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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.

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	Diethyleneglycolmonomethylethersulfate
1-Alkyl-4-fluoroalkyl-1,2,4-triazolium	
Bis(*N*,*N*-dialkyl)dimethylguanidinium	

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 2
Representative physical properties of some room temperature ionic liquids (25 °C unless indicated otherwise).

Ionic liquid	Melting point (°C)	Density (g mL^{-1})	Viscosity (cP)	Temperature limit (°C)
Ethylammonium nitrate	12.5	1.122	32	120
n-Propylammoniun nitrate	4	1.157	67	110
Di-*n*-propylammonium thiocyanate	5.5	0.964	86	130
1-Butyl-3-methylimidazolium				
Hexafluorophosphate	10	1.373	450	349
Tetrafluoroborate	−81	1.208	219	403
Trifluoroacetate		1.209	73 (20 °C)	
Trifluoromethanesulfonate	16	1.290	90 (20 °C)	
Bis(trifluoromethylsulfonyl)imide	−4	1.429	52	
Octylsulfate		1.064	34	
1-Ethyl-3-methylimidazolium				
Trifluoroacetate	−14	1.285	35 (20 °C)	
Bis(trifluoromethylsulfonyl)imide	−39	1.470	37	400
Trifluoromethanesulfonate	−9	1.390	45 (20 °C)	
Trifluoroacetate	−14	1.285	35 (20 °C)	
Tetrafluoroborate	6	1.248 (20 °C)	67 (20 °C)	
Ethylsulfate		1.238	98	
1-Hexyl-3-methylimidazolium				
Bis(trifluoromethylsulfonyl)imide		1.377	71	
Hexafluorophosphate	−61	1.304	585	376
Tetrafluoroborate	−82	1.208	314	
1-Octyl-3-methylimidazolium				
Bis(trifluoromethylsulfonyl)imide	−86	1.310	87	>300
Tetrafluoroborate	−79	1.110	439	
Hexafluorophosphate	−70	1.238	682	

properties in total but systematic changes to the structure of the ionic liquid should allow salts with the desired range of properties to be identified, at least in theory, if not always in practice, at the present time. Low toxicity for all ionic liquids is a debatable issue now that toxicity screening has commenced [42–44] but other properties of ionic liquids should facilitate recycling compared with volatile organic solvents reducing their potential environmental impact. Their negligible vapor pressure minimizes environmental contamination through evaporation, a major concern for conventional organic solvents, allows their use in vacuum systems without appreciable loss, and facilitates product recovery by distillation or sublimation. In addition, ionic liquids are increasingly being studied as solvents for synthesis due to specific advantages in rate, specificity, and yield, as much as for simple replacements for volatile organic solvents [14,45–47]. The presence of a supramolecular structure held together by hydrogen-bonds, in the main, results in a structural directionality that is absent in common isotropic solvents [47]. In other words, ionic liquids can be viewed as a pre-organized medium that can modify molecular reactivity by the formation of "inclusion complexes" between guests (reactive species) and the "host networks" (ionic liquids).

2. Solvent characteristics

The use of a solvent for extraction is determined by a combination of physical properties and solvation characteristics. The physical properties of interest are made up of fundamental characteristics such as density, viscosity, vapor pressure, conductivity, and miscibility with other solvents. Except for mutual solubility (discussed in Section 2.3) these properties were discussed above and point to favorable features of ionic liquids (low vapor pressure and high density), neutral features (high conductivity is relevant in electrochemical applications but does not seem to have a specific role in solvent extraction for neutral organic compounds), and unfavorable features (high viscosity) compared with conventional organic solvents. Solvation behavior is generally characterized by solvent strength (often taken to be synonymous with polarity), solvent selectivity (synonymous with the capability of the solvent to interact with other compounds by defined intermolecular interactions), and solubility. Solubility data is quite sparse for room temperature ionic liquids and insufficient for a detailed discussion [14,48–50], except, it is clear from studies in synthesis that ionic liquids can dissolve a wide and varied range of organic and inorganic compounds in reasonable mole ratios. Also, recent studies demonstrate the suitability of room temperature ionic liquids as solvents for biopolymers as varied as enzymes and wood [51–53]. On the other hand, spectroscopic methods used to establish solvent strength, and chromatographic methods for solvent selectivity, are more numerous and facilitate a broader discussion of the characteristic solvation properties of room temperature ionic liquids and how these properties compare with conventional organic solvents.

2.1. Solvatochromism

The polarity or strength of a solvent is a well-accepted concept but suffers from a rather vague definition. Polarity can be viewed as the capacity of a solvent for all intermolecular interactions between the solvent and solute that do not result in chemical reactions [15,54,55]. In this way the structures of the interacting species are conserved. The interactions involved include several distinct intermolecular forces with the consequence that no single probe molecule is capable of providing a quantitative scale of solvent polarity. From this basis the general concept of solvatochromism and other solvent-induced spectral properties are not exact measures of solvent strength, but with careful interpretation, provide a useful indication of general solvent properties suitable for indicating gross similarities and differences between conventional solvents and room temperature ionic liquids.

Solvatochromism describes the prominent change in the UV–vis absorption spectra observed for probe molecules such as Reichardt's betaine dye [15,55–59], Nile red [15,59] or phenol blue [57] with changes in the solvent strength of the medium. Each indicator dye measures polarity to a different degree determined by the relative contributions from all types of intermolecular interactions. The individual scales are not quantitatively equivalent but indicate broadly similar differences in solvent strength. Probably the most

Table 3
Solvent strength determined by solvatochromism for representative room temperature ionic liquids and traditional organic solvents.

Ionic liquid	Reichardt's dye		Kamlet-Taft		
	$E_{T(30)}$	E_T^N	π^*	α	β
Ethylammonium nitrate	61.6	0.95	1.24	0.85	0.46
n-Propylammonium nitrate	60.6	0.92	1.17	0.88	0.52
Di-*n*-propylammonium thiocyanate	63.3	1.01	1.16	0.97	0.39
1-Butyl-3-methylimidazolium					
Hexafluorophosphate	52.3	0.67	1.03	0.63	0.21
Tetrafluoroborate	52.5	0.67	1.05	0.63	0.38
Trifluoroacetate	51.1	0.63			
Trifluoromethanesulfonate	52.3	0.67	1.01	0.63	0.46
Bis(trifluoromethylsulfonyl)imide	51.5	0.64	0.98	0.62	0.24
1-Butyl-2,3-dimethylimidazolium					
Bis(trifluoromethylsulfonyl)imide	49.3	0.57	0.99	0.45	0.26
Tetrafluoroborate	49.4	0.58	1.08	0.40	0.36
1-Ethyl-3-methylimidazolium					
Bis(trifluoromethylsulfonyl)imide	52.6	0.68			
Tetrafluoroborate	53.7	0.71			
1-Hexyl-3-methylimidazolium					
Bis(trifluoromethylsulfonyl)imide	51.9	0.65	0.98	0.65	0.25
Tetrafluoroborate	53.6	0.71			
Trifluoromethanesulfonate	52.5	0.67	0.98	0.67	0.52
1-Octyl-3-methylimidazolium					
Bis(trifluoromethylsulfonyl)imide	51.0	0.63	0.97	0.60	0.28
Tetrafluoroborate	52.4	0.67			
Hexafluorophosphate	50.0	0.60	0.88		
Water	63.1	1.00	1.09	1.17	0.18
Methanol	55.8	0.77	0.60	0.93	0.62
Acetonitrile	51.9	0.65	0.80	0.35	0.38
Dimethyl sulfoxide	45.0	0.44	1.00	0	0.76
Dimethylformamide	43.8	0.40	0.88	0	0.69

