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Characterizing Ionic Liquids On the Basis of Multiple Solvation Interactions

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Abstract: Room-temperature ionic liquids (RTILs) are useful in many chemical applications. Recent publications have attempted to determine the polarity of RTILs using empirical solvent polarity scales. The results have indicated that most RTILs have similar polarities. Nevertheless, RTILs are capable of behaving quite differently when used as solvents in organic synthesis, matrixes in matrix-assisted laser desorption/ionization (MALDI) mass spectrometry, liquid–liquid extraction, and as stationary phases in gas chromatography. The work presented in this study uses a linear free energy approach to characterize 17 RTILs on the basis of their distinct multiple solvation interactions with probe solute molecules. This model provides data that can be used to help identify the interactions and properties that are important for specific chemical applications.

Introduction

Room-temperature ionic liquids (RTILs) have been the focus of many recent scientific investigations.^{1–21} They have been used as novel solvent systems for organic synthesis,^{3–16} liquid–liquid extraction,^{17–19} in electrochemical studies,²⁰ and as ultralow volatility liquid matrixes for matrix-assisted laser desorption/ionization (MALDI) mass spectrometry.²¹ RTILs have properties that make their application in chemical systems attractive. Some RTILs are immiscible with water and nonpolar organic solvents. They possess good thermal stability (over 300

°C) and yet possess negligible vapor pressure making them “green” solvents in regard to reducing environmental levels of volatile organic carbons (VOCs). RTILs of various viscosities can be easily prepared by simply changing the cation or anion.²² Most ionic liquids are said to have similar polarities, close to those of short chain alcohols.^{24–27} However, their solvent properties can differ considerably from one another as well as from traditional molecular solvents. Clearly, an effective means to characterize RTILs would greatly increase our understanding and effective use of these solvents.

For decades, attempts have been made to develop empirical solvent polarity scales as a means to help explain differences in solvent-mediated reaction pathways, reaction yields, synthesis product ratios, chromatographic retention, and extraction coefficients. An empirical polarity parameter was described by observing the effect of the solvent on a solvent-dependent process such as the rate of a chemical reaction or the absorption of light by a solvatochromic dye.²³ Empirical parameters of solvent polarity were then derived from the rate constants or shifts in absorption maxima. Analogous approaches have been used for RTILs. The solvatochromic effect of Reichardt’s dye²⁴ and Nile Red²⁵ as well as fluorescent probes^{26,27} and the Rohrschneider–McReynolds gas–liquid chromatography (GLC) method¹ have been used to characterize ionic liquids by obtaining a general polarity-based parameter. This “single-parameter-polarity-approach” has not been definitive for RTILs because they all seem to fall within the same narrow range of

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values.^{24–27} Yet, two different ionic liquids that have essentially identical “polarity” ratings or descriptors can produce very different results when used as solvents for organic reactions, gas–liquid chromatography, or extractions.

Clearly, a single “polarity”/“solvent strength”/“interaction” parameter is not sufficient to explain the variation in experimental results in many solvent-mediated processes. Most simple molecular solvents (hexane, for example) are limited in the number and types of solvation interactions possible with dissolved molecules. More complex solvents with additional functional groups are capable of having additional interactions with dissolved molecules. Ionic liquids are among the most complex solvents. Given their structure and diversity of functionality, they are capable of most types of interactions (e.g., dispersive, $\pi-\pi$, $n-\pi$, hydrogen bonding, dipolar, ionic/charge–charge). In every solution, there can be a number of different (in terms of type and strength) and often simultaneous solute–solvent interactions. For any given case, there will be dominant and less-substantial interactions. The various single parameter polarity scales are essentially weighted averages of all possible solute–solvent interactions. Thus, it is not surprising that these averages are similar for any given class of solvents and that they do not adequately explain many experimental observations. For example, despite the fact that the two 1-butyl-3-methyl imidazolium (BMIM) room-temperature ionic liquids ([BMIM][PF₆] and [BMIM][BF₄]) have almost identical E_{TN} values, 0.667 and 0.673, respectively,²⁴ it has been shown that these two RTILs can behave quite differently as reaction solvents.^{10,12} Recently, publications have expressed the need for quantitative parameters to describe the ionic liquids in cases where the individual interactions have a direct effect on the reaction products, product ratio, kinetics, or enzyme activity.^{10,12}

Several approaches have been proposed that allow one to examine and categorize the different solvent–solute interactions. One technique uses several different solvatochromic dyes.^{24,25} Ideally, the behavior of each dye is dominated by a specific type of molecular interaction. The Rohrschneider–McReynolds constants were originally developed to characterize liquid stationary phases for gas chromatography on the basis of several different interaction parameters.¹ They use retention parameters of different probe molecules to thoroughly characterize the liquid. Each probe molecule interacts in a specific way with the liquid. For example, *n*-butanol exhibits acidic properties in the gas state and indicates the hydrogen bonding ability of the liquid.

The solvation parameter model developed by Abraham has been used to characterize either liquid- or gas-phase interactions between solute molecules and liquid phases.^{29–33} Using this approach, we chose a large number of probe molecules capable of a plethora of interactions to characterize the RTIL. Because one probe molecule can be a measure of a specific interaction, it may be considered equivalent to one probe dye molecule, which generally measures many interactions with the RTIL.

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Therefore, a judicious choice of several distinct probe solute molecules can be used to measure all desired interactions, and some redundancy can be included as well. When characterizing RTILs by inverse GC, only small quantities (20 mg) of each RTIL are required and can be examined at different temperatures to illustrate how interactions change with temperature. This property allows for the characterization of RTILs at the higher temperatures commonly used in many organic reactions. Furthermore, the temperatures used in an inverse GC approach volatilize most impurities, including water, allowing for the evaluation of the neat relatively uncontaminated RTIL. Finally, the method uses multiple linear regression analysis (MLRA) and provides statistical treatment of all data.

