

Uses of Ionic Liquids in Analytical Chemistry

A. Berthod, S. Carda-Broch* (*samuel.carda@uv.es*)

*Laboratoire des Sciences Analytiques, CNRS, Université de Lyon 1, Bat CPE-308,
69622 Villeurbanne, France*

ABSTRACT

Room temperature ionic liquids (RTILs) are salts with melting points close or below room temperature. They form liquids in which ions are present. This fact produces interesting solvent properties. RTIL are able to dissolve some apolar molecules as well as some very polar ones. They start to find original use in chemical analysis. Since some RTILs are not soluble in water, they can be used in water/RTIL extractions. The distribution coefficients of a variety of solutes were measured. Our results are presented and discussed along with the results of others. RTILs were also used as electrolytes in capillary electrophoresis. Their low volatility makes them useful as solvent working in high vacuum (MALDI matrixes) or high temperature (GC stationary phases). Examples of such uses were developed and are also discussed.

1. INTRODUCTION

Room temperature ionic liquids (RTILs) are salts with melting points lower than 30°C. They look like a classical liquid but they do not contain any molecules: they are made of ions. The structure of these liquids is completely different from the structure of any other solvents made of molecules. The properties of a given solvent depend on the interaction between the solvent molecules. If there are strong interactions between the solvent molecules, the solvent is called a "polar" solvent, e.g. water, methanol, ethanol. If the interactions between the solvent molecules are weak, it is an "apolar" solvent, e.g. hexane, heptane, petroleum ether. Table 1 lists the properties of some solvents as well as several polarity index values: dipole moment, dielectric constant, Reichardt index and octanol/water partition coefficient (as $\log P_{oct}$). The great originality of RTILs is that they are not made of molecules. Ions are present in the liquid with an exactly equal number of positive and negative ions so that the whole liquid is electrically neutral. Ionic liquids are known for decades, but they were molten salts at very high temperature, e.g. the melting points of sodium, potassium, aluminum and calcium chloride are respectively 801, 770, 190 and 782°C. Most organic molecules are decomposed at these elevated temperatures. The potential of the new solvent class of ionic liquids at room temperature is actively investigated as shown by Figure 1.

The first RTIL was discovered during World War I, in 1914, looking for new explosives. It was ethyl ammonium nitrate with a melting point of 12°C [1]. In the eighties, Seddon and coworkers started to use RTILs as nonaqueous polar-like solvents for electrochemical and spectroscopic studies of transition metal complexes [2-4]. Typically, RTIL consists of nitrogen- or phosphorous-containing organic cations and large organic or inorganic anions [1]. Bulky organic cations such as *N*-alkylpyridinium and 1-alkyl-3-methylimidazolium are combined with inorganic anions such as Cl⁻, Cl⁻/AlCl₃, NO₃⁻, PF₆⁻ and BF₄⁻. Less common anions include bis (trifluoromethanesulfonyl) imide (CF₃SO₂)₂N⁻ and

trifluoromethanesulfonate (CF₃SO₃⁻). The combination of such cations and anions can lead to a large number of ionic liquids that provide considerable flexibility in the selection of the most suitable pair for a specific chemical application.

The main physicochemical properties of RTILs are: (i) under an inert atmosphere, they remain liquid over a temperature range of 200 to 300°C; (ii) they have practically no vapor pressure [5]; (iii) they are reported to have a wide window of electrochemical stability, good electrical conductivity, high ionic mobility and excellent chemical stabilities [6, 7]. With all these properties, it is hoped that they can act as "green solvents" and they will replace volatile organic solvents in several chemical reactions [1, 6].