widely used empirical scale of solvent polarity is the $E_{T(30)}$ scale (or equivalent normalized E_T^N scale) employing changes in the charge transfer π–π^* absorption band for the zwitterionic 2,6-diphenyl-4-(2,4,6-triphenyl-*N*-pyridino)phenolate (Reichardt's betaine dye). This compound exhibits one of the largest solvatochromic effects of any known compound and a large number of values for both room temperature ionic liquids and conventional solvents are available. Some representative values for ionic liquids and common organic solvents are summarized in Table 3 (a more extensive compilations for ionic liquids can be found in Refs. [15,55–57]). The alkylammonium nitrate and thiocyanate ionic liquids have E_T^N values similar to water while the 1,3-dialkylimmidazolium salts are less polar than water with values that cover a similar range to polar organic solvents (e.g., dimethyl sulfoxide at the lower end of the range and short-chain aliphatic alcohols at the higher end) [31]. The introduction of a methyl group at the C-2 position on the imidazole ring of the 1,3-dialkyliidazolium ionic liquids reduces the polarity of the ionic liquid, as would be expected, since the C-2 hydrogen is capable of hydrogen-bonding interactions [57]. It is well known that the E_T^N scale measures preferentially the solvent's dipolarity/polarizability and hydrogen-bond acidity, since the betaine dye is neither a hydrogen-bond donor nor an electron-pair acceptor [54,55]. However, the above indications are entirely compatible with the observations made with Nile red [15] and phenol blue [54], which have a different blend of intermolecular interactions that contribute to the polarity scale. These results are also in agreement with solvent effects on the fluorescence spectra of polycyclic aromatic hydrocarbons [15,60–62] and polar fluorescence probes such as 1-pyrenecarboxaldehyde [15,62].

Also collected in Table 3 are representative values for the solvatochromic parameters, originally developed by Kamlet and co-workers, which have been determined for a number of room temperature ionic liquids as well as numerous organic solvents [15,56,57,62–64]. By this approach solvents are characterized according to their capacity for interactions described as dipolarity/polarizability (π^*), hydrogen-bond acidity (α), and hydrogen-bond basicity (β). These values are determined by absorption measurements for individual or pairs of selected indicator compounds [63] and the scales normalized so that dimethyl sulfoxide for π^*, methanol for α, and hexamethylphosphoramide for β are assigned values of one. The alkylammonium nitrate and thiocyanate salts in Table 3 are slightly more dipolar/polarizable than dimethyl sulfoxide, about as strong a hydrogen-bond acid as an aliphatic alcohol, and moderately hydrogen-bond basic, similar to ethyl acetate [58]. The 1,3-dialkylimidazolium ionic liquids are about as polar/dipolarizable as dimethyl sulfoxide largely indepen-

Table 4
Solute descriptors used in the solvation parameter model.

Descriptor	Solute property
E	Electron lone pair interactions
S	Dipolarity/polarizability
A	Hydrogen-bond acidity
B	Hydrogen-bond basicity
L	Gas–liquid partition coefficient on hexadecane at 25 °C (cavity formation and dispersion interactions)
V	McGowan's characteristic volume (cavity formation and dispersion interactions)

dent of the anion type; are moderate hydrogen-bond acids, if there is a hydrogen atom at the C-2 position, but significantly weaker than aliphatic alcohols; and weak to moderate hydrogen-bond bases depending mainly on the anion type [62].

The main conclusion from all the above studies on the effect of solvation on the spectroscopic properties of probe molecules is that they do not indicate any extraordinary or extreme solvation properties for the room temperature ionic liquids. The room temperature ionic liquids are all dipolar/polarizable and posses a range of hydrogen-bonding properties related to structure but their solvation properties fit quite well into the scales already developed for conventional organic solvents.

2.2. Partition coefficients

There are few comprehensive studies of liquid–liquid or gas–liquid partitioning processes involving room temperature ionic liquids [5,8]. In this section sources of experimental data will be identified and the partitioning data unified through application of the solvation parameter model [15,24,25,65–67]. This model facilitates identification of the contributions from individual intermolecular interactions to the partition process. The solvation parameter model is set out below for partition of neutral compounds between a gas and a liquid

$$\log K = c + e\mathrm{E} + s\mathrm{S} + a\mathrm{A} + b\mathrm{B} + l\mathrm{L} \quad (1)$$

and for partition between two liquid phases

$$\log P = c + e\mathrm{E} + s\mathrm{S} + a\mathrm{A} + b\mathrm{B} + v\mathrm{V} \quad (2)$$

where $\log K$ is the gas–liquid partition coefficient and $\log P$ the liquid–liquid partition coefficient. The contributions to the partition coefficients are made up of a series of product terms where the upper case letters indicate a solute property (descriptors) and the lower case letters in italics the complementary properties of the distribution system (system constants). For the characterization of ionic liquids the solute descriptors are not important. They are defined in Table 4, and are determined by calculation or experimental techniques described elsewhere [65–67]. The system constants describe the capability of the system for electron lone pair interactions, *e*, interactions of a dipole type, *s*, the system acting as a hydrogen-bond base, *a*, or hydrogen-bond acid, *b*, and the requirements for cavity formation and set up of dispersion interactions *l* and *v*, with the *l* term used for transfer from the gas phase to a liquid and the *v* term for transfer between two condensed phase. The system constants are more than mere fitting constants and contain chemical information describing the solvation properties of the system. When transfer occurs from a (near) ideal gas phase to a liquid phase, as is typically the case in gas chromatography, the system constants describe the solvation properties of the liquid phase alone, and thus allow a straightforward comparison of the properties of the liquid phase, albeit a room temperature

Table 5
System constants at 25 °C (except as noted) for ionic liquids and some representative polar non-ionic solvents.