The solvation model of Abraham (eq 1) is a linear free energy relationship that describes the solvation process of a solute as

$$\log k = c + rR_2 + s\pi_2^H + a\alpha_2^H + b\beta_2^H + l \log L^{16} \quad (1)$$

occurring in three stages: (1) a cavity of suitable size is created in the solvent (RTIL), (2) the solvent molecules reorganize around the cavity, and (3) the solute is introduced into the cavity, and the various solute–solvent interactions are allowed to take place.³² Each solute molecule will possess somewhat different solute–solvent interactions due to various acidic, basic, electron-donating, electron-withdrawing, and aromatic functional groups. Specific solute descriptors (see eq 1) have been defined for many molecules.²⁹ They are as follows: R_2 is an excess molar refraction calculated from the solute's refractive index; π_2^H is the solute dipolarity/polarizability; α_2^H and β_2^H are the solute hydrogen bond acidity and hydrogen bond basicity, respectively; and L^{16} is the solute gas-hexadecane partition coefficient at 298 K. For GLC experiments, the dependent variable in eq 1 can be $\log L$, $\log K$, $\log V_g$, or $\log k$ referring to the Ostwald solubility coefficient, gas–liquid partition coefficient, specific retention volume at a given column temperature, or the adjusted relative retention time, respectively.³¹

Table 1 lists the solute descriptors for 36 probe solutes used in this study. The solute retention factor, k , is determined chromatographically. Multiple linear regression analysis (MLRA) is then performed (see Experimental Section) on the set of probe molecule solute descriptors and their retention factors to determine the interaction parameter coefficients (r , s , a , b , l) used to characterize the liquid:²⁹ r is the ability of the RTIL to interact with π - and n -electrons of the solute; s is a measure of the dipolarity/polarizability of the RTIL; a defines the RTIL hydrogen bond basicity (acidic solutes will interact with a basic phase); b is a measure of the hydrogen bond acidity; and l describes dispersion forces and indicates how well the RTIL will separate homologues in any homologous series (e.g., *n*-alkanes). Collectively, the numerical magnitude of each interaction parameter describes the importance of the individual interactions and thereby characterizes the RTIL.

In this paper, we present data obtained using the solvation parameter model for 17 RTILs. Most of the ionic liquids evaluated in the study have been used as solvents in organic synthesis reactions or in other analytical uses (e.g., liquid–liquid extraction, MALDI matrixes, GC stationary phases, capillary electrophoresis (CE) run buffer additive³⁴). By using this

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Table 1. Complete List of All Probe Molecules and Their Solute Descriptors Used To Characterize Each RTIL (Data Obtained from Ref 29)

probe molecule	R_2	π_2^H	α_2^H	β_2^H	$\log L^{16}$
1,2-dichlorobenzene	0.872	0.78	0	0.04	4.518
phenol	0.805	0.89	0.6	0.31	3.766
octylaldehyde	0.16	0.65	0	0.45	4.36
valeraldehyde	0.163	0.65	0	0.45	2.851
<i>o</i> -xylene	0.663	0.56	0	0.16	3.939
<i>p</i> -xylene	0.613	0.52	0	0.16	3.839
cyclohexanol	0.46	0.54	0.32	0.57	3.758
nitrobenzene	0.871	1.11	0	0.28	4.511
<i>N,N</i> -dimethylformamide	0.367	1.31	0	0.74	3.173
<i>m</i> -xylene	0.623	0.52	0	0.16	3.839
2-pentanone	0.143	0.68	0	0.51	2.755
1-nitropropane	0.242	0.95	0	0.31	2.894
toluene	0.601	0.52	0	0.14	3.325
benzaldehyde	0.82	1	0	0.39	4.008
pyridine	0.794	0.87	0	0.62	3.003
aniline	0.955	0.96	0.26	0.53	3.993
butanol	0.224	0.42	0.37	0.48	2.601
acetic acid	0.265	0.65	0.61	0.44	1.75
1-octanol	0.199	0.42	0.37	0.48	4.619
acetophenone	0.818	1.01	0	0.49	4.501
2-chloroaniline	1.033	0.92	0.25	0.31	4.674
methyl caproate	0.08	0.6	0	0.45	3.874
benzene	0.61	0.52	0	0.14	2.786
1-hexyne	0.166	0.23	0.13	0.1	2.51
pyrrole	0.613	0.73	0.41	0.29	2.865
2-propanol	0.212	0.36	0.33	0.56	1.764
benzonitrile	0.742	1.11	0	0.33	4.039
propionitrile	0.162	0.9	0.02	0.36	2.082
1-chlorohexane	0.201	0.4	0	0.1	3.777
ethyl acetate	0.106	0.62	0	0.45	2.314
<i>p</i> -cresol	0.82	0.87	0.57	0.31	4.312
ethylphenyl ether	0.681	0.7	0	0.32	4.242
naphthalene	1.34	0.92	0	0.2	5.161
octylamine	0.187	0.35	0.16	0.61	4.52
dioxane	0.329	0.75	0	0.64	2.892
cyclohexanone	0.403	0.86	0	0.56	3.792

approach to an extensive number of ionic liquids, we can more accurately categorize the types of interactions that they are capable of and effectively delineate their similarities and differences. This information can then be used to understand the effect of different RTILs on reactions and other chemical processes. If a sufficient understanding of the molecular and ionic properties/interactions of RTILs can be obtained, we may eventually be able to pick optimal RTILs for specific applications. In addition, if specific interactions can be attributed to the cationic and/or anionic part of the RTILs, these can be mixed and matched to obtain maximum performance. RTILs are capable of undergoing a multitude of different interactions which makes them more complex and difficult to categorize than more conventional organic solvents but also provides them with a unique and potentially useful set of properties.

