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Analytica Chimica Acta xxx (2005) xxx–xxx

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Analytical applications of room-temperature ionic liquids: A review of recent efforts

Siddharth Pandey *

Department of Chemistry, Indian Institute of Technology, Hauz Khas, New Delhi 110016, India

Received 16 February 2005; received in revised form 10 June 2005; accepted 10 June 2005

Abstract

Room-temperature ionic liquids (RTILs) are solvents that may have great potential in chemical analysis. Recent surge in the number of publications/reports/books/monographs clearly indicate an increasing interest of scientific and engineering community toward these exciting and unique solvents. Consequently, a variety of analytical applications of RTILs have started to emerge. This review presents an account of some of the recent reports on RTILs in major subdisciplines of analytical chemistry. Specifically, recent literature representing the applications of RTILs in chromatography, extraction, electroanalytical chemistry, sensing, and spectrometry is reviewed. With a rapid growth in the number of publications on analytical applications of RTILs, it appears that in the near future these neoteric solvents are definitely going to be a permanent feature in analytical chemistry.

Keywords: RTIL; Volatile organic solvents; Chromatography; Spectrometry

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1. Introduction

During the time span of dramatic development in science and technology that we have witnessed in the last century, certain subjects have evolved over time in an extremely unfortunate way. The earlier periods of the last century appear to contain entirely beneficial developments in science and technology toward mankind, however, as the activities over the later time period unfold, unfortunate long-term environmental consequences can and have become a significant legacy. At the dawn of the new century, it is universally realized that any further development in science and technology has to take into account the concerns and safety of our immediate environment as well as the long-term effects that these developments will have in the future. One of the longest-standing problems facing the chemical industries and academia is continued reliance on huge volumes of toxic, hazardous, flammable, and environmentally damaging organic solvents. These volatile organic solvents (VOCs) are problematic to separate/remove from the products, difficult to recycle/reuse, and impractical to dispose of without incurring substantial costs and/or adversely affecting the environment and/or personnel.

The recently rediscovered (i.e., in their air- and moisture-stable forms) neoteric room-temperature ionic liquids (RTILs), with virtually no vapor pressure, may well be the ace within the deck of solvents of choice (VOC replacements) for the new millennium with potential as environmentally benign media for many industrially important chemical processes [1–5]. RTILs have shown potential as unique solvents with wide range of solubility, miscibility, and other physicochemical properties accompanied by an extremely promising non-volatile behavior. One of the advantages arising from the chemical structures of RTILs is that alteration of the cation or anion can cause changes in properties such as viscosity, melting point, water miscibility, and density. It is not surprising that RTILs have shown tremendous applications in a variety of chemical processes.

The unique molecular architecture combined with the potential uses of RTILs is increasingly piquing the interest of academic researchers and industries alike. Not only is the

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* Tel.: +91 11 26596503; fax: +91 11 26581102.
E-mail address: sipandey@chemistry.iitd.ac.in.

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doi:10.1016/j.aca.2005.06.038

idea of doing chemistry in a non-molecular environment a novel concept, but also relatively little is known about the RTILs themselves. As a consequence, many research groups in the world have embraced research areas dealing with various aspects and applications of RTILs. An exponential growth in the number of publications on RTILs over last 5–6 years is the result of increasing interest in these novel solvents. While a huge number of these publications report chemical syntheses with RTIL as the solvent, number of reports on the applications of RTILs in catalysis is also not far behind. Although recently numerous analytical applications of RTILs have appeared in literature, the full potential of these unique solvents is still unexplored. Initial reports on utilization of RTILs in chromatography and extraction as well as for electroanalytical purposes started to appear in late 1990's, it is safe to say that most publications on analytical applications of RTILs are more recent. It is impossible to include each and every report on analytical applications of RTILs in this review; we have tried to focus more on the recent efforts. We are responsible for the selection of the articles and will be grateful to the readers for any reports of oversight.

It is important to review some of the books, monographs, and conference proceedings published recently that deal with various aspects of RTIL research. In this context, the book edited by Wasserscheid and Welton [6] is an excellent reference for new researchers about to venture in this exciting area of research; the emphasis of this book is mainly on synthetic aspects of RTILs. A variety of preliminary reports encompassing almost all areas of chemical sciences are published in two volumes of ACS Symposium Series [7,8], and a third volume is due to come out in March 2005 [9]. Edited by Rogers and Seddon, these collections contain the key papers presented at three ACS symposia on RTILs, Ionic Liquids: Industrial Applications for Green Chemistry, Ionic Liquids as Green Solvents: Progress and Prospects, and Ionic Liquids: Properties and Structure, respectively. These symposia were organized during the three different National Meetings of the American Chemical Society (ACS) held at San Diego (2001), Boston (2002), and New York (2003), respectively. Another similar monograph, published under NATO Science Series and edited by Rogers, Seddon, and Volkov, also contains some interesting reports on analytical applications of RTILs [10]. Finally, a collection edited by Hiroyuki Ohno titled "Electrochemical Aspects of Ionic Liquids" is scheduled to be released in April 2005 [11]. Although review articles on synthetic aspects of RTILs started to appear in late 1990s [12] (reference 12 is one of the first extensive reviews of its kind), attempts of reviewing analytical applications of these solvents are definitely more recent. A recent article by Poole reviews chromatographic and spectroscopic methods for the determination of solvent properties of RTILs [13]. A more pertinent review of applications of RTILs in analytical chemistry is recently published by Liu and coworkers [14]. This review highlights efforts in RTIL research area in sample preparation, chromatography, and detection. It is important to mention a very comprehensive educational review article describing an analytical view of ionic liquids authored by Baker, Baker, Pandey, and Bright that is recently published [15]. The article chronicles recent progress made in the application of ionic liquids toward analytical problem-solving.