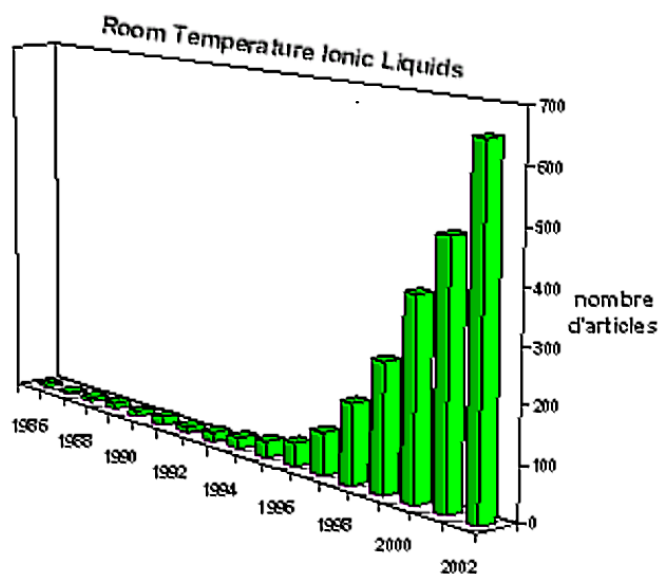


Figure 1: Number of articles published worldwide per year on the subject "room temperature ionic liquids" (2002 = estimate) (Chemical Abstracts, Current Contents and Medline databases).

* on leave on a Marie Curie Fellowship from Area de Química Analítica, Universidad de Jaime I, Castellón, Spain

Solvent	Molecular weight	Density g/cm ³	Viscosity cP	Melting point °C	Boiling point °C	Refractive index	Dipole moment debye	Dielectric constant	Solubility %w/w		Log <i>P</i> _{oct}	Polarity Reichardt
									Solvent in water	Water in solvent		
Acetic acid	60	1.049	1.1	16.7	118	1.3719	1.74	6.15	∞	∞	-0.20	65
Acetone	58	0.790	0.33	-94.7	56.1	1.3587	2.69	20.7	∞	∞	-0.22	35.5
Acetonitrile	41	0.782	0.36	-43.8	81.6	1.3441	3.44	37.5	∞	∞	-0.34	46
Benzene	78	0.876	0.65	5.5	80.1	1.5011	0	2.28	0.18	0.063	2.15	11
1-butanol	74	0.810	2.95	-88.6	118	1.3993	1.75	17.5	7.8	20.1	0.88	60
2-butanol	74	0.807	3.78	-115	99.5	1.3970	1.64	15.8	12.5	44.1	0.78	50.5
chloroform	119	1.489	0.58	-63.5	61.2	1.4892	1.15	4.9	0.815	0.056	1.97	26
diethyl ether	74	0.713	0.23	-116	34.4	1.3524	1.15	4.34	6.9	1.3	0.83	11.5
dimethylformamide	73	0.949	2	-60.4	153	1.4305	3.86	36.7	∞	∞	-1.00	40.5
dimethyl sulfoxide	78	1.095	2.2	18.5	189	1.4793	4.30	48.7	∞	∞	-1.30	44.5
ethanol	46	0.789	1.2	-114	78.3	1.3610	1.66	26.6	∞	∞	-0.70	65.5
ethyl acetate	88	0.901	0.45	-83.5	77.1	1.3724	1.88	6.0	8.7	3.3	0.78	23
heptane	100	0.684	0.41	-90.6	98.4	1.3876	0	1.92	0.0003	0.01	4.28	1.2
hexane	86	0.659	0.32	-95.3	68.7	1.3749	0.08	1.88	0.001	0.01	3.52	0.9
methanol	32	0.791	0.55	-98	64.5	1.3284	2.87	32.7	∞	∞	-0.80	76
methyl ethyl ketone	72	0.805	0.43	-86.7	79.6	1.3788	2.76	15.2	24	10	0.30	33
methyl isobutyl ketone	100	0.801	0.60	-84	116	1.3597	2.70	13.1	1.7	1.9	1.30	27
methyl- <i>t</i> -butyl ether	88	0.741	0.27	-108	55.2	1.3689	1.32	4.5	4.8	1.5	1.38	15
octanol	130	0.827	7.2	-16.7	194.5	1.4295	1.76	10.3	0.054	4.1	3.18	34
1-propanol	60	0.804	2.3	-126	97.1	1.3856	3.10	20.3	∞	∞	0.34	62
tetrahydrofuran	72	0.888	0.55	-108	66	1.4072	1.75	7.6	∞	∞	0.54	20.5
toluene	92	0.867	0.59	-95	111	1.4969	0.31	2.38	0.074	0.03	2.70	10
water	18	0.998	1.0	0	100	1.3330	1.87	80.1	-	-	-1.48	100
BMIM-PF ₆ ionic liquid	284	1.362	300*	-8	dec.	1.4110	ions	cond.	1.8	1.4	-0.69	65

