n*-dodecane, 7, 4-chloroaniline, and 8, *n*-tridecane.

phases as well as squalane and the DB-5 stationary phase. The more nonpolar and nonionizable compounds are listed toward the beginning of Table 4, while the ionizable and more polar compounds are listed afterward. All four GLC columns tended to have similar retention factors for the neutral, less polar compounds. The relative retention on the ionic liquid stationary phases increases with the more polar alcohols and formamids. This increase is even more dramatic for the amines and particularly the phenols and organic acids (Table 4). The observed retention behavior corresponds well with that predicted by the previously mentioned Rohrschneider-McReynolds constants. Also apparent from the data in Table 4 is that the nature of the anionic portion of the ionic liquids can have a profound effect on retention and selectivity.

Effect of the Anion. The cationic portion of both ionic liquids in this study consists of the 1-butyl-3-methylimidazolium ion (see Experimental Section and Tables 2–4). Both ionic liquids have approximately the same average polarity (see the "Average" in Table 3). However, it is clear from the data in Table 4 that there are significant differences in the chloride versus the hexafluorophosphate ionic liquids. The data shows that some classes of compounds interact more strongly with the hexafluorophosphate ionic liquid, while other classes of compounds interact more strongly with the chloride-containing ionic liquid (Table 4). Indeed, it appears that GLC may be a very useful tool to study differences in the properties of various ionic liquids as well as how they interact with molecules.

Molecules that do not contain good proton-donating or -accepting groups (e.g., aliphatic and aromatic compounds, esters, aldehydes, and ketones) are more strongly retained on the [BuMIm][PF₆] stationary phase. This is true even for the more polar haloalkanes. However, all compounds with proton-donor groups (e.g., alcohols, diols, phenols, and carboxylic acids) interact much more strongly with the chloride-containing [BuMIm][Cl] ionic liquid (Table 4). Amines also prefer the [BuMIm][Cl].

An examination of the Rohrschneider-McReynolds constants (Table 3) confirms the experimental observations in Table 4. The constant for proton-donor activity (i.e., the Y terms in Table 3) was far and away the most dominant feature of [BuMIm][Cl]. Conversely, constants for dispersive and dipolar interactions (i.e., the X and U terms in Table 3) were more prominent for [BuMIm]-[PF₆]. Clearly, GLC can be a useful tool to evaluate and compare ionic liquids. As indicated in this study, one can focus on the nature of specific anions (or cations in other instances). Such information could be useful in a number of areas other than separations, where a knowledge of salt–organic interactions and/ or relative-ion behaviors are important.

The only compounds that were retained to a greater extent on the less polar squalane and DB-5 columns than on the ionic liquid columns were the unsubstituted alkanes, the smaller chloroalkanes, and a few of the esters, aldehydes, and ketones.

CONCLUSIONS

Room-temperature ionic liquids (RTILs) act as nonpolar stationary phases when separating nonpolar analytes or somewhat polar analytes that are not proton-donor or -acceptor molecules. However, they act in the opposite manner (i.e., are highly interactive and retentive) when used to separate molecules with somewhat acidic or basic functional groups. Thus, molecules with proton-donor or -acceptor characteristics tend to be spatially resolved, as a group, from nonpolar analytes. The dual nature of ionic liquid stationary phases also is evident from the Rohrschneider-McReynolds constants. Inverse GLC also is a good way to examine the nature of different ionic liquids. It is apparent that the chloride-containing ionic liquid interacted much more strongly with proton-donor and -acceptor molecules. The hexafluorophosphate-containing ionic liquid tended to be somewhat less polar and interacted more strongly with nonpolar solutes. GLC with ionic liquids is an effective way to study differences in ions as well to study interactions between ions and organic molecules. RTILs often can solubilize complex macrocyclic molecules such as cyclodextrins and their derivatives and macrocyclic antibiotics. As a result of their novel properties, RTILs may be useful in many separation methods.

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