In this review, we focus on recent analytical applications of air- and moisture-stable RTILs as they are of particular interest because they can be easily handled and used in wide variety of environments. We have tried to incorporate most of the recent publications on analytical application of these RTILs to the best of our effort. However, very few reports on other aspects of RTIL research such as, synthesis/catalysis and structure/property elucidation of RTILs are selected for inclusion in this review. These are judiciously selected publications that either directly or indirectly deal with analytical applications of RTILs.

2. Chromatographic applications of ionic liquids

RTILs have been used in a variety of chromatographic methods as novel materials. It appears that unusual properties of these neoteric solvents could impart potential benefits to many areas of separation science. Most work on applications of RTILs in gas chromatography (GC) to date has been conducted by Armstrong group. As one of the early reports of the use of RTILs as stationary phase in GC, this group has examined the behavior of two common RTILs, $bmimPF_6$ and bmimCl (bmim = 1-butyl-3-methylimidazolium), when coated onto fused silica capillary [16]. It was observed that the wetting ability and the viscosity of RTILs make them ideal coating stationary phases in various GC applications. Using inverse GC, the authors compared the performance of aforementioned RTILs versus a popular commercial polysiloxane as stationary phases. They discovered that RTILs act as low-polarity stationary phases to nonpolar compounds, however, more interestingly; solutes containing strong proton-donor groups were efficiently retained. Further, the change of anion was shown to affect selectivity and the solubilizing capacity of RTIL stationary phases. In a separate investigation by the same group, RTIL bmimCl was used as a solvent to dissolve per- and di-methylated β-cyclodextrins to prepare stationary phases for capillary columns in GC for chiral separation [17]. Performance of the commercial cyclodextrin columns was compared with RTIL cyclodextrin columns and it was found that the efficiency of chiral separation of bmimCl cyclodextrin column was significantly inferior. The reason for this observation was proposed to be the possibility of the formation of an inclusion complex between bmim and cyclodextrin cavity thus hindering the process of chiral recognition. Later, two new RTILs containing bulky imidazolium cations, 1-benzyl-3-methylimidazolium trifluoromethanesulfonate and 1-(4-methoxyphenyl)-3-methylimidazolium trifluoromethanesulfonate, synthesized by Anderson and Armstrong showed improved thermal stability as stationary phases in GC [18]. In a very recent collaborative effort, Ding, Welton, and Armstrong have presented the first enantiomeric separations using chiral RTIL stationary phases in GC [19]. The chiral RTIL-coated stationary phases were shown to separate many solutes including alcohols, diols, alkoxides, sulfoxides, epoxides, and acetylated amines.

Before reviewing important contributions on applications of RTILs in high performance liquid chromatography (HPLC), it is important to mention a recently published review article by Stalcup and Cabovska in this area [20]. This review presents some important work on applications of RTILs in liquid chromatography. In an earlier attempt, chromatographic behavior of ephedrines on a C18 column was investigated with different concentrations of bmimBF_4 as the eluent at pH 3.0 [21]. Addition of RTIL resulted in decreased band tailing, reduced band broadening, and improved resolution. Retention times were observed to first increase and than decrease with increasing concentration of RTIL. This was partly attributed to the competition between imidazolium cations and the polar groups of the analyte for the silanol group on the alkyl silica surface along with the formation of weak bilayer electronic structure on the C18 column. In another report, similar studies were performed with 1-alkyl-3-methylimidazolium and *N*-butylpyridinium salts as new mobile phase additives for separation of catecholamines in reversed-phase HPLC [22]. Separations with good efficiencies were achieved. In another report by the same group, amines were separated using RTILs as additives for the mobile phase in HPLC [23]. Effects of RTIL alkyl chain length, counterion, and concentration were also reported. A comparison with tetrabutylammonium bromide suggested that RTILs behave as ion-pair reagents, however, their H-bonding ability and hydrophobicity plays a major role. Recently, RTIL chemically modified silica particles were used for the first time as the stationary phase in HPLC for the separation of alkaloids [24]. The problem encountered in liquid chromatography during the separation of basic compounds due to the surface acidity of silica-based stationary phases was dealt recently by adding imidazoliumBF_4 RTILs [25]. It was observed that addition of 0.5–1.5% (v/v) of such RTILs blocked silanols and provided efficient separations of strongly basic drugs using thin layer chromatography. These drugs were hard to elute even with acetonitrile as the mobile phase. Application of bmimPF_6 as a novel solvent in countercurrent chromatography (CCC) is reviewed by Berthod and Carda-Broch [26]. They investigated the partitioning of 38 aromatic derivatives possessing acidic, basic, or neutral moieties between bmimPF_6 and water. It was observed that the high viscosity inherent to neat bmimPF6 limits its use as a solvent in CCC; however, addition of a third low viscosity solvent could alleviate this problem. In a subsequent and more recent investigation, the same authors utilized a 40:20:40% (w/w) water:acetonitrile:bmimPF_6 biphasic liquid system in CCC [27]. It was again demonstrated that the major drawback in using RTIL was its high viscosity. Among minor drawbacks, significant UV absorbance by RTILs limited the use of UV detector and non-volatile nature precluded the use of evaporative light-scattering detector for continuous detection in CCC.