BMIM = butyl methyl imidazolium hexafluorophosphate, * dry ionic liquid, dec. = decomposes, cond. = conduct electrical current.

Table 1 : Physico-Chemical properties of some solvents at 20°C

The physicochemical properties of RTILs depend on the nature and size of both their cation and anion constituents. Table 2 lists some data for several RTILs formed by the 1-butyl-3-methyl imidazolium cation associated with different anions, and for various bis(triflyl)amide ($(CF_3SO_2)_2N^-$) ionic liquid salts with different cations [1, 8-11]. This table shows that it is difficult to relate the physicochemical properties of a given RTIL to its chemical structure [8]. The polarity of RTILs was estimated using the solvatochromic effect of the Reichardt's dye (E_T^N scale) [11]. A remarkable constancy was found for imidazolium based ionic liquids, all values falling between 64 and 68 [11, 12]. For comparison, the E_T^N values the common solvents toluene, acetone, acetonitrile, ethanol and methanol are respectively 10, 36, 46, 65 and 76 [13] (Table 1). The solubility of the RTILs in organic solvents depends on the dielectric constant, ϵ , of the solvent. Most RTILs are fully miscible with solvents with a ϵ value higher than 6 (e.g. water, dimethylformamide, ethanol, acetone, Table 1) [1]. However the water solubility of RTILs is highly dependent on the anion. Chloride, bromide, trifluoroacetate ionic liquids are water-soluble. Hexafluorophosphate and bis(triflate) amide salts often form two phases with water [1].

1-butyl-3-methyl imidazolium salts					
gegenion	m.p. °C	d g/cm ³	N	Viscosity cP 20°C	Conductivity S/cm
BF ₄ ⁻	-82 (g)	1.17	1.429	233	0.17
PF ₆ ⁻	-8	1.36	1.411	312	0.14
Cl ⁻	65	1.10*	solid	solid	solid
CF ₃ COO ⁻	-40 (g)	1.21	1.449	73	0.32
CF ₃ SO ₃ ⁻	16	1.29	1.438	90	0.37
(CF ₃ SO ₂)N ⁻	-4	1.43	1.427	52	0.39
C ₂ F ₅ COO ⁻	-40 (g)	1.33	1.414	182	0.10
C ₆ F ₅ SO ₂ ⁻	20	1.47	1.405	373	0.045
bis-(trifluoromethyl sulfonyl) amide salts					
1-methyl-3-methyl imidazolium	22	1.56	1.422	44	0.84
1-ethyl-3-methyl imidazolium	-3	1.52	1.423	34	0.88
1-ethyl-3-ethyl imidazolium	14	1.45	1.426	35	0.85
1-butyl-3-methyl imidazolium	-4	1.43	1.427	52	0.39
1-isobutyl-3-methyl imidazolium	-30 (g)	1.43	1.429	83	0.26
1-butyl-3-ethyl imidazolium	-30 (g)	-	1.428	-	-
1-methoxyethyl-3-methylimidazolium	-30 (g)	1.50	1.429	54	0.42
1-methyl-2-methyl-3-ethylimidazolium	20	1.51	1.430	88	0.32
1-trifluoroethyl-3-methyl imidazolium	-30 (g)	1.66	1.409	248	0.10
1-ethyl-3-ethyl-4-methyl imidazolium	-22	1.43	1.430	36	0.62
1-methyl-3-ethyl-4-methyl imidazolium	-3	1.47	1.427	37	0.66

Data from Refs 1, 8-11; * supercooled liquid at 25°C ; (g) glass transition, ~ approximate value (+/- 10°C)

Table 2 : Effect of the nature of the anion on physicochemical properties of 1-butyl-3-methyl imidazolium salts and of the cation of the bis (triflyl)amide salts (20°C).