Experimental Section

All probe molecules (Table 1) were purchased from Aldrich (Milwaukee, WI) and were used as received. Figure 1 displays the RTILs examined in this study. Class I RTILs were prepared as previously reported in the literature.^{1,9,11,24,26} Most RTILs in this class were prepared using the BMIM chloride salt. Because of the fact that residual chloride impurities can have a large effect on the physical properties of the RTILs,³⁵ extra care was taken to ensure all other ionic liquids were free of chloride ion. Forming the desired RTIL by metathesis exchange of BMIM-Cl with the silver salt of the anion of

interest yielded a product with low levels of chloride ion. Further washes were then performed and treated with silver nitrate to detect silver chloride precipitate. Finally, purity was examined using ion chromatography to check for residual chloride ion impurities. In all cases, the residual chloride concentration was less than 1 ppm. In addition, it was observed that BMIM-SbF₆ produced small amounts of fluoride ion over time due to its sensitivity to air. Class II RTILs were prepared by dissolving ~0.5 g of the respective acid in 15 mL of methanol. After equimolar base was added, the mixture was sonicated for 5 min, then filtered, and vacuum evaporated to remove solvent. Because none of these RTILs were produced from chloride salts, the presence of contaminating chloride was not a problem.

Untreated fused silica capillary tubing (0.25-mm i.d.) was purchased from Supelco (Bellefonte, PA). Five-meter capillary columns were coated at 40 °C by the static method using a 0.24% (w/v) solution of each RTIL in dichloromethane. Coated columns were flushed with dry helium gas and conditioned overnight from 30 to 100 °C at 1 °C/min. Column efficiency was tested with naphthalene at 100 °C. All columns had efficiencies between 1700 and 2400 plates/meter. The retention time of naphthalene at 100 °C was recorded for each column before and after evaluating all probe molecules at three column temperatures to ensure that the coated layer of the RTIL had not changed during the chromatographic study.

Mixtures of probe compounds were dissolved in dichloromethane. Some probe molecules with very low boiling points (e.g., ethyl acetate, benzene, 1-hexyne) eluted with the RTIL column void volume (i.e., were unretained) at 100 °C. Obviously, they could not be included in the linear regression analysis. Conversely, at 40 °C some RTILs tenaciously retained a few other probe molecules which did not elute after 180 min.

Gas chromatographic measurements were made using a Hewlett-Packard model 6890 gas chromatograph and a Hewlett-Packard 6890 series integrator. Helium was used as the carrier gas at a column inlet pressure of 3.1 psi and flow rate of 1.0 mL/min. Split injection and flame ionization detection were utilized with injection and detection temperatures of 250 °C. Methane was used to determine the dead volume of each column at the respective temperature.

Multiple linear regression analysis (MLRA) and statistical calculations were performed using the program Analyze-it (Microsoft, USA). Figure 2 illustrates a typical regression line consisting of all probe molecules with a high correlation coefficient (0.98).

Results and Discussion

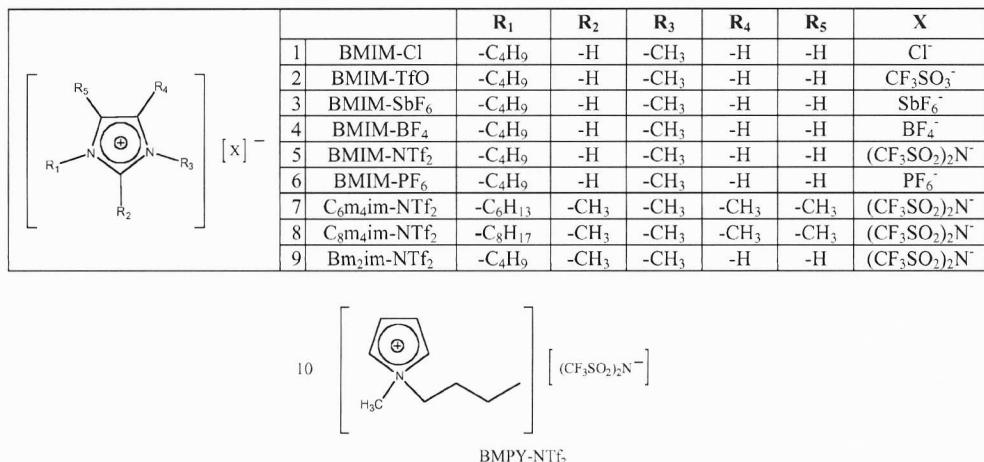
The interaction capabilities of most RTILs were evaluated at three different temperatures (40, 70, and 100 °C) using 36 probe molecules (Table 1). By examining the probe molecules on each RTIL at three different temperatures, the interaction parameters could be compared to ensure that the solvation model adequately characterized the RTILs and that the integrity of the ionic liquid had not been compromised.

Two classes of RTILs were evaluated in this study. The first class consisted of ionic liquids frequently used and reported in the literature as solvents for organic synthesis^{3–16} and for liquid–liquid extractions.^{17–19} The second class of RTILs was lower molecular weight substances previously reported in the literature as matrixes for MALDI.²¹

Table 2 lists the interaction parameters obtained for each ionic liquid. These data indicate that the most dominant interaction constants for RTILs are strong dipolarity (*s*), hydrogen bond basicity (*a*), and dispersion forces (*l*). Figure 3 is a plot of the interaction parameters for each ionic liquid at 70 °C. It allows a quick comparison of different RTILs and visualization of trends. While the dispersion forces (*l*) were nearly constant for every RTIL evaluated (Figure 3), the hydrogen bond basicity