Ionic liquid	System constants					
	c	*e*	*s*	*a*	*b*	*l*
1-Butyl-3-methylimidazolium						
Bis(trifluoromethylsulfonyl)imide	−0.366	0.148	1.946	2.261	0.872	0.688
Trifluoromethanesulfonate	−0.449	0.567	1.987	3.615	0.857	0.584
Tetrafluoroborate	−0.576	0.605	2.278	3.427	0.471	0.590
Hexafluorophosphate	−0.602	−0.087	2.841	2.785	0.140	0.631
1,3-Dimethylimidazolium						
Dimethyl phosphate (39 °C)	−0.61	0.86	2.59	7.27	0	0.35
1-Ethyl-3-methylimidazolium						
Diethyl phosphate (39 °C)	−0.09	0.26	1.97	6.90	0	0.54
Trifluoroacetate	−0.810	0	2.694	5.462	0.734	0.669
Ethylsulfate	−0.709	0.137	2.544	5.262	0.042	0.592
Bis(trifluoromethylsulfonyl)imide	−0.499	0.205	2.304	2.194	1.072	0.641
Trihexyl(tetradecyl)phosphonium						
Bis(trifluoromethylsulfonyl)imide	−0.447	−0.619	1.666	2.262	0.03	0.957
1-Hexyl-3-methylimidazolium						
Bis(trifluoromethylsulfonyl)imide	−0.170	−0.116	2.079	2.141	0.429	0.704
Trimethylbutylammonium						
Bis(trifluoromethylsulfonyl)imide	−0.288	0.115	2.047	2.152	0.723	0.627
1-Octyl-3-methylimidazolium						
Tetrafluoroborate	−0.268	−0.100	1.800	3.224	0.453	0.722
4-Methyl-*N*-butylpyridinium						
Tetrafluoroborate	−0.611	0.487	2.484	3.190	0.558	0.606
1,2-Dimethyl-3-ethylimidazolium						
Bis(trifluoromethylsulfonyl)imide	−0.565	0.214	2.347	2.075	0.896	0.655
Acetonitrile	−0.007	−0.595	2.461	2.085	0.418	0.738
Chloroform	0.168	−0.595	1.259	0.280	1.370	0.981
Acetone	0.154	−0.277	1.522	3.258	0.078	0.863
Ethyl acetate	0.203	−0.335	1.251	2.949	0	0.917
Nitrobenzene	−0.295	0.121	1.682	1.247	0.370	0.915
N,*N*-Dimethylformamide	−0.174	−0.339	2.315	4.112	0	0.830
N-Methylpyrrolidinone	−0.293	0.253	2.210	5.094	0	0.818
Dimethyl sulfoxide	−0.619	0.131	2.811	5.474	0	0.734
Methanol	−0.004	−0.215	1.173	3.701	1.432	0.769
Butan-1-ol	−0.039	−0.276	0.539	3.781	0.995	0.934
Octan-1-ol	−0.120	−0.203	0.560	3.560	0.702	0.939
2,2,2-Trifluoroethanol	−0.092	−0.547	1.339	2.213	3.807	0.645
Water	−1.271	0.823	2.743	3.904	4.814	−0.213

ionic liquid or molecular organic solvent. When transfer occurs between two condensed phase the system constants describe the difference in solvation properties for the two phases and are only simple to compare for systems with a common phase as reference. For room temperature ionic liquids there is a significant amount of data collected by gas–liquid chromatography either as partition coefficients or as parameters that can be converted to a partition coefficient, for example, activity coefficients. The system constants for various ionic liquids studied by gas chromatography at 25 °C are summarized in Table 5. The data for the 1,3-dimethylimidazolium [63], 1-ethyl-3-methylimidazolium [68–71], 1-butyl-3-methylimidazolium [70–73], 1-hexyl-3-methylimidazolium [72], 1-octyl-3-methylimidazolium [72], 1,2-dimethyl-3-ethylimidazolium [68], trimethylbutylammonium [72], 4-methyl-*N*-butylpyridinium [72] cations with various anions and for the polar organic solvents [67,72] were taken from the sources indicated. The system constants for the room temperature ionic liquids fall into the range $e = -0.62$ to 0.86, $s = 1.7$–2.8, $a = 2.1$–7.3, $b = 0$–1.07, and $l = 0.35$–0.96. This can be compared with the range for the polar organic solvents $e = -0.60$ to 0.82, $s = 0.54$–2.8, $a = 0.28$–5.50, $b = 0$–4.8, and $l = -0.21$ to 0.98. There is more or less a quantitative overlap of the two ranges supporting the conclusion from the studies of solvatochromism that the solvation properties for the room temperature ionic liquids are not extraordinary and fit quite well into the scales developed for polar molecular solvents. The room temperature ionic liquids are about as dipolar/polarizable as acetonitrile and dimethyl sulfoxide, span a wide range of hydrogen-bond basicity, and depending on the anion, can be slightly more hydrogen-bond basic than dimethyl sulfoxide and *N*-methylpyrrolidinone, and are weak to moderate hydrogen-bond acids, similar to the aliphatic alcohols. They are generally cohesive solvents but no more so than polar non-ionic solvents. There are only a limited number of anions included in Table 5, and it is likely based on what can be inferred from general studies of stationary phases at higher temperatures that the hydrogen-bond basicity of ionic liquids may extend beyond the range observed for molecular solvents [15,74]. The hydrogen-bond acidity of the ionic liquids in Table 5 depends largely on the cation and is considerably less for the 1,3-dialkylimidazolium salts with an alkyl group at C-2, identifying the C-2 hydrogen as the most hydrogen-bond acidic of the ring hydrogen atoms. The dialkyl phosphate anion stands out for its high hydrogen-bond basicity and its affect on the cohesion of the ionic liquid compared to the predominantly highly fluorinated anions in Table 5.

To increase the variety of ionic liquids used for comparisons the system constants for further ionic liquids determined at 40 °C are summarized in Table 6 [69,75–78]. The system constants are temperature dependent and generally decline with temperature (except for the *e* system constant) in a non-linear manner over a sufficiently wide temperature window [79–82]. In the case of the 40 °C data it is reasonable to make a semi-quantitative comparison with the results in Table 5. The system constants for the ionic liquids fall into the range $e = 0$–0.86, $s = 1.40$–3.10, $a = 2.30$–7.60, $b = 0$–1.81, and $l = 0.35$–0.72. The *b* system constant for 1-ethyl-3-methylimidazolium trifluoroacetate is suspiciously high compared with the other imidazolium salts. The trifluoroacetate anion is not expected to contribute to the hydrogen-bond acidity of the ionic liquid and a value closer to the other 1-ethyl-3-methylimidazolium

Table 6
System constants for ionic liquids at 40 °C.