Since pioneering works of Ford [14], Hussey [15] and Seddon [16], the ionic liquids are actively studied by several researchers groups worldwide working in all fields of chemistry. Recently, several researchers have reported uses for RTILs in chemical analysis. They have been used as stationary phases in gas chromatography [17] and mobile phases in liquid chromatography [18], they were able to dissolve chiral selectors to make chiral stationary phases [19] and they were used as unique running electrolytes in the separation of phenolic compounds by capillary electrophoresis [20].

The RTILs are used in chemistry such as [21]:

(i) non-volatile solvents in organic synthesis, catalyzed

reactions, electrochemistry and spectroscopy; (ii) non-molecular environment; and (iii) room temperature chemistry. The very low vapor pressure of RTILs makes them possible candidates for matrixes in matrix-assisted laser desorption/ionization mass spectrometry (MALDI) experiments. The MALDI matrix should absorb the light energy, transfer it to the analyte and ionize it (adding a proton) so it can fly in the high vacuum the tube of time-of-flight (TOF) mass spectrometer. As some ionic liquids are non-miscible with water, they could be also used in countercurrent chromatography in a biphasic liquid system, since in this technique both phases, stationary and mobile, are liquids.

2. USES OF IONIC LIQUIDS IN CHEMICAL ANALYSIS

We thought that the unique properties of RTILs will be useful in chemical analysis. The main property is the original polarity of the RTILs used as solvent. The liquid salts associate ionic interaction with hydrophobic interaction (alkyl tail of the imidazolium ring). RTILs are able to solubilize inorganic as well as organic compounds. The thermal stability and low volatility of RTILs will also be used in chemical analysis.

2.1. Liquid-liquid extractions with ionic liquids

Solute distribution in a biphasic liquid system

In liquid-liquid extraction, two immiscible or partially miscible solvents are used. Solutes will distribute or partition between the two liquid phases. Different solutes will partition differently between the same liquid phases allowing to separate them. We used the 1-butyl-3-methyl imidazolium hexafluorophosphate (BMIM-PF₆) ionic liquid as a typical example of a RTIL forming a biphasic liquid system with water in liquid-liquid extractions [22]. We synthesized our own ionic liquid because it is difficult to find at a reasonable price. We reacted butyl chloride with 1-methyl imidazole for 72 h at 70°C to obtain BMIM-Cl with a 95% yield. A metathesis was done with hexafluorophosphoric acid at room temperature producing two phases: BMIM-PF₆ and an acidic aqueous solution. The distribution between the ionic liquid and the aqueous phase of a large variety of compounds bearing different functionalities was studied at several pH values [22].

Ionic liquid/water distribution coefficients

We determined the water / BMIM-PF₆ distribution coefficients for 45 aromatic compounds. High performance liquid chromatography (HPLC) was the analytical technique used to measure the solute concentration in each phase. After a thorough equilibration (20 min under vigorous shaking), the two liquid phases are let standing for one night. 0.5 mL of the aqueous upper phase and 0.5 mL of the ionic liquid lower

phase are collected separately. The RTIL phase is too viscous to be injected directly in the HPLC system. It was diluted with 1 mL methanol to form 1.5 mL of fluid solution. 20 μ L of the solution are injected in the HPLC system (column 15 cm with octadecyl silane (ODS) bonded silica particles, methanol/water 70/30 mobile phase at 1 mL/min, UV detection at 254 nm). The peak areas of the solutes were used to quantitate the solute concentrations in each phase. The ratio of (solute peak area in the ionic liquid phase \times 3) over (solute peak area in the aqueous phase) gave the ionic liquid/water distribution coefficients.

