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Review

Extraction of organic compounds with room temperature ionic liquids[☆]

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ABSTRACT

Room temperature ionic liquids are novel solvents with a rather specific blend of physical and solution properties that makes them of interest for applications in separation science. They are good solvents for a wide range of compounds in which they behave as polar solvents. Their physical properties of note that distinguish them from conventional organic solvents are a negligible vapor pressure, high thermal stability, and relatively high viscosity. They can form biphasic systems with water or low polarity organic solvents and gases suitable for use in liquid–liquid and gas–liquid partition systems. An analysis of partition coefficients for varied compounds in these systems allows characterization of solvent selectivity using the solvation parameter model, which together with spectroscopic studies of solvent effects on probe substances, results in a detailed picture of solvent behavior. These studies indicate that the solution properties of ionic liquids are similar to those of polar organic solvents. Practical applications of ionic liquids in sample preparation include extractive distillation, aqueous biphasic systems, liquid–liquid extraction, liquid-phase microextraction, supported liquid membrane extraction, matrix solvents for headspace analysis, and micellar extraction. The specific advantages and limitations of ionic liquids in these studies is discussed with a view to defining future uses and the need not to neglect the identification of new room temperature ionic liquids with physical and solution properties tailored to the needs of specific sample preparation techniques. The defining feature of the special nature of ionic liquids is not their solution or physical properties viewed separately but their unique combinations when taken together compared with traditional organic solvents.

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1. Introduction

Solvent extraction remains one of the most widely used sample preparation techniques for chromatographic analysis [1,2]. The main reason being the versatility, simplicity, and effectiveness of extraction methods at reducing sample complexity, combined with the convenience of liquid sample concentration and injection techniques. In a general sense all solvent extraction methods are based on contacting and mixing the sample with a suitable solvent and/or distribution of the sample in a biphasic system composed of two or more solvents with limited mutual solubility. The large number of possible solvents with varied properties and the many possible approaches available to accomplish the extraction step are the features that maintain interest in the current and future development of solvent extraction methods. In this review we will focus on the use of room temperature ionic liquids as a new type of solvent to enhance the capabilities and applications of solvent extraction methods [3–12].

Ionic liquids are low-melting salts that form liquids composed entirely of ions. Historically the term ionic liquids was used quite broadly to include all types of thermally stable organic and inorganic melts, but for laboratory applications the emphasis has changed to low-melting point, organic, air stable salts with wide temperature-stable liquid ranges. A broadly accepted definition of an ionic liquid in contemporary practice is any salt with a melting point below 100 °C [13,14]. The room temperature ionic liquids are simply a subset of these salts, which have melting points below room temperature, and are the most interesting for solvent extraction. More than two hundred room temperature ionic liquids are known and an increasing number are now commercially available [15,16].

The main types of room temperature ionic liquids are alkylammonium, tetraalkylammonium, tetraalkylphosphonium, 1,3-dialkylimidazolium, and *N*-alkylpyridinium salts formed with weak nucleophilic anions such as bis(trifluoromethylsulfonyl)imide, hexafluorophosphate, tetrafluoroborate, perfluoroalkylsulfonate, etc. (Table 1) [15]. The liquid range for an ionic liquid is defined approximately by its melting point at the low end and vapor pressure or thermal breakdown at the upper end of the temperature scale. Methods to predict melting points (and other physical properties of ionic liquids) using quantitative structure–property relationships are poorly developed and indicate the need for further work if the goal of designing task-specific ionic liquids from ion structures is to become a reality [17–22]. Qualitatively it seems that low symmetry and effective charge delocalization or shielding for one or both ions together with weak hydrogen-bonding between ions, favors the formation of salts with low melting points [18,23]. High order and symmetry in the crystal lattice and a uniform (isotropic) charge dislocation, allows for better packing, and is associated with high melting crystalline phases. Relatively large asymmetric ions with high vibrational freedom and charge delocalization disrupt the lattice structure, increasing intercharge distances, thereby lowering the stability of the crystalline phase and its melting point. Ionic liquids with weak basic anions exhibit exceptional thermal stability in an inert atmosphere allowing applications at temperatures above 250 °C, such as in gas chromatography [8,10,12,15,24–27]. Several 1-alkyl-3-methylimidazolium salts containing highly delocalized anions are stable to distillation at reduced pressure (e.g., 300 °C and 10^{-4} bar) in which the vapor phase contains only neutral ion pairs [28]. Normal vaporization temperatures of ionic liquids are inherently high because the long range Coulombic forces prevent ions escaping into the gas phase. More commonly, the thermal stability of an ionic liquid is established by the onset of decomposition at elevated temperatures. Important factors in this case are the ability of the anion to participate in dealkylation reactions and the tolerance of the cation towards alkyl migration or elimination reactions [26,27,29]. For protic ionic liquids (formed by proton transfer between a weak acid and a weak base) decomposition with formation of two neutral products (the free base and acid) occurs at relatively modest temperatures [28]. The lack of significant vapor pressure over wide temperature ranges is one of the outstanding characteristic properties of ionic liquids.