One of the earlier reports of the use of RTIL buffer electrolytes in non-aqueous capillary electrophoresis (NACE) demonstrated the separation of water-insoluble dyes in acetonitrile that were previously not accessible using conventional CE methodology [28]. It was reported that the anionic part of the RTIL changed the general electrophoretic mobility of the system and the separation of analytes was achieved due to the dissociation of analytes in the presence of RTILs in the separating medium. Application of 1-alkyl-3-methylimidazolium RTILs in CE was reported by Stalcup et al. [29]. Phenolic compounds found in grape seed extracts were resolved using these RTILs as running electrolytes. Authors propose the separation mechanism to involve association between imidazolium cations and the polyphenols. In another study, Warner and coworkers reported the use of RTILs as modifiers in the separation of achiral and chiral analytes in micellar electrokinetic chromatography along with polymeric surfactants [30]. RTILs may show the ability to assist in the separation of hydrophobic mixtures while maintaining adequate background current. Their investigation showed that presence of RTILs rendered improved resolution and peak efficiency. In a different type of application, two groups have reported to utilize the RTIL-coated capillary during CE separations [31,32]. In the first investigation, RTIL-coated capillary was prepared and investigated for DNA separation. The experiments indicated that the performance of these capillaries was stable in the run buffer for at least 96 h with no noticeable deterioration in performance [31]. In the second report, a CE method in which 1-alkyl-3-methylimidazolium RTILs were used as the running electrolytes to separate basic proteins such as, lysozyme, cytochrome *c*, trypsinogen, and α-chymotyypsinogen A, was established [32]. Baseline separation, high efficiencies, and symmetrical peaks were obtained during the separation of the four proteins. Again, the separation mechanism was suggested to involve association between imidazolium cations and proteins.

3. Ionic liquids as solvents for extraction

Some of the initial reports on utilization of RTILs for extraction purposes came from Robin Rogers and collaborators. In one of the first reports, this group studied the partitioning of substituted benzene derivatives between water and bmimPF_6 [33]. In a subsequent and more detailed investigation, utilizing an indicator dye thymol blue Rogers group demonstrated the reversible pH-dependent liquid/liquid partitioning for RTIL-containing systems [34]. Possibility of the fine-tuning of the partitioning process by varying RTIL structure was also presented. 18-Crown-6 family crown ethers were dissolved in 1-alkyl-3-methylimidazolium PF_6 and investigated for the extraction of Na^+, Cs^+, and Sr^{2+} from aqueous solutions [35]. In the presence of crown ethers in

RTIL-based liquid/liquid separations, the resulting metal ion partitioning depended on the hydrophobicity of the crown ether and the composition of the aqueous phase. In comparison to traditional solvent extraction behavior, RTILs showed exceptional behavior and possibility of significantly complicated partitioning mechanism. It is important to mention that another report from a different research group also described unprecedented large distribution coefficients achieved by using RTILs as extraction solvents for separation of metal ions by crown ethers [36]. Bartsch group also reported on the influence of structural variations in RTIL on the selectivity and efficiency of competitive alkali metal salt extraction by crown ethers [37]. They showed that extraction efficiency generally diminished as the length of the 1-alkyl group on RTIL was increased. To further expand the utility of RTILs in metal ion extraction, other well-known organic and inorganic extractants were also utilized [38]. It was demonstrated that metal ion affinity for the hydrophobic phase necessitates the presence of an extractant. Later, in an exciting communication, Rogers and Davis, Jr. introduced task-specific RTILs for extraction of metal ions from aqueous milieu [39]. In such applications, imidazolium cations were derivatized to include task-specific functionalities, such as metal ligating groups that when used as part of the solvent or doped in the less expensive RTILs could dramatically enhance the extraction of targeted metal ions.

Fadeev and Meagher reported the potential of RTILs as extractants in recovery of butyl alcohol from fermentation broth [40]. By measuring the partition coefficient between water and two RTILs (log P), Abraham et al. showed that an increase in solute hydrogen bond basicity and solute volume led to a decrease and increase in log P, respectively [41]. Similarly, an increase in solute hydrogen bond acidity also decreased log P. Surprisingly, RTILs showed to have an increased affinity for polyaromatic hydrocarbons as compared to traditional organic solvents. RTIL, 1-octyl-3-methylimidazoliumPF_6 was demonstrated to be excellent extraction solvent in both direct-immersion and headspace liquid phase microextraction (LPME) [42]. Model solutes, polycyclic aromatic hydrocarbons, were rapidly and conveniently enriched in a 3 μL drop of aforementioned RTIL suspended on the tip of a microsyringe followed by a liquid chromatographic determination. Similar results were also reported for other solutes, 4-nonylphenol and 4-*tert*-octylphenol [43]. RTIL bmimPF_6 in concert with dithizone metal chelator was demonstrated to form neutral metal–dithizone complexes with heavy metal ions such as to extract heavy metal ions from aqueous solution into bmimPF_6 [44]. Distribution ratios of heavy metal complexes between bmimPF_6 and water were found to be high and extraction efficiencies pH dependent. In more recent studies, novel crown ethers (*N*-alkyl aza-18-crown-6 series) and calixarenes crown ethers (calix[4]arene-bis(*tert*-octylbenzo-crown-6)) were synthesized and used in RTILs as recyclable extractants for separation of Sr^{2+} and Cs^+ from aqueous solutions [45,46]. The strong dependence of selectivity on the type of RTIL indicated the important role played by solvation in solvent extraction processes based on RTILs. Shimojo and Goto found that a calix[4]arene-bearing pyridine was soluble in 1-alkyl-3-methylimidazolium PF_6 and showed a high extraction ability and selectivity for Ag^+ [47]. The extraction performance of pyridinocalix[4]arene was reported to be greatly enhanced by dissolution in RTILs in comparison to chloroform.