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Class I RTILs



Class II RTILs

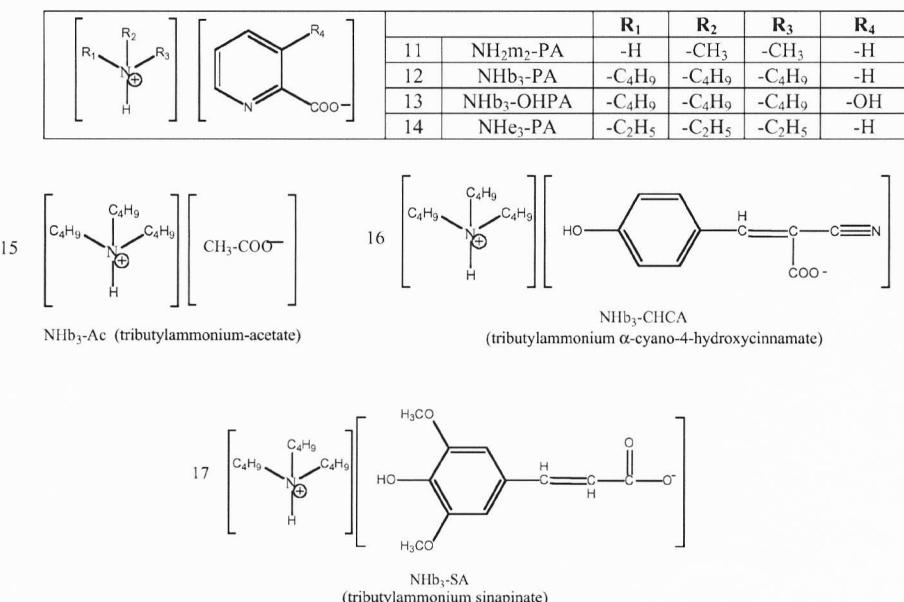


Figure 1. Structural description of RTILs evaluated in this study.

(*a*) and dipolarity (*s*) terms seemed to vary for each ionic liquid. In most cases, when the RTIL hydrogen bond basicity was very high (e.g., BMIM-Cl, BMIM-SbF₆), the RTIL hydrogen bond acidity was negative. The anionic portion of the RTIL appears to control its hydrogen bond basicity. A plot of the two dominant interaction parameters, dipolarity (*s*) and hydrogen bond basicity (*a*), is shown in Figure 4. Clearly, four groups or clusters of RTILs with similar *a* and *s* values are observed. This classification scheme is very useful in comparing the hydrogen bond basicity characteristics of the RTILs. The hydrogen bond basicity, while the most significant interaction of the RTILs, plays an important role in the RTIL's usefulness as an organic solvent and as a GLC stationary phase.

RTILs with the same cation (BMIM) and different anions exhibited different basicity and dipolarity values. However, when the same anion (NTf₂) was evaluated with different cations, the effect of the cation on hydrogen bond basicity and dipolarity was quite small (Figure 3, Table 2). Clearly, the anion

has a greater influence on the overall hydrogen bond basicity of the RTIL.

Only three of the examined Class I RTILs exhibited significant hydrogen bond acidity (*b*), with BMIM-NTf₂ exhibiting the highest value (see Figure 3). This parameter appears to be affected by both the RTIL's cation and the RTIL's anion. Also, only three RTILs (BMIM-Cl, C₈m₄im-NTf₂, C₆m₄im-NTf₂) exhibited significant ability to interact with the probe molecules via nonbonding or π -electrons, as specified by the *r*-term in eq 1. In the case of the C₈m₄im-NTf₂ and C₆m₄im-NTf₂ RTILs, each alkyl substituent on the imidazole ring inductively donates electrons to the aromatic π system. This can accentuate nonbonding to π and π to π interactions between ionic liquids and solutes that contain nonbonding and π electron systems. It appears that RTILs which have a cationic moiety with an electron-rich aromatic π -system produced stronger interactions (higher retention factors) for solute molecules capable of undergoing π - π and n- π interactions (e.g., 2-chloroaniline,

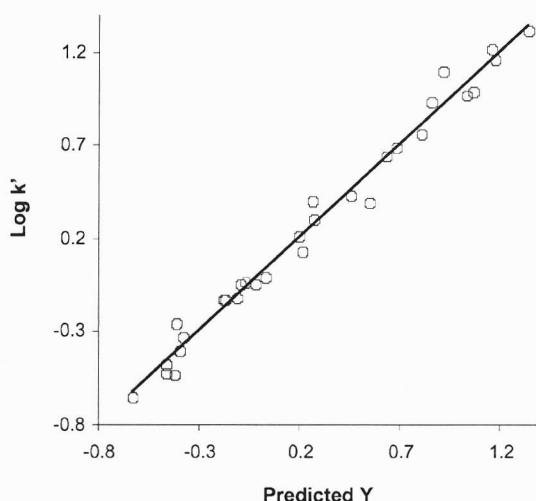


Figure 2. Multiple linear regression plot ($R^2 = 0.98$) of BMIM-PF₆ at 100 °C. The solute descriptors and retention factors of 32 solute probe molecules are fitted by MLRA to obtain each interaction parameter shown in eq 1.

p-cresol, aniline). It was also observed that the BMIM-Cl RTIL tenaciously retained these same probe molecules. Although the BMIM cation does not have the analogous electron-rich aromatic system, it appears that the chloride anion (with nonbonding electrons), in combination with the BMIM cation, forms a RTIL that exhibits significant ability to interact with π -systems of probe molecules. Similar behavior but of much smaller magnitude was observed for the BMIM-SbF₆ and BMIM-TfO salts, both of which have anions exhibiting large hydrogen bond basicity. Most other RTILs exhibited zero or negative *r* values. It has been noted previously that negligible and negative *r* values are due to repulsive interactions between fluorinated moieties of the anion and the probe solute molecules.³²

Although capabilities for dispersion interactions were considerable for all RTILs in this study, they showed only slight variability. Thus, while dispersion interactions between solutes and ionic liquids are important, they usually cannot be used to distinguish between RTILs. However, dispersion forces play an important role in solute—solvent interactions in that they aid all RTILs in distinguishing between similar molecules (i.e., homologous series of alkanes). Probe molecules that primarily interact with RTILs via dispersion interactions (i.e., hydrocarbons) will behave similarly with all RTILs. Likewise, solvatochromic dyes which interact with RTILs primarily by dispersive interactions would show similar trends in their behavior.