Ionic liquid	System constants					
	c	*e*	*s*	*a*	*b*	*l*
1-Ethanol-3-methylimidazolium						
Hexafluorophosphate	−1.14	0	3.03	2.89	1.13	0.47
Tetrafluoroborate	−1.35	0	3.03	3.64	0.76	0.50
1,3-Dimethylimidazolium						
Dimethyl phosphate	−0.61	0.86	2.59	7.57	0	0.35
1-Ethyl-3-methylimidazolium						
Diethyl phosphate	−0.09	0.26	1.97	6.90	0	0.54
4-Toluenesulfonate	−0.84	0.54	2.40	4.81	0.17	0.48
Bis(trifluoromethylsulfonyl)imide	−0.44	0.15	2.28	2.17	1.04	0.63
Trifluoroacetate	−0.92	0.61	1.63	4.21	1.81	0.58
1-Butyl-3-methylimidazolium						
Tetrafluoroborate	−0.72	0.56	2.82	3.27	0.48	0.50
Octylsulfate	−0.24	0	1.47	4.05	0	0.68
Trifluoromethanesulfonate	−0.78	0.40	2.03	3.49	0.68	0.65
1-Acryloyloxypropyl-3-methylimidazolium						
Bromide	−1.03	0	2.88	5.50	0	0.48
1-Methacryloyloxyhexyl-3-methylimidazolium						
Bromide	−0.87	0	2.46	5.36	0	0.57
1-Propenyl-3-methylimidazolium						
Bromide	−1.86	0	2.16	5.19	0	0.53
1-Propenyl-3-octylimidazolium						
Bromide	−1.60	0	1.72	4.96	0	0.57
1-Propenyl-3-decylimidazolium						
Bromide	−1.58	0	1.73	4.89	0	0.66
1-Propenyl-3-dodecylimidazolium						
Bromide	−1.51	0	1.44	4.87	0	0.72
1,2-Dimethyl-3-ethylimidazolium						
Bis(trifluoromethylsulfonyl)imide	−0.57	0.21	2.35	2.08	0.90	0.66
Triethylsulfonium						
Bis(trifluoromethylsulfonyl)imide	−0.80	0.11	2.37	2.34	0.70	0.64

Table 7
Ion-specific system constants for ionic liquids at 25 °C.

	c	*e*	*s*	*a*	*b*	*l*
Cation						
1-Ethyl-3-methylimidazolium	−0.520	0.248	2.286	2.319	1.047	0.641
1-Ethyl-2,3-dimethylimidazolium	−0.611	0.188	2.380	2.101	0.899	0.667
1-Propyl-2,3-dimethylimidazolium	−0.863	0.820	2.317	3.216	1.092	0.513
1-Butyl-3-methylimidazolium	−0.427	0.137	1.961	2.179	0.946	0.694
1-Hexyl-3-methylimidazolium	−0.395	−0.062	1.975	2.234	0.621	0.768
1-Octyl-3-methylimidazolium	−0.266	−0.218	1.218	1.642	1.317	0.832
Trimethylbutylammonium	−0.457	−0.005	2.188	2.375	0.663	0.668
N-Ethylpyridinium	−0.668	0.246	2.399	2.403	0.936	0.672
4-Methyl-*N*-butylpyridinium	−0.489	0.257	2.127	1.878	1.133	0.674
Trihexyl(dodecyl)phosphonium	−0.406	−0.547	1.602	2.338	−0.009	0.959
Anion						
Bis(trifluoromethylsulfonyl)imide	0	0	0	0	0	0
Tetrafluoroborate	−0.162	0.177	0.411	1.309	−0.574	−0.055
Hexafluorophosphate	−0.085	−0.297	0.730	0.070	−0.629	−0.054
Ethylsulfate	−0.151	−0.232	0.259	2.995	−1.034	−0.054
Trifluoromethanesulfonate	−0.283	−0.023	0.391	1.782	−0.446	0.012
Trifluoroacetate	−0.299	−0.242	0.395	3.148	−0.291	0.033
Octylsulfate	0.291	−0.312	−0.041	2.510	−1.205	0.128
Thiocyanate	−0.667	−0.200	1.477	3.385	−1.640	−0.022

salts would be expected. This value apart, the range of the system constants falls within or close to the range for the polar molecular solvents determined at 25 °C, indicating that there is no reason to imply exceptional solvation properties for these additional ionic liquids.

Once a model has been established further partition coefficients can be predicted for other compounds so long as the descriptor values for those compounds fall roughly into the descriptor space used to build the model. This approach, however, would not allow partition coefficients to be predicted for additional room temperature ionic liquids until the new ionic liquids have been characterized experimentally. It would not allow partition coefficients to be estimated for room temperature ionic liquids yet to be synthesized. To get around this problem, Acree and co-workers [75,83–85] split the individual system constants of Eqs. (1) and (2) into ion-specific system constants. Thus, they re-write Eq. (1) as

$$\log K = c_C + c_A + (e_C + e_A)\mathrm{E} + (s_C + s_A)\mathrm{S} + (a_C + a_A)\mathrm{A} + (b_C + b_A)\mathrm{B} + (l_C + l_A)\mathrm{L} \quad (3)$$

where subscript *C* represents the cation and subscript *A* the anion contribution to the solvation property of the ionic liquid. The system constants in Eq. (2) can be split in a similar way. In splitting the system constants into ion-specific contributions it is assumed that each solute–ion interaction is unaffected by the nature of the other co-ion present in the ionic liquid. To establish a common reference point for the ion-specific contributions to the solvation process the bis(trifluoromethylsulfonyl)imide anion was assigned a value of zero for each ion-specific system constant. To date, ion-specific system constants at 25 °C have been established for the 10 cations and 8 anions summarized in Table 7 [83–86]. Internal validation indicated that the use of the ion-specific system constants resulted in only a small loss in predictive ability compared with the general model [86]. For now, it is somewhat unclear if the ion-specific system constants retain relevant chemical information or are merely regression constants. For example, the *b* system constants for all anions other than bis(trifluoromethylsulfonyl)imide have negative signs. The bis(trifluoromethylsulfonyl)imide anion has no hydrogen atoms and, therefore, cannot function as a hydrogen-bond acid, so it is difficult to conceive how say the tetrafluoroborate anion (which also contains no hydrogen atoms) could be a significantly weaker hydrogen-bond acid. The descriptor space for the calculation of ion-specific system constants remains quite narrow for some ions and some of the experimental partition coefficients used to establish the system constants may be affected by interfacial adsorption. The latter is a common problem for the measurement of gas–liquid partition coefficients for compounds of low solubility (e.g., *n*-alkanes in polar solvents) but can be corrected using suitable experimental techniques [15,86–88]. Molecular simulation studies and results from mass spectrometry indicate medium range ordering for imidazolium-based ionic liquids, resulting in microphase segregation into polar and non-polar domains [89–91]. This would suggest that solute–solvent interactions are domain selective, and for data based on a varied group of compounds, would not support splitting the system properties into ion-specific terms. Models using ion-specific system constants have also been obtained for the Goss-modified Abraham model and for the transfer of neutral compounds from water to dry room temperature ionic liquids [83–86]. The latter are simply hypothetical models if mutual solubility of the two phases is significant. Their principal use is to facilitate the calculation of ion-specific system constants by increasing the size of the partition constant databases.