Utilization of supercritical carbon dioxide ($scCO_2$) in concert with various popular ionic liquids is shown to have modified and enhanced the overall extraction capabilities and applications of these neoteric solvents [48–52]. In an initial report by Brennecke group, recovery of organic products from ionic liquids using $scCO_2$ is demonstrated [48]. Recovery rates of various aromatic and aliphatic solutes from bmimPF_6 in the presence of environmentally benign $scCO_2$ are presented. In a subsequent study, interesting outcomes showing utility of $scCO_2$ as a separation switch for ionic liquid/organic mixtures were published by the same group [49]. Ian another report, Brennecke and coworkers have shown that liquid/liquid extraction with water resulted in the loss of some ionic liquid, whereas a variety of solutes could be extracted from ionic liquids with $scCO_2$ without cross-contamination [50]. Recently, enantioselective hydrogenation of *N*-(1-phenylethylidene)aniline using cationic iridium complexes with chiral phosphinooxazoline ligands is studied as a chemical probe to assess the potential of ionic liquid/CO_2 media for multiphase catalysis by Leitner and coworkers [51]. They observed that the products are readily isolated from the catalyst solution by CO_2 extraction without cross-contamination of ionic liquid or catalyst. During the electro-oxidation of benzyl alcohol by electrolysis in an ionic liquid/$scCO_2$ system in an undivided cell, Zhao et al. also demonstrated that the products could be easily recovered from the ionic liquid by using $scCO_2$ extraction after the electrolysis, and the ionic liquid could be reused [52].

4. Electroanalytical applications of ionic liquids

In one of the earlier reports, McEwen and coworkers explored electrochemical properties of some common RTILs with an eye toward their applications in electrochemical capacitor [53]. Later, in a series of papers published in the journal *Electrochemistry*, detailed preliminary investigations of the potential of RTILs toward electroanalytical applications were reported by many research groups [54–61]. Among others, potential of RTILs as electrolytes, their use in photoelectrochemical solar cells, their applications in double-layer capacitors, as electrolytes in rechargeable cells, in electrodeposition of metals and alloys were discussed. Other similar reports also hinted toward their applications as solvents for the electrodeposition of metals, semiconductors, germanium nanoclusters, and germanium on Au(III) [62–64]. In an exciting report, a RTIL electrolyte constituted of 1-methyl-3-propylimidazolium iodide, 1-methyl-3-

ethylimidazolium dicyanamide, and lithium iodide was combined with an amphiphilic polypyridyl ruthenium sensitizer to obtain a solar cell based on a solvent-free electrolyte with good efficiencies [65]. These unprecedented efficiencies for dye-sensitized solar cells with pure RTIL electrolyte demonstrated one of the major electroanalytical applications of RTILs. The voltammetry of ferrocene and ferrocene$^+$ was studied in RTIL bmimPF$_6$ when solid was adhered to glassy carbon or platinum disk electrodes [66]. Voltammograms of adhered ferrocene and ferrocene$^+$ were obtained and analyzed in detail. Extensive studies on other redox-active solids suggested that voltammograms of solid particles adhered to the electrode surface in contact with RTILs mostly exhibited classical behavior associated with solution-phase diffusion-controlled voltammetry.

In a more recent investigation, conductivity property of carbon nanotubes/RTILs and carbon microbeads/RTILs composite materials was studied utilizing *ac* impedance technology [67]. It was demonstrated that enzyme coated by RTILs-modified gold and glassy carbon electrodes allow efficient electron transfer between the electrode and the protein and also catalyze the reduction of molecular oxygen and hydrogen peroxide. Recently, the electrochemistry of cesium was investigated at Hg electrodes in RTIL tri-1-butylmethylammonium bis((trifluoromethyl)sulfonyl)imide by using cyclic staircase voltammetry, rotating disk electrode voltammetry, and chronoamperometry [68]. It was observed that reduction of cesium showed quasireversible behavior with bulk deposition and stripping experiments conducted at a rotating Hg film electrode showing an average recovery of 97% of the electrodeposited Cs. In another investigation, electrodeposition of Pd-Au alloy was studied within 1-ehtyl-3-methylimidazolium chloride tetrafluoroborate system containing Pd(II) and Au(I) [69]. Authors demonstrated that galvanostatic electrolysis of the solution resulted in a compact alloy deposition. Martiz et al. reported electrogeneration of diorganylsilanones from difunctional precursors in the presence of hexamethyldisiloxane and hexamethylcyclotrisiloxane within three RTILs [70]. High solubility of oxygen and inertness toward superoxide anion associated with the RTILs selected allowed functionalized siloxanes to be produced selectively in good isolated yields. In an exciting interdisciplinary report, single-wall carbon nanotubes, fullerene peapods, and double-wall carbon nanotubes were charged electrochemically in 1-butyl-3-methylimidazolium tetrafluoroborate/hexafluorophosphate [71]. It was observed that the electrochemistry of nanotubes and peapods is dominated by their capacitive double-layer charging.

It is important to mention the two very recent review articles published on electrochemical applications of RTILs; one by Buzzeo et al. [72], and the other by Endres [73]. These two reviews provide a detailed account of the utilization of RTILs in a variety of electrochemical processes. Readers are guided to these two informative reviews for further information on electroanalytical applications of RTILs.

5. Sensing within ionic liquids

Applications of RTILs in chemosensing are recently being explored by many researchers. In one of the earlier reports, Dai and coworkers have developed and evaluated the performance of a quartz crystal microbalance device employing RTILs as the sensing materials for organic vapors [74]. The sensing mechanism was shown to be based on the rapid decrease in the viscosity of RTIL membrane due to solubilization of analytes in RTILs. It was further observed that this change in viscosity was specific to the gaseous chemical species as well as to the type of RTIL. The sensor was shown to have a rapid response (<2 s) with excellent reversibility due to the fast diffusion of analytes in RTILs.