Ionic Liquid Model. The results obtained from this study have shown that RTILs can be classified on the basis of their interactions with a variety of solute probe molecules. Because a large variety of probe molecules capable of undergoing specific interactions were chosen, the data obtained should provide an adequate characterization of each ionic liquid. These data can then be used to indicate optimal uses for specific RTILs (such as solvents for organic synthesis, extraction solvents, matrixes for MALDI, and stationary phases for GLC, see Figure 3).

Organic Synthesis. The use of ionic liquids as solvents in organic chemistry has increased dramatically. As compared to conventional organic solvents, it has been shown that RTILs are capable of undergoing many types of interactions resulting in enhanced material dissolution, distinct reaction product ratios,

Table 2. Interaction Parameters Obtained from the Solvation Model for 17 RTILs^a

temperature (°C)	Class I RTILs							
	interaction parameters							
	<i>c</i>	<i>r</i>	<i>s</i>	<i>a</i>	<i>b</i>	<i>l</i>	<i>n</i>	<i>R</i> ²
BMIM-SbF ₆	-2.441	0	1.875	3.085	-0.325	0.587	30	0.97
	-2.688	0	1.808	2.704	-0.365	0.509	31	0.97
	-2.854	0	1.659	2.276	-0.332	0.456	30	0.95
BMIM-Cl	-3.095	0.237	2.247	7.030	-0.358	0.627	15	0.97
	-2.841	0.291	2.007	5.230	-0.320	0.445	22	0.98
	-3.099	0.408	1.826	4.860	-0.121	0.392	23	0.98
BMIM-TfO	-2.428	0	1.862	3.023	0	0.607	30	0.98
	-2.639	0	1.727	2.713	0	0.516	31	0.99
	-2.764	0	1.386	2.353	0	0.485	32	0.96
BMIM-BF ₄	-2.656	0	1.647	2.219	-0.102	0.644	31	0.98
	-2.740	0	1.456	1.967	-0.127	0.569	33	0.98
	-2.724	-0.141	1.365	1.660	-0.283	0.473	31	0.96
BMIM-NTf ₂	-2.868	0	1.889	2.016	0.362	0.634	33	0.99
	-3.025	0	1.671	1.752	0.378	0.557	35	0.99
	-3.130	0	1.596	1.551	0.235	0.487	32	0.98
BMIM-PF ₆	-2.607	0	1.914	1.887	0	0.620	29	0.98
	-2.622	0	1.695	1.579	0	0.515	33	0.99
	-2.677	0	1.540	1.369	0	0.439	32	0.98
C ₈ m ₄ im-NTf ₂	-2.893	0.222	1.678	1.944	0	0.715	30	0.98
	-3.017	0.170	1.525	1.827	0	0.633	34	0.98
	-3.090	0.133	1.396	1.562	0	0.551	31	0.98
C ₆ m ₄ im-NTf ₂	-2.801	0.206	1.717	1.966	0	0.701	31	0.98
	-2.908	0.173	1.579	1.848	0	0.611	34	0.98
	-2.902	0.243	1.398	1.563	0	0.496	31	0.99
Bm ₂ im-NTf ₂	-2.934	0.073	1.964	2.033	0.125	0.636	32	0.98
	-3.140	0.082	1.750	1.790	0.159	0.569	34	0.98
	-3.152	0.092	1.581	1.566	0.113	0.478	31	0.98
BMPY-NTf ₂	-2.779	0	1.688	2.083	0.159	0.677	34	0.98
	-2.799	0	1.533	1.775	0	0.561	34	0.99
	-2.920	0	1.442	1.547	0	0.484	32	0.99
Class II RTILs								
temperature (°C)	interaction parameters							
	<i>c</i>	<i>r</i>	<i>s</i>	<i>a</i>	<i>b</i>	<i>l</i>	<i>n</i>	<i>R</i> ²
NH ₂ m ₂ -PA	-3.605	-0.238	0.776	1.173	0	0.763	29	0.94
	-3.532	-0.233	0.781	0.797	0	0.613	21	0.93
NHb ₃ -PA	-2.649	-0.126	0.590	1.506	-0.349	0.741	30	0.95
	-2.700	0	0.498	1.508	-0.374	0.624	30	0.95
NHb ₃ -OPHA	-2.897	-0.126	0.476	1.076	-0.158	0.749	32	0.98
	-3.008	0	0.373	0.935	-0.146	0.636	27	0.97
NHe ₃ -PA	-3.136	0	0.516	1.350	0	0.713	30	0.95
	-2.704	-0.102	0.576	0.843	0	0.486	23	0.96
NHb ₃ -Ac	-3.413	-0.249	0.734	1.343	-0.216	0.827	32	0.98
	-3.626	-0.243	0.654	1.054	-0.213	0.738	23	0.98
NHb ₃ -CHCA	-3.829	0.323	1.373	2.209	1.086	0.676	27	0.93
	-3.350	0.257	1.340	2.178	1.037	0.553	30	0.96
NHb ₃ -SA	-4.28	0.160	1.880	2.851	1.382	0.768	30	0.94
	-4.08	0.240	1.743	2.691	1.132	0.673	31	0.96

^a Note: *n* = number of probe molecules subjected to multiple linear regression analysis. *R*² = statistical correlation coefficient.

and reaction kinetics.^{3–16} In this section, we examine whether the values of the interaction parameters obtained in this work support the qualitative observations and results of previous studies.