Data for liquid–ionic liquid partition coefficients is even more sparse than for gas–ionic liquid partition coefficients. Partition coefficients for several organic compounds were reported for the biphasic systems containing ethylammonium nitrate, *n*-propylammonium nitrate, or di-*n*-propylammonium thiocyanate and hexane, toluene, octan-1-ol, or dichloromethane [8,31,92]. In general, compounds capable of strong hydrogen-bonding interactions were selectively extracted by the room temperature ionic liquids while compounds of low polarity remained largely in the organic phase. The largest number of partition coefficients is available for the biphasic systems formed by 1-butylammonium-3-methylimidazolium hexafluorophosphate and water or heptane [8,93–96]. In addition, Liu et al. [97] have determined partition coefficients for 15 polycyclic aromatic hydrocarbons in the 1-octyl-3-methylimidazolium hexafluorophosphate–water biphasic system and Berthod and Carda-Broch [38] for varied compounds in the biphasic system formed by 1-butyl-3-methylimidazolium hexafluorophosphate–acetonitrile–water. *N*-Alkylisoquinolinium hexafluorophosphate ionic liquids (alkyl = octyl and tetradecyl) were shown to be more effective at extracting simple organic compounds from water than 1-butyl-3-methylimidazolium hexafluorophosphate [98]. In general, for ionizable compounds transfer from the aqueous phase to the room temperature ionic liquid is more efficient for the neutral form of the compound. Manipulation of the pH of the aqueous phase is an effective means of adjusting selectivity for extraction by room temperature ionic liquids, as

Table 8
System constants for liquid–liquid partition between 1-alkyl-3-methylimidazolium hexafluorophosphate and water or *n*-heptane.

System constant	1-Butyl-3-methylimidazolium			1-Hexyl-3-methylimidazolium
	Water [96]	Water [103]	Heptane [96]	Water [103]
e	1.29	0.45	3.28	0.05
s	−0.73	0.23	−0.75	0.40
a	−0.76	−1.76	2.77	−1.48
b	−2.39	−1.83	2.46	−2.11
v	0.64	2.15	−2.80	2.30
c	1.79	−0.17	−0.10	−0.13

is the case for non-ionic solvents [93,95,99]. Ionic liquids containing the hexafluorophosphate and tetrafluoroborate anions undergo a slow hydrolysis in the presence of water, producing hydrogen fluoride and other hydrolysis products [100–102]. This may be a problem for some applications using these ionic liquids in biphasic systems containing water.

The solvation parameter model, Eq. (2), was used to model the partition coefficient data for the water–1-butyl-3-methylimidazolium hexafluorophosphate system [96,103], water–1-hexyl-3-methylimidazolium hexafluorophosphate system [103], and the *n*-heptane–1-butyl-3-methylimidazolium hexafluorophosphate system [96]. In these reports only a subset of all data currently available was used. When partition coefficients from several studies were combined a poor model was obtained [13]. This was likely because of the inhomogeneity in the quality of the literature values for the partition coefficients. The models obtained for the data subsets are summarized in Table 8 [13]. There is only poor agreement for the water–1-butyl-3-methylimidazolium hexafluorophosphate systems. The system constants for the model of the Carda-Broch et al. [96] data are difficult to rationalize in chemical terms and are based on a small data set of 12 compounds with high cross-correlation between the E and S descriptors ($r = 0.85$). We have not placed any confidence in these results. The model proposed by Abraham et al. [103] makes chemical sense, and is based on a collection of partition coefficients obtained from a single source. Interpretation of Abraham et al.'s model indicates that 1-butyl-3-methylimidazolium hexafluorophosphate saturated with water is less cohesive and hydrogen-bond acidic than water, but slightly more dipolar/polarizable and has a greater affinity for electron lone pair interactions. Solute properties that favor extraction into the ionic liquid phase from water are increasing size and dipolarity/polarizability (higher values for V, E, and S). Properties that diminish extraction into the ionic liquid phase are the solute's capacity for hydrogen-bonding interactions (higher values for A and B). The model for the heptane–1-butyl-3-methylimidazolium hexafluorophosphate system is poor, which is likely for the same reasons discussed above for the biphasic system for this room temperature ionic liquid formed with water [13,96]. The indication that the *n*-heptane phase saturated with ionic liquid is more dipolar/polarizable than the ionic liquid phase is difficult to defend. Partition coefficients for a wider range of varied compounds and of a higher quality are required to establishing suitable models for predicting further partition coefficients for biphasic systems formed with room temperature ionic liquids and organic solvents.

2.3. Mutual solubility in biphasic systems

Most ionic liquids are fully or partially miscible with polar organic solvents (e.g., methanol, acetonitrile, tetrahydrofuran, dichloromethane, acetone, etc.). Biphasic systems are commonly formed with organic solvents of low polarity (e.g., hexane, toluene, alkyl ethers) or with water. A table of solvent miscibility for room temperature ionic liquids is given in Poole [15]. General guidelines for predicting mutual solubility of ionic liquids and water have been suggested by Seddon et al. [104]. 1,3-Dialkylimidazolium salts with halide, ethanoate, nitrate and trifluoroacetate anions are, in general, completely miscible with water. The salts formed with the hexafluorophosphate and bis(trifluoromethylsulfonyl)imide anions are generally immiscible with water, while the salts formed with the borontetrafluoride and trifluoromethylsulfonate anions range from totally soluble to immiscible with water depending on the length of the alkyl chains on the cation. All 1,3-dialkylimidazolium tetrafluoroborates are generally miscible with acetone and dichloromethane. 1-Ethyl-3-methylimidzolium, *N*,*N*-dialkylpyrrolidinium, and tetralkylammonium dicyanamide ionic liquids are completely miscible with water and most organic solvents except for hexane and toluene [105]. The 1,3-dialkylimidazolium methanesulfonate and ethanesulfonate ionic liquids are miscible with water and most common polar organic solvents [106]. Mutually immiscible pairs of ionic liquids (e.g., 1-ethylpyridinium bis(trifluoromethylsulfonyl)imide and trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide) have also been described [107], but no solute partitioning data was discussed. Although not specifically discussed in this section, in recent years there has been a significant increase in the reporting of liquid–liquid equilibrium data for binary and ternary solvent system formed mainly by 1,3-dialkylimidazolium-based ionic liquids with either organic solvents or water [8,15,108,109]. Good progress has been made for system containing ionic liquids in predicting phase separation using the nonrandom two-liquid segment activity coefficient model [110], UNIQUAC [111] and COSMO-RS [112].