In a separate investigation, Compton and coworkers have demonstrated the use of RTILs in gas sensor design [75]. While comparing the attainable steady-state limiting currents and time responses of membrane-covered and membrane-independent gas sensors constituted of a variety of electrodes and electrolyte materials, these researchers considered a new design of membrane-free microelectrode modified with a thin layer of a RTIL. It was concluded that the use of RTIL as an electrolyte eliminates the need for a membrane and supporting electrolyte, however, slower time responses resulted due to higher viscosities of RTILs. It was suggested that these types of RTIL-based sensors may operate better in extreme operating conditions (e.g., high temperature and pressure) due to thermal stability and extreme low volatility of RTILs. Toward more specific gas sensing applications, a solid-state amperometric O_2 sensor was built by using supported hydrophobic bmimPF$_6$ porous polyethylene membrane as a solid-state electrolyte [76]. This RTIL-based O_2 gas sensor showed a wide detection range and high stability. In a similar investigation, the same group utilized a different hydrophilic RTIL, 1-ethyl-3-methylimidazolium tetrafluoroborate, to fabricate a solid-state amperometric sensor for O_2 detection [77].

Recently, Bennett and Leo have shown the application of RTILs as stable solvents for ionic polymer transducers [78]. They explored to replace water with highly stable RTILs to saturate Nafion™ membranes, which are known to operate as electromechanical actuators and sensors. Their experimental results demonstrated that Nafion™ transducers solvated with RTIL 1-ethyl-3-methylimidazolium trifluoromethylsulfonate have improved stability when operated in air as compared to the same materials solvated with water. However, the reduction in the speed of the response as compared to water was also noteworthy. Finally, a critical evaluation of RTILs containing lithium methylsulfonyl group in ethanol sensing is reported by Lee and Chou [79]. These RTILs were prepared from the precursors poly(propylene glycol)-block-(ethylene glycol)-block-(propylene glycol)-bis(2-aminopropyl ether) with different molecular weights. In order to establish the sensitivity of an ethanol sensor by using these RTILs, they were subjected into sequential electrochemical tests with Ni electrodes which performed at high sensitivity for the ethanol sensor.

However, it was reported that only the derivative with low molecular weight could detect ethanol. A linear relationship was established between response current and ethanol concentration with detection limit around 0.13% (v/v) and 336 s response time.

6. Ionic liquids in spectrometry

The use of RTILs in mass spectrometric analysis is rapidly increasing. In one of the first reports of its kind, application of RTILs as matrixes for ultraviolet matrix-assisted laser desorption/ionization (UV-MALDI) mass spectrometry (MS) was established by Armstrong's group [80]. All RTILs-based matrixes tested showed excellent solubilizing properties and vacuum stability compared to other frequently employed solid and liquid matrixes. It was observed, however, that these matrixes varied widely in their ability to produce analyte gas-phase ions. In a more recent effort, performances of various RTIL MALDI–MS matrixes were assessed and compared with frequently used conventional matrixes [81]. It was demonstrated that vacuum-stable, liquid consistency of RTIL matrix sample preparations considerably enhanced MALDI–MS analysis in terms of shot-to-shot reproducibility. It was also shown that solvent properties and MALDI matrix properties of RTILs, such as 2,5-dihydroxybenzoic acid butylamine, can be combined to enable fast and direct screening of an enzymatic reaction. Quantitative MALDI-ToF (time-of-flight) MS using isotopic labeled internal standards and ionic liquid matrixes was applied for the screening of 10 pyranose oxidase variants using aliquots of enzyme reaction mixtures without prepurification steps [82]. In another application, fast screening of low molecular weight compounds (three arborescidine alkaloids, the anesthetics levobupivacaine and mepivacaine, and the antibiotic tetracycline) was performed by thin-layer chromatography (TLC) followed by direct on-spot MALDI-ToF MS identification with nearly "matrix-free" mass spectra using an UV-absorbing RTIL matrix, triethylamine/α-cyano-4-hydroxycinnamic acid [83]. The technique was demonstrated to be fast and sensitive, required little sample preparation and manipulation. The problem of inhomogeneous distribution of analytes and matrixes in solid sample preparation for quantitative measurements encountered in MALDI MS was partly solved by the use of RTILs as matrixes [84]. Researchers prepared RTIL matrixes composed of equimolar combinations of classical MALDI matrices with organic bases in quantitative and qualitative analysis of low molecular weight compounds such as amino acids, sugars, and vitamins. RTIL-based matrix systems allowed a homogeneous sample preparation leading to a facilitated quantitative and qualitative measurement of the analytes compared with classical solid matrixes. In a recent communication, Dyson and coworkers demonstrated that electrospray ionization MS of neat RTILs did not require continuous sample injection. They also showed that the presence of a molecular solvent facilitated the analysis of RTIL as well as analytes dissolved in RTILs [85]. The task of identifying catalysts in RTILs using in situ NMR spectroscopy is problematic because of the requirement of deuterated RTILs. Zhao has demonstrated that since many of the catalysts used in RTILs are ionic in nature, electrospray ionization (ESI) MS could be used to detect such catalysts in RTILs [86]. The characterization of a ruthenium catalyst immobilized in a RTIL was described in detail.

Analysis of gold by inductively coupled plasma atomic emission spectrometry (ICP-AES) in aqueous solution in the presence of up to 50% (w/v) of various RTILs is recently reported [87]. The presence of RTILs is shown to alter the nebulization efficiency and sample transport properties. As a consequence of the higher viscosities associated with most RTILs, the AES signal intensity and apparent concentration of gold in solution is reported to be usually suppressed. Further, the use of the standard addition method to compensate for matrix error in the presence of RTILs was shown to be effective. There are many reports in the literature on detecting a variety of species and impurities within RTILs using different atomic spectroscopic techniques; however, these reports are about RTIL characterization and therefore are not discussed in this review.