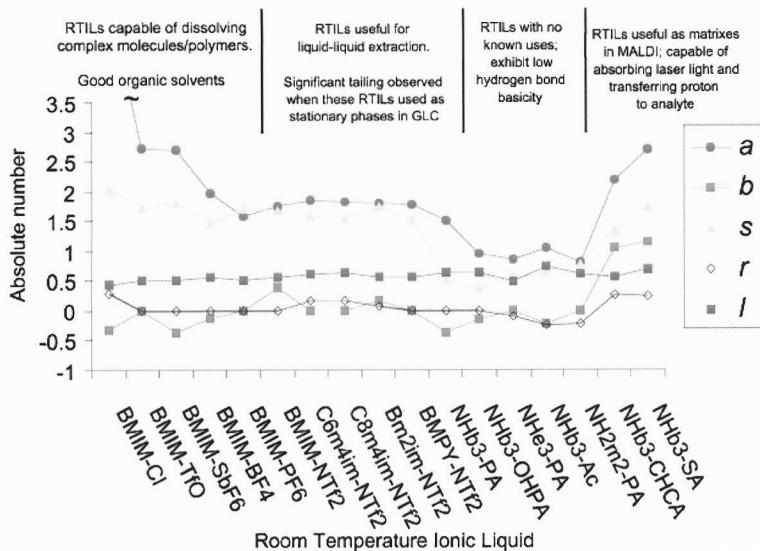


Figure 3. Plot illustrating the magnitude of each interaction parameter at 70 °C: hydrogen bond basicity (*a*), hydrogen bond acidity (*b*), interaction via nonbonding and π -electrons (*r*), dipolarity/polarizability (*s*), and dispersion forces (*l*).

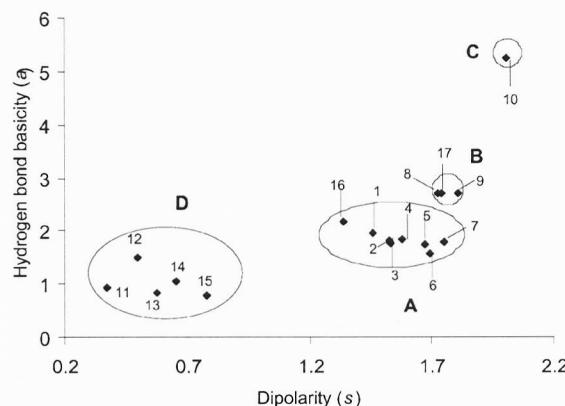


Figure 4. Plot illustrating the grouping of the 17 tested RTILs based upon their hydrogen bond basicity and dipolarity characteristics. 1, [BMIM][BF₄]; 2, [C₆m₄im][NTf₂]; 3, [BMPY][NTf₂]; 4, [C₆m₄im][NTf₂]; 5, [BMIM][NTf₂]; 6, [BMIM][PF₆]; 7, [Bm₂im][NTf₂]; 8, [BMIM][TfO]; 9, [BMIM][SbF₆]; 10, [BMIM][Cl]; 11, [NH₂m₂][PA]; 12, [NHb₃][PA]; 13, [NHb₃][OHPA]; 14, [NH₃][PA]; 15, [NHb₃][Ac]; 16, [NHb₃][CHCA]; 17, [NHb₃][SA].

Recently, it was reported that cellulose could be dissolved up to 25 wt % in BMIM-Cl.³⁶ However, it was noted that BMIM-BF₄ and BMIM-PF₆ did not dissolve pulp cellulose. Our data indicate that the BMIM-Cl ionic liquid has the largest hydrogen bond basicity, suggesting that the anion plays a key role in the dissolution of the cellulose. We have previously reported the solubility of other complex compounds in BMIM-Cl, BMIM-PF₆, and BMIM-BF₄ RTILs.¹ Native α , β , and γ cyclodextrins exhibited the best solubility in the BMIM-Cl RTIL (~30% w/w), while the BMIM-BF₄ and BMIM-PF₆ RTILs demonstrated only 1% solubility. Important macrocyclic antibiotics such as vancomycin, teicoplanin, rifamycin B, and avoparcin were soluble in BMIM-Cl but sparingly soluble in the BMIM-PF₆ and BMIM-BF₄ RTILs. These compounds contain many free hydroxyl groups as a consequence of the carbohydrate moieties that are part of the molecule. Recent observations by our group have shown that if the sugar moieties

are removed from teicoplanin (resulting in the macrocyclic aglycone), the solubility in BMIM-Cl drops by nearly 60%. Indeed, the role of the chloride anion and its hydrogen bond basicity behavior is crucial in achieving dissolution of compounds capable of hydrogen bonding to the RTIL.

Reynolds et al. recently reported that the photoreduction of benzophenones by amines is possible using RTILs as solvents.¹⁰ Because the photoreduction of a substrate produced a mixture of benzhydrol and benzpinacol, the authors explored the effect of the RTILs on the product ratio obtained from the reaction. They discovered that the yield of benzhydrol was highest in the BMIM-PF₆ solvent and lowest in the BMIM-TFO salt (BMIM-PF₆ > BMIM-BF₄ > BMIM-TFO). According to our data, this reaction favored a solvent with the lowest hydrogen bond basicity, while increasing basicity had a detrimental effect on the yield of benzhydrol. This same trend was discussed by Ohara et al., where ionic liquid solvents were used in the ferric ion-catalyzed cycloaddition of styrene derivatives.²⁸ They discovered that the reaction rate was strongly dependent on the anion of the imidazolium salt and that the optimal rate was achieved when using BMIM-PF₆ as the solvent. A significant drop in the reaction rate was observed for the BMIM-BF₄ salt, while no reaction was achieved using the BMIM-TFO solvent system. It is possible that RTILs with strong hydrogen bond basicity interact with the ferric ion catalyst or otherwise interfere with the reaction.