A useful collection of solubility data for ionic liquids in water was prepared by Ranke et al. [113]. Representative data for the mutual solubility of room temperature ionic liquids and water are summarized in Table 9 [112–119]. Although biphasic systems can be formed when "hydrophobic" room temperature ionic liquids are mixed with water, the mutual solubility can be quite large [102,114]. On a mole fraction basis the solubility of water in ionic liquids is several orders of magnitude higher that the solubility of water in the ionic liquids [112]. For the 1,3-dialkylimidazolium salts increasing the alkyl chain length decreases solubility of the ionic liquid in water and of water in the ionic liquid [114,117]. The decrease in ionic liquid solubility in water is driven by a decrease in the entropy of solution [119]. Anion–water interactions are most important in establishing mutual solubility but the cation also has an influence. The introduction of an alkyl group at the C-2 position on the imidazole ring reduces hydrogen-bonding interactions with water and decreases the mutual solubility of these ionic liquids and water [112,118].

3. Applications

3.1. Extractive distillation

Distillation is a widely used separation process where volatile substances are separated based on differences in their volatility. Fractional distillation is generally inefficient for the separation of mixtures of similar volatility and impossible for azeotropes. Extrac-

Table 9
Mutual solubility of ionic liquids and water at 25 °C.

Ionic liquid	Solubility of ionic liquid in water		Solubility of water in ionic liquid	
	Mole fraction	Weight fraction (%)	Mole fraction	Weight fraction (%)
1-Ethyl-3-methylimidazolium				
Bis(trifluoromethylsulfonyl)imide	8.38×10^{-4}	1.81	0.298	1.94
Tetracyanoborate		4.2		11.7
1-Butyl-3-methylimidazolium				
Hexafluorophosphate	1.21×10^{-3}	2.0	0.272	2.3
Tricyanomethane	6.22×10^{-3}		0.857	
Bis(trifluoromethylsulfonyl)imide	3.07×10^{-4}	0.72	0.257	1.48
Tris(trifluoromethylsulfonyl)methide		0.11		0.53
1-Butyl-2,3-dimethylimidazolium				
Hexafluorophosphate	8.17×10^{-4}	1.60		
Bis(trifluoromethylsulfonyl)imide		0.61		
1-Hexyl-3-methylimidazolium				
Hexafluorophosphate	4.34×10^{-4}		0.229	
Bis(trifluoromethylsulfonyl)imide	9.58×10^{-5}	0.24	0.208	1.05
1-Octyl-3-methylimidazolium				
Hexafluorophosphate	1.27×10^{-4}	0.7	0.205	1.3
Tetrafluoroborate	1.17×10^{-3}	1.8	0.63	10.8
Bis(trifluoromethylsulfonyl)imide	3.36×10^{-5}	0.09	0.187	0.87
1-Methyl-3-propylpyridinium				
Bis(trifluoromethylsulfonyl)imide	3.75×10^{-4}		0.236	

tive distillation is used in this case and relies on the introduction of a liquid or salt (referred to as an entrainer) to the mixture that causes a significant change in the relative volatility of the components of the mixture when present at moderate concentrations [120–122]. A suitable entrainer should possess both a high selectivity and a high solvent capacity for the components to be separated. In the absence of a complete liquid–vapor diagram for the mixture and entrainer the selectivity of the system is usually determined by the ratio of the infinite dilution activity coefficients for the components of the mixture with the entrainer as the stationary phase using inverse gas chromatography for entrainers of low volatility [69,75–77]. The ratio of activity coefficients represents the maximum selectivity since the experimental selectivity at finite dilution will usually be different. Representative examples of ionic liquids used in extractive distillation are summarized in Table 10 [123–135]. The ionic liquid may form a single phase with the mixture in which it has a higher affinity for one component over the other (often hydrogen-bonding more strongly with one component than the other); or may cause phase separation in which the more volatile component is enriched in the upper phase and recovered in high purity by distillation and the lower phase leaves the column with the ionic liquid from the bottom of the distillation tower and is recovered in a second distillation; or the ionic liquid is used to establish a biphasic system in which the components of the mixture are distributed favorably between the two phases and recovered separately in high purity by subsequent distillation from each phase. The principal advantages of ionic liquids for extractive distillation are their virtual absence of vapor pressure, ability to dissolve a wide range of materials, relatively low viscosity at operating temperatures, and their low corrosivity compared with other materials. Compared to inorganic salts they are more soluble in a wider range of materials and their systems are easier to optimize. These properties suggest that ionic liquids will find further applications in extractive distillation once more is understood about their solvation properties, particularly how to identify the best choice ionic liquid for a particular application, and methods to model process conditions are developed that incorporate the typical physical and chemical properties characteristic of ionic liquids.

3.2. Aqueous biphasic systems

Aqueous biphasic systems are usually formed by combining either two incompatible and water-soluble polymers or a water-soluble polymer and a salt in water above a certain critical concentration [136]. Phase separation occurs on mixing at appropriate temperatures in which two water-containing phases are

Table 10
Ionic liquids used to separate azeotropic or close boiling mixtures by extractive distillation.

Mixture	Ionic liquid	Reference
Toluene + *n*-heptane	1-Ethyl-3-methylimidazolium triiodide	[123]
Ethanol + *n*-heptane	1-Hexyl-3-methylimidazolium hexafluorophosphate	[124]
	1,3-Dimethylimidazolium methanesulfonate	[131]
Ethanol + *n*-hexane	1-Butyl-3-methylimidazolium methanesulfonate	[133]
Aromatics + alkanes	1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[125]
Ethyl acetate + ethanol	1-Allyl-3-methylimidazolium bromide	[126]
	1-Ethyl-3-methylimidazolium tetrafluoroborate	[127]
Chloroform + ethanol	1-Ethyl-3-methylimidazolium trifluoromethylsulfonate	[128]
Water + ethanol	1-Ethyl-3-methylimidazolium acetate, or tetrafluoroborate	[122,129]
Water + tetrahydrofuran	1-(2-hydroxyethyl)-3-methylimidazolium chloride	[130]
Water + 2-propanol	1-Ethyl-3-methylimidazolium acetate	[135]
Water + *tert*-butanol	1-Ethyl-3-methylimidazolium chloride	[131]
n-Hexane + 1-hexene	1-Octylquinolinium bis(trifluoromethylsulfonyl)imide	[132]