A brief review of the recent research on RTIL in molecular fluorescence spectrometry is provided by Warner and coworkers [88]. In an attempt to demonstrate the applications of RTILs toward solute solvation, many research groups have investigated the dynamic and static solvation processes for a variety of solutes within RTILs. Pandey and coworkers observed the behavior of several electronic absorption and fluorescence solvatochromic probes within RTIL [89], RTIL + water [90,91], RTIL + ethanol [92], RTIL + water + ethanol [93], and RTIL + RTIL [94] systems. Their investigations indicated that the solvation environment afforded by RTILs is similar to that of short-chain alcohols. It was also demonstrated that addition of a cosolvent can drastically alter the physicochemical properties of RTILs and hence increase their overall analytical utility toward solute solvation. In an attempt to increase solubilization capacity and capability of RTILs the same group provided preliminary evidence of the formation of molecularly organized assemblies by nonionic surfactants within a low-viscosity RTIL [95]. Temperature-dependent solvent properties of neat $\mathrm{bmimPF_6}$ [96], $\mathrm{bmimPF_6}$ + water [96], and $\mathrm{bmimPF_6} + \mathrm{CO_2}$ [97] were explored by Bright group utilizing different solvatochromic probes. They also investigated the effect of water on relaxation dynamics surrounding a fluorescence probe within $\mathrm{bmimPF_6}$ [98]. Baker and coworkers used fluorescence correlation spectroscopy to determine the translational diffusion coefficients of three differently charged fluorescent probes dissolved within $\mathrm{bmimPF_6}$ [99]. In a recent communication, they synthesized a series of RTIL-inspired *N*-alkyl-*N*-methylpyrrolidinium halides and showed them to aggregate when dissolved in water [100]. It is important to mention here that many other research groups, namely those of Brennecke, Samanta, Maroncelli, Seddon, Tran, Hamaguchi, Welton, McLean, Gordon, Pagni, Kazarian, Eckert, Sarkar, Petrich, Armstrong, Billard, among others, have also employed different spectroscopic probes to extensively characterize solvation within RTIL-based systems; however, due to the lack of space it is impossible to incorporate even brief accounts of their significant work in this review.

Baker and coworkers reported a self-referencing optical thermometer based on a reversible, temperature-dependent monomer–excimer interconversion of 1,3-bis(1-pyrenyl)propane dissolved in a RTIL [101]. Monomer-to-excimer fluorescence intensity ratio of 1,3-bis(1-pyrenyl)propane was shown to vary dramatically in the 25–140 °C temperature range. In another interesting investigation, they demonstrated, using the single tryptophan residue in the sweet protein monellin as a spectroscopic handle, that RTIL affords extreme thermodynamic stabilization to the protein as compared to water [102]. Pandey group showed that bmimPF$_6$ can be used as a solvent to discriminate between alternant and nonalternant polycyclic aromatic hydrocarbons (PAHs) from a mixture [103]. Nitromethane was observed to selectively quench the fluorescence from alternant PAHs (PAHs containing only benzenoid structures), while fluorescence from nonalternant PAHs (PAHs containing five-membered rings as well) was not quenched at all. Finally, in a recent effort, Baker group has presented a simple spectroscopic colorimetric method that can be used to assess the relative intrinsic hydrolytic stabilities of water-miscible and water-immiscible ionic liquids [104].

7. Conclusions

Due to their unusual characteristics as well as potential environment-friendly behavior, RTILs are finding more and more applications in a variety of analytical processes, such as, separation, extraction, electroanalysis, sensing, and spectrometry, among others. It is safe to say that once the physicochemical properties of these neoteric solvents are well-established, number of analytical applications of RTILs will increase dramatically as researchers are discovering more and more about these exciting solvents. There is no doubt that, in the near future, RTILs will establish themselves as important solvents in chemical analysis.

Acknowledgement

The author would like to thank Department of Science and Technology (DST), India for the support under the scheme SR/S1/PC-38/2004.