Comparison with the octanol/water distribution coefficients

The solute distribution between octanol and water is used as a reference scale for hydrophobicity [13]. Figure 2 shows the ionic liquid/water distribution constants of the molecular forms of the aromatic compounds plotted versus their respective octanol/water coefficients with a logarithm scale. A reference line with a slope of unity (*i.e.*, the ionic liquid coefficient is exactly equal to the octanol/water coefficient) is included in this plot. As can be seen in Figure 2, the ionic liquid/water distribution coefficients of the amine-containing compounds are slightly higher than the octanol/water coefficients. Conversely, the ionic liquid/water distribution coefficients of the acidic and phenolic compounds are significantly lower than the corresponding octanol/water coefficients. The neutral compounds and the ionizable compounds with both basic and acid functionalities show similar distribution behavior in both the ionic liquid/water and octanol/water systems.

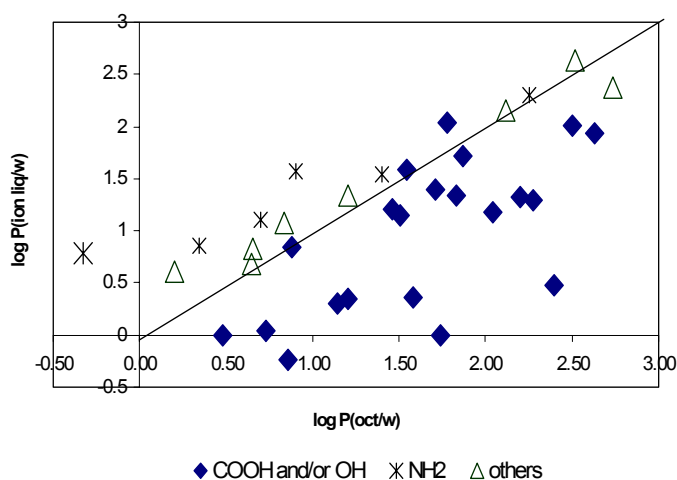


Figure 2 : Ionic liquid/water distribution coefficients compared to the octanol/water values (log scale). Crosses: amino-aromatic compounds, open triangles: neutral compounds or compounds with both acidic and basic substituents, filled-diamond: acidic and/or phenolic compounds.

A polarity of ethanol with a low water solubility

Our study showed that the polarity of the BMIM PF₆ ionic liquid is comparable to that of ethanol, but without being soluble in water or in apolar solvents. The

viscosity of the water-saturated ionic liquid phase was 10 times lower than the pure ionic liquid. It can be generalized that the physicochemical properties of the pure ionic liquid are significantly modified by the mutual saturation occurring in liquid-liquid extraction processes [23].

Heptane is an apolar solvent not soluble with water (Table 1) nor with ionic liquids. A three-phase system can be obtained with heptane, BMIM-PF₆ and water. The ionic liquid phase can also be sandwiched between a denser liquid phase such as chloroform and a lighter aqueous phase. A triphasic liquid system made of BMIM-PF₆, water and cyclohexane was used to perform Heck reactions (coupling of alkenes with aryl halides or benzoic anhydride) in BMIM-PF₆ [24].

2.2. Additive in HPLC

Poole *et al* [18,25] studied the properties of tetraalkylammonium nitrate and thiocyanate ionic liquids in gas and liquid chromatography. These salts show very strong orientation and proton acceptor interactions with weak proton donor capacity and can be used in the temperature range from around room temperature to 150-180°C, at which temperature they exhibit significant vapor pressure. Their viscosity is conveniently controlled by working at elevated temperatures or through dilution with a cosolvent.

In HPLC, they showed that ionic liquid containing mobile phases rapidly deteriorated the silica-based column packing (ODS). They used them as liquid mobile phase with unbounded silica packing. It was shown recently that BMIM-PF₆ could be used with pure water to separate polar basic drugs. The screening of the silanol groups by the imidazolium cation was not clearly different from the screening obtained with amines (*e.g.* triethylamine).