formed with different compositions. Solutes distribute themselves between the two aqueous phases depending on their relative affinity for each phase. The technique is widely used for purifying biopolymers where advantages include favorable selectivity, low cost, rapid phase disengagement, adaptable to continuous sample processing, and retention of biological activity. However, most of the phase forming polymers (typically poly(ethylene glycols)) have high viscosity, form an opaque solution, and sometimes interfere with the analysis of extracted compounds. Most water-soluble room temperature ionic liquids tend to be water-destructuring salts (chaotropic salts) and are capable of being salted out by water-structuring salts (kosmotropic salts) forming aqueous biphasic systems [137–141]. Alternatively, sugars (e.g., fructose and sucrose) have been used as water-structuring agents to form biphasic systems with aqueous solutions of 1-butyl-3-methylimidazolium tetrafluoroborate [142,143]. In ionic liquid + inorganic salt + water solutions the driving force for phase separation is the competition between the ionic liquid and inorganic salt for water molecules. The higher affinity of the inorganic salt for water induces a migration of water away from the ions of the ionic liquid and towards those of the inorganic salt. This, in turn, decreases the hydration of the ionic liquid and reduces its solubility in water. Consequently, a phase rich in the salted-out ionic liquid separates from the rest of the solution. The inorganic salts typically employed are ammonium, potassium or sodium salts of multiply charged anions, such as phosphate, sulfate, carbonate, or citrate. For the 1,3-dialkylimidazolium-based water-soluble salts their ability to form two phases is roughly inversely proportional to their solubility in water with 1-butyl-3-methylimidazolium chloride and bromide room temperature ionic liquids together with the inorganic salts potassium phosphate or potassium hydrogen phosphate being the most widely used systems [139]. Unlike polymer-based biphasic systems applications employing room temperature ionic liquids include extraction studies with a significant number of low molecular mass compounds (e.g., tryptophan [139], opium alkaloids [144], and testosterone and epitestosterone [145]). Typical partition coefficients fall into the range of 10–125 with recoveries > 85% in a single extraction. The ionic liquid-rich aqueous phase is compatible with liquid chromatography and detection limits (UV detection) were suitable for analyzing real samples. An imidazolium-terminated poly(ethylene glycol) was used to efficiently (≈96%) extract penicillin in an aqueous biphasic system [146]. The penicillin was recovered from the polymer phase in a second aqueous biphasic system formed by adjusting the pH to slightly basic and adding 1-butyl-3-methylimidazolium hexafluorophosphate. This allowed recycling of the imidazolium-terminated polymer. The extraction of proteins by water-insoluble ionic liquids is limited by the low solubility of proteins in this type of room temperature ionic liquid and by concerns for activity loss. Aqueous biphasic systems containing water-soluble ionic liquids are likely to be more suitable for the isolation of proteins [147–150]. Model proteins have been recovered from ionic liquid–inorganic salt biphasic systems with an efficiency of 75–100% and with retention of biological activity. Hydrogen-bonding between proteins and ionic liquids was identified as the likely cause of protein unfolding [150]. The high volume fraction of water in the ionic liquid-rich phase is thought to depress the extent of protein-ionic liquid hydrogen-bonding interactions promoting preservation of the protein structure. Ionic liquid and salt aqueous biphasic systems showed a higher recovery of model proteins than methods employing poly(ethylene glycols) and salt systems as well as possessing improved processing properties, such as lower viscosity, little emulsion formation, and quick phase separations [149,150]. The results obtained so far for the extraction of both low and high molecular mass compounds by aqueous biphasic systems containing room temperature ionic liquids are encouraging and indicate a general potential for wider use as a sample preparation tool for both analysis and process chemistry. There is still limited information for partition coefficients for varied compounds from which one might assess the effect of ionic liquids on selectivity and phase diagrams are only available for a limited number of biphasic systems.

3.3. Liquid–liquid extraction

There is a general lack of a significant body of partition coefficients for biphasic systems containing ionic liquids (see Section 2.2). In this section the studies described fall into two general categories. An evaluation of the potential of ionic liquids for sample preparation purposes in which a few compounds are utilized with a single or limited range of ionic liquids. Secondly, the selective isolation of a single compound at finite dilution in studies in process chemistry in which ternary liquid–liquid equilibrium diagrams are used to evaluate the feasibility of separating a binary mixture into relatively pure single component fractions. In early studies it was shown that the ionic liquid di-*n*-propylammonium thiocyanate extracts a larger amount of all organic compounds than ethylammonium and *n*-propylammonium nitrates from hexane [92]. Compounds extracted by the ionic liquid could be recovered by back extraction into an organic solvent after dilution of the ionic liquid phase with water or buffer for analysis by gas chromatography. Alternatively, extractive derivatization (e.g., alkylation, acylation, silylation, etc., of compounds in the ionic liquid phase) facilitated recovery of the less polar derivatives from the ionic liquid phase by back extraction into an immiscible organic solvent. These steps were necessary to avoid direct introduction of the ionic liquids into the gas chromatograph. Because of their low volatility ionic liquids tend to accumulate in the injector and column resulting in an unsatisfactory separation performance.

Matsumoto et al. [151] studied the extraction of short-chain aliphatic carboxylic acids (acetic, glycolic, propanoic, lactic, pyruvic, and butyric) from water by 1-alkyl-3-methylimidazolium hexafluorophosphates. The distribution constants for the organic acids were generally quite small ($K \approx 0.02$–1.06) and varied only slightly with the alkyl chain length (butyl, hexyl or octyl) of the room temperature ionic liquid. Khachatryan et al. [152] demonstrated nearly quantitative extraction of phenols from aqueous solution adjusted to a pH < pK_a by 1-butyl-3-methylimidazolium hexafluorophosphate. Partition coefficients varied from about 11 to 97 for benzene and naphthalene compounds with a single phenolic group. For some phenols (e.g., picric acid) significant extraction by the ionic liquid was observed for conditions in which the phenol was in an ionized form. In this case, it was suggested that extraction occurs by an ion exchange mechanism in which to maintain electroneutrality for each phenolate anion transferred to the ionic liquid an equal number of hexafluorophosphate anions must enter the aqueous phase. Vidal et al. [153] evaluated a series of 1-alkyl-3-methylimidazolium hexafluorophosphate and tetrafluoroborate room temperature ionic liquids for the extraction of phenol, tyrosol and p-hydroxybenzoic acid from aqueous solution. A near quantitative extraction of the three phenols was obtained using the room temperature ionic liquid 1-octyl-3-methylimidazolium tetrafluoroborate (the results were similar to those observed using *n*-octanol). Fan et al. [154] reported similar results for the extraction of phenol, bisphenol A, pentachlorophenol, 4-octylphenol, and 4-nonylphenol for the same series of ionic liquids. The increase in extraction efficiency for the room temperature ionic liquids with the longest alkyl chain attached to the cation was assigned to the considerable importance of solute hydrophobicity on the extraction mechanism. The higher distribution constants observed for the room temperature ionic liquids containing the tetrafluoroborate anion compared with the hexafluorophosphate anion was assigned to the stronger hydrogen-bonding interactions of the phe-

nols with the tetrafluoroborate anion. The ionic liquids were more than 10-fold more efficient at extracting the phenols from water than dichloromethane. It has also been shown that phenol can be extracted from water efficiently ($K \approx 17$) by several dicationic ionic liquids containing the bis(trifluoromethylsulfonyl)imide anion [155].