References

[1] J.S. Wilkes, M.J. Zaworotko, Chem. Commun. (1992) 965.
[2] J. Fuller, R.T. Carlin, H.C. De Long, D. Haworth, Chem. Commun. (1994) 299.
[3] Y. Chauvin, H. Olivier-Bourbigou, CHEMTECH Sep. (1995) 26.
[4] K.R. Seddon, J. Chem. Tech. Biotechnol. 68 (1997) 351.
[5] J.S. Wilkes, Green Chem. 4 (2002) 73.
[6] P. Wasserscheid, T. Welton (Eds.), Ionic Liquids in Synthesis, Wiley-VCH, 2003.
[7] R.D. Rogers, K.R. Seddon (Eds.), Ionic Liquids: Industrial Applications for Green Chemistry, ACS Symposium Series 818, American Chemical Society, Washington, DC, 2002.
[8] R.D. Rogers, K.R. Seddon (Eds.), Ionic Liquids as Green Solvents: Progress and Prospects, ACS Symposium Series 856, American Chemical Society, Washington, DC, 2003.
[9] R.D. Rogers, K.R. Seddon (Eds.), Ionic Liquids III: Fundamentals, Challenges, and Oppurtunities, ACS Symposium Series, American Chemical Society, Washington, DC, 2005.
[10] Green industrial applications of ionic liquids, in: R.D. Rogers, K.R. Seddon, S. Volkov (Eds.), NATO Science Series II: Mathematics, Physics, and Chemistry, Kluwer Academic, 2003.
[11] H. Ohno (Ed.), Electrochemical Aspects of Ionic Liquids, Wiley-Interscience, 2005.
[12] T. Welton, Chem. Rev. 99 (1999) 2071.
[13] C.F. Poole, J. Chromatogr. A 1037 (2004) 49.
[14] J.F. Liu, J.A. Jonsson, G.B. Jiang, Trends Anal. Chem. 24 (2005) 20.
[15] G.A. Baker, S. Baker, S. Pandey, F.V. Bright, Analyst 130 (2005) 800.
[16] D.W. Armstrong, L.F. He, Y.S. Liu, Anal. Chem. 71 (1999) 3873.
[17] A. Berthod, L.F. He, D.W. Armstrong, Chromatographia 53 (2001) 63.
[18] J.L. Anderson, D.W. Armstrong, Anal. Chem. 75 (2003) 4851.
[19] J. Ding, T. Welton, D.W. Armstrong, Anal. Chem. 76 (2004) 6819.
[20] A.M. Stalcup, B. Cabovska, J. Liq. Chromatogr. Rel. Tech. 27 (2004) 1443.
[21] L.J. He, W.Z. Zhang, L. Zhao, X. Liu, S.X. Jiang, J. Chromatogr. A. 1007 (2003) 39.
[22] W.Z. Zhang, L.J. He, Y.L. Gu, X. Liu, S.X. Jiang, Anal. Lett. 36 (2003) 827.
[23] X. Xiaohua, Z. Liang, L. Xia, S.X. Jiang, Anal. Chim. Acta 519 (2004) 207.
[24] S.J. Liu, F. Zhou, L. Zhao, X.H. Xiao, X. Liu, S.X. Jiang, Chem. Lett. 33 (2004) 496.
[25] R. Kaliszan, M.P. Marszall, M.J. Markuszewski, T. Baczek, J. Pernak, J. Chromatogr. A 1030 (2004) 263.
[26] A. Berthod, S. Carda-Broch, J. Liq. Chromatogr. Rel. Tech. 26 (2003) 1493.
[27] A. Berthod, S. Carda-Broch, Anal. Bioanal. Chem. 380 (2004) 168.
[28] M. Vaher, M. Koel, M. Kaljurand, Chromatographia 53 (2001) 302.
[29] E.G. Yanes, S.R. Gratz, M.J. Baldwin, S.E. Robison, A.M. Stalcup, Anal. Chem. 73 (2001) 3838.
[30] S.M. Mwongela, A. Numan, N.L. Gill, R.A. Agbaria, I.M. Warner, Anal. Chem. 75 (2003) 6089.
[31] W. Qin, S.F.Y. Li, Analyst 128 (2003) 37.
[32] T.F. Jiang, Y.L. Gu, B. Liang, J.B. Li, Y.P. Shi, Q.Y. Ou, Anal. Chim. Acta 479 (2003) 249.
[33] J.G. Huddleston, H.D. Willauer, R.P. Swatloski, A.E. Visser, R.D. Rogers, Chem. Commun. (1998) 1765.
[34] A.E. Visser, R.P. Swatloski, R.D. Rogers, Green Chem. 2 (2000) 1.
[35] A.E. Visser, R.P. Swatloski, W.M. Reichert, S.T. Griffin, R.D. Rogers, Ind. Eng. Chem. Res. 39 (2000) 3596.
[36] S. Dai, Y.H. Ju, C.E. Barnes, J. Chem. Soc., Dalton Trans. (1999) 1201.
[37] S. Chun, S.V. Dzyuba, R.A. Bartsch, Anal. Chem. 73 (2001) 3737.
[38] A.E. Visser, R.P. Swatloski, S.T. Griffin, D.H. Hartman, R.D. Rogers, Sep. Sci. Tech. 36 (2001) 785.
[39] A.E. Visser, R.P. Swatloski, W.M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J.H. Davis Jr., R.D. Rogers, Chem. Commun. (2001) 135.