2.3. Electrolyte in Capillary Electrophoresis

In some capillary electrophoresis (CE) studies, alkylammonium salts have been used as electroosmotic flow (EOF) modifiers [26-28]. Yanes *et al* [29] reported the development of a fairly robust capillary electrophoretic method for the separation of polyphenols found in grape seed extracts that uses tetraethylammonium tetrafluoroborate (TEA-BF₄) as the only electrolyte in the background electrolyte. They showed that the cation not only acted as an EOF modifier but also played an active role through association with polyphenols. The excellent reproducibility was attributed to the coating of the capillary wall by the tetraalkylammonium cations with a permanent charge group not subject to pH-induced variations in ionization.

Stalcup *et al* [20] used alkyl-methyl imidazolium ionic liquid salts with different anions as running electrolytes in CE to separate polyphenolic neutral molecules. They found that the polyphenols eluted after

the EOF marker as if they were positively charged. The separation mechanism relies on the association of the polyphenols with the imidazolium cations either coating the capillary wall or electrophoretically migrating in the bulk solution. The cation has a significant effect on the electropherogram acting on the retention times. The anion has much less effect. The larger polyphenols were the most retained.

2.4. Matrixes for MALDI-TOF MS

In Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS), the role of the matrix is:

- (i) to absorb strongly the laser UV light and convert it in enough heat so that the solute will be vaporized,
- (ii) to ionize the solute so it can fly if an electrostatic field is applied.

The MALDI technique involves the process of desorption, dissociation and ionization of the analyte and the matrix under the condition of high laser energy density. The matrix should not be volatile, dissolve (liquid matrix) or cocrystallize (solid matrix) with the sample. It should protonate the solute, stifle both chemical and thermal degradation of the sample and produce homogeneous mixtures (10000 to 100000/1 matrix/solute ratio). These requirements make ionic liquids possible candidates for MALDI matrixes. As liquids, they will produce much more homogeneous mixtures of greater vacuum stability than any solid matrixes and they are good solvents for a variety of organic, inorganic and polymeric substances, etc, but they should protonate the sample.

Many conventional solid MALDI matrixes are acids such as sinapinic acid, α -cyano-4-hydroxycinnamic acid, 2,5-dihydroxybenzoic acid and 3-hydroxypicolinic acid (3-HPA). The classical ionic liquids failed to produce signal in MALDI experiments because they were unable to protonate the solute. Associating the efficient acid solid matrixes with bases producing liquid salts, useful ionic liquid matrixes were obtained for protein and polymer molecular weight measurements. Armstrong *et al.* [30] demonstrated that ionic liquids and solids may make the most useful MALDI matrixes. With ionic matrixes, it is possible to combine the beneficial qualities of liquid and solid matrixes. Ionic liquids produce a much more homogeneous sample solution (as do all liquid matrixes) yet have greater vacuum stability than most solid matrixes. In most cases, an ionic matrix can be found that produces greater spectral peak intensities and lower limits of detection than comparable solid matrixes. Most ionic liquids readily dissolve biological oligomers, proteins, and polymers. However, ionic liquids can vary tremendously in their ability to promote analyte ionization. Both the cationic and anionic portion of the ionic matrix must be chosen with a consideration

for the special requirements of UV-MALDI detection. The ionic matrix must have significant absorbance at the desired wavelength, but also available protons. Most conventional ionic liquids that lack these properties are ineffective as MALDI matrixes.

In the quest for a good MALDI matrix, it is not possible to predict:

- (i) which salt will be efficient
- (ii) which salt will be liquid.

For protein MALDI detection [30], 38 combinations were tested: 18 salts failed to produce any MALDI signal, and 20 salts were successful, of which only 9 were liquids. We tried to find ionic matrixes that could be used in MALDI-TOF to determine deoxyribonucleic acid (DNA)-oligomers directly, improving the results obtained for the 3-HPA conventional matrix. For DNA MALDI detection, 33 combinations were tested: 19 salts failed, 14 salts produced a MALDI signal with DNA oligomers but none of them were liquid [31]. In most cases, an ionic matrix produced greater spectral intensities than comparable solid matrixes. Since all ionic matrixes working were solids, the spectra that gave the best intensity only could be obtained after several attempts to find appropriate "hot spots" [31].