Chauvin et al. used RTILs based on 1-butyl-3-methylimidazolium salts as nonaqueous solvents in Rh-catalyzed two phase hydrogenation, isomerization, and hydroformylation of unsaturated substrates.³⁷ Because RTILs can easily dissolve charged species, the hydrogenation of 1-pentene using a cationic catalyst precursor was explored. The results indicated that the BMIM-SbF₆ RTIL produced hydrogenation rates nearly 5 times higher than comparable homogeneous reactions in acetone and considerably higher turnover frequencies than the BMIM-PF₆ and BMIM-BF₄ RTILs. Our data (see Table 2 and Figure 4) indicate the much higher hydrogen bond basicity character of BMIM-

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SbF_6 as compared to BMIM-PF₆ and BMIM-BF₄. In comparing the latter two RTILs, their published experimental results indicated a much lower activity with the BMIM-BF₄ salt that was attributed to its hydrophobic nature and the presence of trace amounts of chloride ion. Indeed, it is very important to evaluate RTILs free of any chloride ion as trace amounts greatly influence the hydrogen bond basicity character of the RTIL (see Experimental Section).

The Class II ionic liquids examined in this study possess small hydrogen bond basicity constants and may be useful for organic reactions in which the hydrogen basicity of the anion is preferred to have little influence on the reaction rate, product yield, or product ratio. Although these ionic liquids decompose at a lower temperature as compared to Class I RTILs, their possible usefulness should not be ignored.

Matrix-Assisted Laser Desorption/Ionization (MALDI)

Matrixes. MALDI mass spectrometry has proved to be a successful soft ionization method for analyzing polar, nonvolatile, and thermally labile biomolecules and synthetic polymers with high molecular weight.^{38–41} Two of the fundamental properties that every effective matrix must possess are the ability to absorb ultraviolet laser light (i.e., have a chromophore) and also transfer a proton to the analyte after excitation. Also, it is crucial that the matrix be nonvolatile so that it can exist under the high-vacuum conditions used in mass spectrometry.

Two effective and five ineffective RTILs used as MALDI matrixes were evaluated using the solvation model. Ideally, the interaction parameters could predict whether the RTIL would be an effective MALDI matrix by demonstrating substantial hydrogen bond acidity (as the matrix must transfer a proton to the analyte to form the intact molecular ion) and a significant *r*-term signifying an aromatic moiety (i.e., chromophore). Clearly, the data show that only the effective RTILs (tributylammonium α -cyano-4-hydroxycinnamate (NHb₃-CHCA) and tributylammonium sinapinate acid (NHb₃-SA)) have appreciable hydrogen bond acidity (*b*-term) and significant ability to interact with *n* and π -electrons (*r*-term) as illustrated in Figure 3. These characteristics are absolutely necessary for a MALDI matrix to be effective. All other RTILs with zero or negative *r*-terms failed to provide adequate signals probably due to a lack of ionization of the solute.²¹ Obviously, the solvation model allows one to examine a potential MALDI matrix largely on the basis of two interaction parameters, *b* and *r*. This demonstrates the usefulness and robustness of the model to properly evaluate all solvation interactions of the RTIL.

Gas Chromatography Stationary Phases. We have previously reported the retention behavior of various solute molecules on a BMIM-Cl and a BMIM-PF₆ GLC stationary phase and indicated that RTILs have an apparent “dual nature”.¹ As illustrated in Figure 5a, low polarity compounds (i.e., hydrocarbons) exhibited relatively small retention factors but good selectivity (i.e., peak to peak separation). In fact, the RTILs interact with nonpolar molecules as if they were nonpolar liquid stationary phases where dispersive interactions dominate. Conversely, compounds capable of donating protons, and to a lesser

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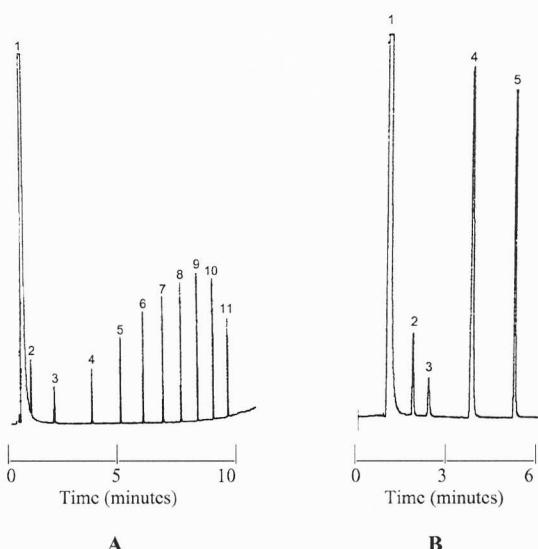


Figure 5. Chromatograms demonstrating the dual nature of RTILs. (A) A homologous mixture of *n*-alkanes is subjected to a 15 meter BMIM-TfO column. 1, CH_2Cl_2 ; 2, hexane; 3, heptane; 4, octane; 5, nonane; 6, decane; 7, undecane; 8, dodecane; 9, tridecane; 10, tetradecane; 11, pentadecane. Conditions: initial, 30 °C for 3 min; ramp, 15 °C/min to 170 °C. (B) A mixture of small chain alcohols is separated by the same BMIM-TfO column. 1, CH_2Cl_2 ; 2, methanol; 3, ethanol; 4, propanol; 5, butanol. Conditions: initial, 35 °C for 3 min; ramp, 15 °C/min to 170 °C.

extent proton acceptors, were tremendously retained, as if the RTILs were very polar liquids (i.e., carboxylic acids, phenols, and alcohols, Table 3). This dual behavior is illustrated in Figure 5a and b where the BMIM-TfO RTIL separated a mixture of *n*-alkanes (as if it was a nonpolar stationary phase) and also demonstrated excellent selectivity in separating a mixture of small chain alcohols (as if it was a polar stationary phase).