[40] A.G. Fadeev, M.M. Meagher, Chem. Commun. (2001) 295.
[41] M.H. Abraham, A.M. Zissimos, J.G. Huddleston, H.D. Willauer, R.D. Rogers, W.E. Acree Jr., Ind. Eng. Chem. Res. 42 (2003) 413.
[42] J.F. Liu, G.B. Jiang, Y.G. Chi, Y. Cai, Q. Zhou, J.T. Hu, Anal. Chem. 75 (2003) 5870.
[43] J.F. Liu, Y.G. Chi, G.B. Jiang, C. Tai, J.F. Peng, J.T. Hu, J. Chromatogr. A 1026 (2004) 143.
[44] G.T. Wei, Z. Yang, C.J. Chen, Anal. Chim. Acta 488 (2003) 183.
[45] H. Luo, S. Dai, P.V. Bonnesen, Anal. Chem. 76 (2004) 2773.
[46] H. Luo, S. Dai, P.V. Bonnesen, A.C. Buchanan III, J.D. Holbrey, N.J. Bridges, R.D. Rogers, Anal. Chem. 76 (2004) 3078.
[47] K. Shimojo, M. Goto, Anal. Chem. 76 (2004) 5039.
[48] L.A. Blanchard, J.F. Brennecke, Ind. Eng. Chem. Res. 40 (2001) 287.
[49] A.M. Scurto, S.N.V.K. Aki, J.F. Brennecke, J. Am. Chem. Soc. 124 (2002) 10276.
[50] J.F. Brennecke, L.A. Blanchard, J.L. Anthony, Z.Y. Gu, I. Zarraga, D.T. Leighton, Clean solvents, ACS Symp. Ser. 819 (2002) 82.
[51] M. Solinas, A. Pfaltz, P.G. Cozzi, W. Leitner, J. Am. Chem. Soc. 126 (2004) 16142.
[52] G.Y. Zhao, T. Jiang, W.Z. Wu, B.X. Han, Z.M. Liu, H.X. Gao, J. Phys. Chem. B. 108 (2004) 13052.
[53] A.B. McEwen, H.L. Ngo, K. LeCompte, J.L. Goldman, J. Electrochem. Soc. 146 (1999) 1687.
[54] M. Matsunaga, Electrochemistry 70 (2002) 126.
[55] R. Hagiwara, Electrochemistry 70 (2002) 130.
[56] H. Ohno, Y. Yoshizawa, Electrochemistry 70 (2002) 136.
[57] A. Noda, M. Watanabe, Electrochemistry 70 (2002) 140.
[58] H. Matsumoto, T. Matsuda, Electrochemistry 70 (2002) 190.
[59] M. Ue, M. Takeda, Electrochemistry 70 (2002) 194.
[60] S. Tobishima, Electrochemistry 70 (2002) 198.
[61] N. Koura, Y. Suzuki, F. Matsumoto, Electrochemistry 70 (2002) 203.
[62] F. Endres, CHEMPHYSCHEM 3 (2002) 144.
[63] F. Endres, S.Z. El Abedin, Chem. Commun. (2002) 892.
[64] F. Endres, S.Z. El Abedin, Phys. Chem. Chem. Phys. 4 (2002) 1640.
[65] P. Wang, S.M. Zakeeruddin, J.E. Moser, M. Gratzel, J. Phys. Chem. B 107 (2003) 13280.
[66] J. Zhang, A.M. Bond, Anal. Chem. 75 (2003) 2694.
[67] F. Zhao, X. Wu, M. Wang, Y. Liu, L. Gao, S. Dong, Anal. Chem. 76 (2004) 4960.
[68] P.Y. Chen, C.L. Hussey, Electrochim. Acta 49 (2004) 5125.
[69] F.Y. Su, J.F. Huang, I.W. Sun, J. Electrochem. Soc. 151 (2004) 811.
[70] B. Martiz, R. Keyrouz, S. Gmouh, M. Vaultier, V. Jouikov, Chem. Commun. (2004) 674.
[71] L. Kavan, L. Dunsch, H. Kataura, Carbon 42 (2004) 1011.
[72] M.C. Buzzeo, R.G. Evans, R.G. Compton, CHEMPHYSCHEM 5 (2004) 1107.
[73] F. Endres, Zeitschrift Fur Physikalische Chemie 218 (2004) 255.
[74] C. Liang, C.Y. Yuan, R.J. Warmack, C.E. Barnes, S. Dai, Anal. Chem. 74 (2002) 2172.
[75] M.C. Buzzeo, C. Hardacre, R.G. Compton, Anal. Chem. 76 (2004) 4583.
[76] R. Wang, S. Hoyano, T. Ohsaka, Chem. Lett. 33 (2004) 6.
[77] R. Wang, T. Okajima, F. Kitamura, T. Ohsaka, Electroanalysis 16 (2004) 66.
[78] M.D. Bennett, D.J. Leo, Sens. Actuators A 115 (2004) 79.
[79] Y.G. Lee, T.C. Chou, Biosens. Bioelectron. 20 (2004) 33.
[80] D.W. Armstrong, L.K. Zhang, L. He, M.L. Gross, Anal. Chem. 73 (2001) 3679.
[81] M. Mank, B. Stahl, G. Boehm, Anal. Chem. 76 (2004) 2938.
[82] D. Bungert, S. Bastian, D.M. Heckmann-Pohl, F. Giffhorn, E. Hinzle, A. Tholey, Biotechnol. Lett. 26 (2004) 1025.
[83] L.S. Santos, R. Haddad, N.F. Hoehr, R.A. Pilli, M.N. Eberlin, Anal. Chem. 76 (2004) 2144.
[84] M. Zabet-Moghaddam, E. Heinzle, A. Tholey, Rapid Commun. Mass Spectrom. 18 (2004) 141.
[85] P.J. Dyson, I. Khalaila, S. Luettgen, J.S. McIndoe, D.B. Zhao, Chem. Commun. (2004) 2204.
[86] D.B. Zhao, Aust. J. Chem. 57 (2004) 509.
[87] J.A. Whitehead, G.A. Lawrance, A. McCluskey, Aust. J. Chem. 57 (2004) 151.
[88] A.M. Powe, K.A. Fletcher, N.N. St. Luce, M. Lowry, S. Neal, M.E. McCarroll, P.B. Oldham, L.B. McGown, I.M. Warner, Anal. Chem. 76 (2004) 4614.
[89] K.A. Fletcher, I.K. Storey, A.E. Hendricks, S. Pandey, S. Pandey, Green Chem. 3 (2001) 210.
[90] K.A. Fletcher, S. Pandey, Appl. Spectrosc. 56 (2002) 266.
[91] S. Pandey, K.A. Fletcher, S.N. Baker, G.A. Baker, Analyst 129 (2004) 569.
[92] K.A. Fletcher, S. Pandey, Appl. Spectrosc. 56 (2002) 1498.
[93] K.A. Fletcher, S. Pandey, J. Phys. Chem. B. 107 (2003) 13532.
[94] K.A. Fletcher, S.N. Baker, G.A. Baker, S. Pandey, New J. Chem. 27 (2003) 1706.
[95] K.A. Fletcher, S. Pandey, Langmuir 20 (2004) 33.
[96] S.N. Baker, G.A. Baker, F.V. Bright, Green Chem. 4 (2002) 165.
[97] S.N. Baker, G.A. Baker, M.A. Kane, F.V. Bright, J. Phys. Chem. B 105 (2001) 9663.
[98] S.N. Baker, G.A. Baker, C.A. Munson, F. Chen, E.J. Bukowski, A.N. Cartwright, F.V. Bright, Ind. Eng. Chem. Res. 42 (2003) 6457.
[99] J.H. Werner, S.N. Baker, G.A. Baker, Analyst 128 (2003) 786.
[100] G.A. Baker, S. Pandey, S. Pandey, S.N. Baker, Analyst 129 (2004) 890.
[101] G.A. Baker, S.N. Baker, T.M. McCleskey, Chem. Commun. (2003) 2932.
[102] S.N. Baker, T.M. McCleskey, S. Pandey, G.A. Baker, Chem. Commun. (2004) 940.
[103] K.A. Fletcher, S. Pandey, I.K. Storey, A.E. Hendricks, S. Pandey, Anal. Chim. Acta 453 (2002) 89.
[104] G.A. Baker, S.N. Baker, Aust. J. Chem. 58 (2005) 174.