2.5. Gas Chromatography Stationary Phases

Armstrong *et al* [17] showed that RTILs could act as non-polar stationary phases in gas chromatography (GC) when separating volatile non-polar analytes such as the linear alkanes shown in Figure 3-A. Polar analytes that are proton-donor or acceptor molecules were separated by the RTIL GC column in a way similar to what is obtained with an apolar classical GC stationary phase (e.g. dimethylpolysiloxane OV1 or OV101). The unique point is that the same RTIL stationary phase was also able to separate perfectly polar molecules with somewhat acidic or basic functional groups. These molecules were highly retained similarly to what is obtained with a polar classical GC stationary phase (e.g. carbowax). Figure 3-B shows the separation of some light linear alcohols. Thus, molecules with proton-donor or acceptor characteristics tend to be spatially resolved, as a group, from nonpolar analytes.

Inverse GC also is a good way to examine the nature of different ionic liquids. Preparing different capillary GC column with different ionic liquids, it is possible to establish some ionic liquid physico chemical properties by studying the way a variety of solutes are retained by the different columns at different temperature. The chloride-containing ionic liquid interacted much more strongly with proton-donor and acceptor solutes. The hexafluorophosphate-containing ionic liquid tended to be somewhat less polar and interacted more strongly with nonpolar solutes.

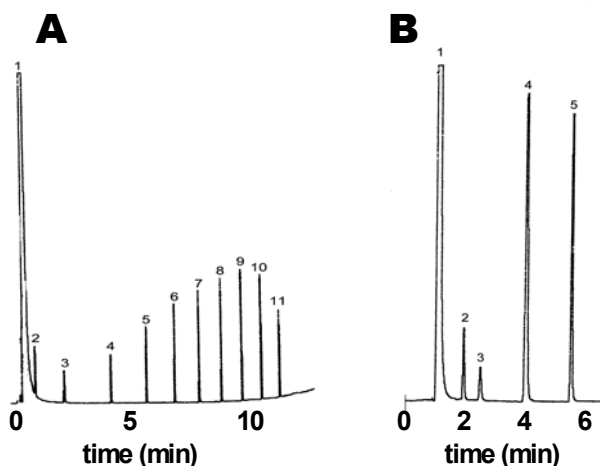


Figure 3 : Gas chromatograms obtained on an ionic liquid coated capillary column. A- Linear alkanes 1- solvent peak, 2-pentane, 3-hexane, 4-heptane, 5-octane, 6-nonane, 7-decane, 8-undecane, 9-dodecane, 10-tridecane, 11-tetradecane. B- Linear alcohols, 1- solvent peak, 2-methanol, 3-ethanol, 4-propanol, 5-pentanol. Column 15 m long, 200 μm i.d., BMIM-triflate ionic liquid coated in ~ 1 μm film, helium carrier gas, 100°C isotherm for 4 min, next 10°C/min temperature gradient.

Since RTILs are non volatile and can solubilize molecules, we thought to use them as solvents for original molecules and to test the new stationary phase in GC. BMIM-Cl [19] was able to dissolve cyclodextrins, a sugar derivative. Cyclodextrins can be used as chiral selectors. BMIM-Cl can dissolve up to 25% w/w of derivatized cyclodextrin. Such ionic liquid solution was used to coat the internal wall of a 25 m capillary column. The chiral GC column obtained was proved to be able to separate some volatile racemic mixtures with a good kinetics in the solute-stationary phase exchange process and consequently, sharp peaks were obtained [19].

3. CONCLUSIONS

To conclude this work, it is important to point out that the new class of solvents called "room temperature ionic liquid" has really unique properties. Ionic liquids have, at the same time, some properties found in polar solvents or in apolar solvent. They were called "green" solvents because they have a very low vapor pressure that minimizes the release of chemical in the atmosphere when they are used as solvent [4-6]. As analytical chemists, we would like to temper too much enthusiasm for such solvents. To select them to replace classical (volatile) organic solvents, the synthesis route to make ionic liquid and the way to dispose of them should both be evaluated. In a global view, perfluorinated ions may not be as "green" as too often stated.