Representative physical properties for some room temperature ionic liquids used in solvent extraction are summarized in Table 2 [15,30–35]. In some cases the melting points indicated refer to the glass transition temperature, which is not a true thermodynamic parameter, since this value depends on the thermal history of the sample. The density of most common room temperature ionic liquids is typically greater than water but usually declines with increasing ion size [36]. Fluorine-containing ionic liquids generally have the highest densities. The typical density difference between ionic liquids and common organic solvents as well as water favors rapid settling in phase separation devices used in some extraction methods. The choice of anion seems to have a strong influence on the viscosity of ionic liquids [16,30,36–39]. Low viscosity is associated with small anions with a diffuse negative charge and a limited capability for hydrogen bonding. Low is a relative term, however, since most room temperature ionic liquids have viscosities > 30 cP at room temperature. These high viscosities facilitate suspending larger drops at the tip of a capillary or needle for liquid-phase microextraction but otherwise contribute to poor penetration of porous solid materials and restrict mass transfer at solvent interfaces [11]. Sample preparation procedures that depend on pumping ionic liquids with common laboratory devices require viscosities < 5 cP for normal operation [26]. This is a limitation for some methods such as countercurrent chromatography The viscosity of ionic liquids can be lowered into a useful range for some applications by increasing the temperature or by dilution with a miscible solvent [31,38,39]. Flashpoints for 1,3-dialkylimidazolium salts are generally at least 100 °C higher than for conventional organic solvents reducing the risk of accidental combustion [40]. Although ionic liquids, in general, are associated with low flammability, ionic liquids containing energetic groups are combustible [41].

Ionic liquids have attracted interest as green solvents for chemical processes, for minimizing solvent waste, reducing exposure to hazardous vapors, and are considered environmentally benign (low toxicity). For these applications their favorable properties include low or negligible vapor pressure, an ability to dissolve a wide range of inorganic and organic compounds, high thermal stability, a large electrochemical window, high conductivity, high heat capacity, and low flammability [14,16]. No single ionic liquid possess all these

Table 1
Typical cations and anions used in the synthesis of room temperature ionic liquids.

Cations	Anions
Alkylammonium	Bis(trifluoromethylsulfonyl) imide
Tetraalkylammonium	Hexafluorophosphate
Tetraalkylphosphonium	Tetrafluoroborate
1,3-Dialkylimidazolium	Alkylsulfate
1,2,3-Trialkylimidazolium	Perfluoroalkylsulfonate
1-(Alkoxyalkyl)-3-alkylimidazolium	Alkylcarboxylate
1-(Hydroxylalkyl)-3-alkylimidazolium	Perfluoroalkylcarboxylate
N-Alkylimidazolium	Dicyanamide
N-Alkylisoquinolinium	Nitrate
N-Alkylpyridinium	Dialkylphosphate
1-Alkylpiperidinium	Thiocyanate
2,3-Dialkylindolinium	Diethyleneglycolmonomet hylethersulfate
1-Alkyl-4-fluoroalkyl-1,2,4-triazolium	
Bis(*N*,*N*-dialkyl)dimethylguanidinium	