Although there appear to be only slight differences regarding the polarity of ionic liquids,¹⁶ using single parameter polarity scales, it seems from our results that RTILs may be capable of acting as quite polar solvents in the presence of more polar molecules and conversely acting as a nonpolar solvent for nonpolar solutes. This dual nature of RTILs makes them attractive not only as novel organic solvents, but also as stationary phases in GLC. Indeed, it may be possible to design a single RTIL stationary phase that is capable of separating a greater variety of compounds than any existing stationary phase or perhaps combination of stationary phases.

RTIL anions consisting of weak bases capable of accepting a proton from a carboxylic acid or alcohol exhibited poor chromatographic mass transfer on all RTIL stationary phases with the bis[(trifluoromethyl)sulfonyl]imide (NTf₂) anion. This phenomenon was apparent by inverse GLC and is shown in Figure 6 where 1-octanol was eluted from the BMIM-NTf₂ stationary phase. Although the retention time was only a few minutes, the resulting analyte peak was very broad and exhibited severe tailing (as compared to Figure 5a). The mass transfer problem may be due to the solute molecule hydrogen bonding to the delocalized negative charge across the S-N-S moiety as described previously by crystallographic experiments.⁴² This is supported by molecular orbital calculations of proton dissociation and hydration which indicate a proton dissociation

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Table 3. Retention Factors Obtained at 70 °C for Select Probe Molecules on All RTIL Phases Examined^a

	aniline	2-chloroaniline	1-octanol	p-cresol	acetic acid	1-chlorohexane
BMIM-SbF ₆	*	91.3	16.3	*	9.5	1.1
BMIM-Cl	*	*	73.1	*	*	**
BMIM-TfO	*	119.4	21.2	*	13.7	1.3
BMIM-BF ₄	77.8	54.7	11.1	90.2	2.8	1.2
BMIM-PF ₆	59.8	70.8	10	96.0	2.1	1.4
BMIM-NTf ₂	57.3	53.3	9.5	100.8	1.5	0.6
C ₈ m ₄ im-NTf ₂	106.1	116.5	14.1	198.4	1.2	1.0
C ₆ m ₄ im-NTf ₂	127.3	128.7	14.8	225.8	1.4	1.2
Bm ₂ im-NTf ₂	62.3	55.1	7.4	105.6	1.1	0.5
BMPY-NTf ₂	68.7	59.3	10.5	121.6	1.4	0.9
NH ₂ m ₂ -PA	0.31	0.91	0.79	0.90	**	0.10
NHb ₃ -PA	1.88	6.96	3.62	20.20	0.50	0.64
NHb ₃ -OHPA	0.82	2.59	1.89	3.86	0.10	0.33
NHe ₃ -PA	0.63	1.40	1.30	2.07	**	0.22
NHb ₃ -Ac	0.73	2.14	1.70	2.96	**	0.24
NHb ₃ -CHCA	17.31	43.5	19.1	101.6	3.8	0.43
NHb ₃ -SA	6.8	17.9	7.6	42.8	1.0	**

^a Note: * indicates the solute molecule did not elute from the stationary phase before 180 min. ** indicates the solute molecule eluted with the dead volume.

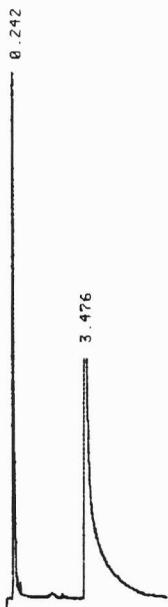


Figure 6. Chromatogram illustrating poor mass transfer between the RTIL stationary phase (BMIM-NTf₂) and 1-octanol.

energy of -0.7 kcal/mol for the bis[(trifluoromethyl)sulfonyl]-imide anion after the addition of two water molecules.⁴³

Conclusions

Room-temperature ionic liquids (RTILs) have been used in many areas of chemistry. As compared to conventional organic

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solvents, RTILs are much more complex solvent systems capable of undergoing many types of interactions. Characterizing them with a single “polarity” term fails to describe the type and magnitude of individual interactions that make each RTIL unique. The solvation model uses many solute probe molecules in conjunction with inverse GC to quantitatively determine the importance of different RTIL interactions as a function of temperature. These results are especially useful in explaining different solvent behavior between broad classes of RTILs.

The anion had the greatest effect on the hydrogen bond basicity of the RTIL, while the effect of the cation was generally quite small. The penta-substituted imidazolium salts (C₆m₄im-NTf₂ and C₈m₄im-NTf₂) demonstrated strong $\pi-\pi$ interactions by tenaciously retaining probe molecules containing electron-rich aromatic systems. RTILs exhibited multiple behaviors, which explains why many RTILs act as polar solvents in organic reactions containing polar molecules and as less polar solvents in the presence of less polar molecules. In addition, the solvation model adequately characterized two effective MALDI matrixes by demonstrating their ability to absorb laser light (i.e., existence of a chromophore, *r*-term) as well as their ability to transfer a proton to an analyte (*b*-term). The two effective MALDI matrixes were the only two RTILs to exhibit significant hydrogen bond acidity values. The classification of the RTILs based upon dipolarity and basicity provides a model that can be used to pick RTILs for specific organic reactions, liquid extractions, or GLC stationary phases.

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