4. ACKNOWLEDGMENTS

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5. REFERENCES

- [1] Wassercheid P., Keim W. (2000) *Angew. Chem. Int. Ed.* 39:3772-3789.
- [2] Appleby D., Hussey C.L., Seddon K.R., Turp J.E. (1986) *Nature* 323:614-616.
- [3] Seddon K.R. (1996) *Kinet. Catal.* 37:693-697.
- [4] Earle N.J., Seddon K.R. (2000) *Pure Appl. Chem.* 72:1391-1398.
- [5] Welton T. (1999) *Chem. Rev.* 99:2071-2083.
- [6] Chauvin Y., Olivier-Bourbigou H. (1995) *Chemtech* 25:26-30.
- [7] Ngo H.L., LeCompte K., Hargens L., McEwen A.B. (2000) *Thermochim. Acta* 357:97-102.
- [8] Bonhôte P., Dias A.P., Papageorgiou N., Kalyanasundaram K., Grätzel M. (1996) *Inorg. Chem.* 35:1168-1178.
- [9] Hagiwara R., Ito Y. (2000) *J Fluorine Chem* 105:221-227.
- [10] Gordon C.M., Holbrey J.D., Kennedy A.R., Seddon K.R. (1998) *J. Mater. Chem.* 8:2627-2636.
- [11] Muldoon M.J., Gordon C.M., Dunkin I.R. (2001) *J. Chem. Soc. Perkin Trans 2*:433-435.
- [12] Park S., Kazlauskas R.J. (2001) *J. Org. Chem.* 66:8395-8401.
- [13] Berthod A. (1995) in Foucault A.P. (ed) *Centrifugal Partition Chromatography* M Dekker NY Chromatogr. Sci. Ser. 68:167-197.
- [14] Ford W.T., Haurj R.J., Hart D.J. (1973) *J. Org. Chem.* 38:3976-3983.
- [15] Hussey C.L. (1983) *Adv. Molten Salt Chem.* 5:185-199.
- [16] Appleby D., Hussey C.L., Seddon K.R., Turp J.E. (1986) *Nature* 323:614-616.
- [17] Armstrong D.W., He L., Liu Y.S. (1999) *Anal. Chem.* 71:3873-3876.
- [18] Poole C.F., Kersten B.R., Ho S.S.J., Coddens M.E., Furton K.J. (1986) *J. Chromatogr.* 352:407-425
- [19] Berthod A., He L., Armstrong D.W. (2001) *Chromatographia* 53:63-68.
- [20] Yanes E.G., Gratz S.R., Baldwin M.J., Robinson S.E., Stalcup A.M. (2001) *Anal. Chem.* 73:3838-3844.
- [21] Crabb C. (2001) *C&En News* March 23:33-37.
- [22] Carda-Broch S., Berthod A., Armstrong D.W. (2003) *Anal. Bioanal. Chem.* 375:191-199.
- [23] Holbrey J.H., Seddon K.R. (1999) *J. Chem. Soc. Dalton Trans.* 2133-2139.
- [24] Carmichael A.J., Earle M.J., Holbrey J.D., McCormac P.B., Seddon K.R. (1999) *Org. Lett.* 1:997-1000.
- [25] Poole S.K., Shetty P.H., Poole C.F. (1989) *Anal. Chim. Acta* 218:241-264.
- [26] Huang X., Luckey J.A., Gordon M.J., Zare R.N. (1989) *Anal. Chem.* 61:766-770.
- [27] Harrold M.P., Wojtusik M.J., Riviello J., Henson P. (1993) *J. Chromatogr.* 640:463-471.
- [28] Quang C., Khaledi M.G., (1993) *Anal. Chem.* 65:3354-3358.
- [29] Yanes E.G., Gratz S.R., Stalcup A.M. (2000) *Analyst* 125:1919-1923.
- [30] Armstrong D.W., Zhang L., He L., Gross M.L. (2001) *Anal. Chem.* 73:3679-3686.
- [31] Carda-Broch S., Berthod A., Armstrong, D.W. (2003) *Rapid Comm. Mass Spec.* 17:553-560.