An ion exchange mechanism was used to explain the high extraction efficiency of amino acids by 1-butyl-3-methylimidazolium hexafluorophosphate containing the crown ether dicyclohexano-18-crown-6 [156]. In the absence of the crown ether the extraction of amino acids was rather low. Studies of pH confirmed a common mechanism involving binding of an ammonium group on the amino acid to the dicyclohexano-18-crown-6 ether. Electroneutrality requires that if the amino acid transfers to the ionic liquid phase as a cation, an equal amount of 1-butyl-3-methylimidazolium cations must enter the aqueous phase. At an optimum pH the extraction of tryptophan, leucine, alanine, glycine, arginine and lysine from water was nearly quantitative in the above system. Wang et al. [157] studied the extraction of the amino acids (valine, leucine, tyrosine, phenylalanine, and tryptophan) from aqueous solution using the ionic liquids 1-butyl-3-methylimidazolium hexafluorophosphate, 1-hexyl-3-methylimidazolium hexafluorophosphate and tetrafluoroborate, and 1-octyl-3-methylimmidazolium tetrafluoroborate. For all ionic liquids the partition coefficients for the aromatic amino acids were higher than those for the aliphatic amino acids and fell into the range of 0.005–10 as a function of pH. The partition coefficients of the amino acids are small in the range $pH < pK_{a1}$, and almost reach a plateau for $pK_{a1} < pH < pK_{a2}$. In the range $pH < pK_{a1}$ the amino acids are predominantly in the cation form suggesting that the two main factors contributing to the extraction efficiency by the ionic liquids are the hydrophobicity of the amino acid (amino acids with polar functional groups tend to exhibit smaller partition coefficients) and the strength of electrostatic interactions between the cation of the amino acids and the anion of the ionic liquids. In general, room temperature ionic liquids containing a tetrafluoroborate anion exhibit higher extraction efficiency than ionic liquids containing the hexafluorophosphate anion in keeping with the stronger effective charge on the tetrafluoroborate anion. Increasing the alkyl chain length of the cation resulted in a general decrease in the partition coefficients. Soto et al. [158] demonstrated the efficient extraction of the antibiotics amoxicillin and ampicillin from aqueous solution at pH = 8 by 1-octyl-3-methylimidazolium tetrafluoroborate. At this pH the antibiotics are expected to exist in the anionic form with approximately two negative charges suggesting an anion-exchange mechanism is responsible for the high extraction efficiency ($K \approx 3$–20 depending on conditions).

Rogers and co-workers [98] reported the partitioning of simple benzene derivatives between water and 1-butyl-3-methylimidazolium hexafluorophosphate and compared the results with extraction into octan-1-ol. It was shown that the distribution ratios in the water–ionic liquid system correlated with the corresponding water–octanol partition coefficients, but are about an order of magnitude smaller. Rogers and co-workers [99] also demonstrated the reversible pH-dependent partitioning of thymol blue between water and 1-butyl-3-methylimidazolium hexafluorophosphate.

Vijayaraghavan et al. [159] employed the ionic liquid *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide for the extraction of azo dyes (naphthalenesulfonic acids) from aqueous solution. The dyes were extracted in an ionized form and had a distribution constant of about 2. With two or three extractions about 95% of the dye could be extracted into the ionic liquid phase. Li et al. [160] demonstrated the quantitative extraction of acid dyes from water by 1-butyl-3-methylimidazolium hexafluorophosphate. An ion exchange mechanism similar to that discussed for the amino acids and phenols above was invoked to explain the favorable distribution constants for the dyes. For reactive dyes containing an ethylsulfone group the addition of dicyclohexyl-18-crown-6 to the aqueous phase enhanced the extraction into the ionic liquid.

Table 11
Range of distribution constants for organic compounds extracted from water by nine ionic liquids (see text for identity) compared to the values for octanol [161].

Compound	Distribution constants (K)	
	Ionic liquids	*n*-Octanol
Toluene	13–200	2.73
Cyclohexanone	3–15	0.81
1-Nonanol	5–410	3.77
Acetic acid	N.E.–6	−0.17
Hexanoic acid	N.E.–25	1.92

McFarlane et al. [161] studied the extraction of toluene, cyclohexanone, nonan-1-ol, acetic acid and hexanoic acid by nine room temperature ionic liquids (1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide with alkyl = butyl, hexyl, and octyl, 1-butyl-3-methylimidazolium hexafluorophosphate, trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, trihexyltetradecylphosphonium dodecylbenzenesulfonate, tributyltetradecylphosphonium dodecylbenzenesulfonate, and trihexyltetradecylphosphonium methanesulfonate) from water under various conditions of pH, temperature, and sodium chloride concentration. The distribution constants for the ionic liquids covered a wide range as can be seen in Table 11. The room temperature ionic liquids, in general, were more efficient at extracting the neutral compounds from water than *n*-octanol, and some of the ionic liquids proved more successful at extracting the carboxylic acids than *n*-octanol. Mixtures of the room temperature ionic liquids and 1-nonanol were generally more effective for extracting the carboxylic acids than the ionic liquids alone. These authors also discussed the potential problems of using the above room temperature ionic liquids for process applications. They identified the non-negligible solubility of the ionic liquids in water, the instability of the hexafluorophosphate anion, and the high viscosity of ionic liquids at room temperature as the main problems. Future use in process applications would also have to consider the potential toxicity of the ionic liquids and the relatively high cost of most ionic liquids. Room temperature ionic liquids with quaternary ammonium cations, such as tetrahexylammonium dihexylsulfosuccinate and trioctylmethylammonium salicylate, represent low cost alternatives to the common 1,3-dialkylimidazolium-based ionic liquids for extraction, which from a process point of view have the added advantage of significantly lower solubility in water [162]. These two ionic liquids were used successfully to extract phenols and amines from an aqueous solution after adjusting the pH to ensure that the analytes were predominantly in the neutral form. Phenols could be extracted both in the neutral form and as anions (by an anion-exchange mechanism) but the extraction efficiency was significantly higher when the phenols were in the neutral form. The amines were only poorly extracted when pH conditions were adjusted to favor formation of the protonated cation. As demonstrated by the results in Table 12, the extraction of phenols and amines by the quaternary ammonium-based room temperature ionic liquids was considerably higher than observed for *n*-octanol. For the phenols and amines in Table 12 the distribution constants are generally a factor of 5–10-fold greater than observed for common 1,3-dialkylimidazolium-based room temperature ionic liquids. Yung et al. [163] concluded that 1-butyl-3-methylimidazolium hexafluorophosphate was a poor choice for the extraction of the amines tyramine and 2-methoxyphenethylamine from water due

Table 12
Extraction of phenols and amines from aqueous solution as the predominantly neutral species by quaternary ammonium-based ionic liquids compared with *n*-octanol [162].

Compound	Distribution constant (log *D*)		
	Tetrahexylammonium dihexylsulfosuccinate	Trioctylmethylammonium salicylate	*n*-Octanol
Phenol	2.5	2.1	1.46
4-Nitrophenol	3.6	3.4	1.91
2,4-Dintrophenol	4.1	3.5	1.67
2,6-Dinitrophenol	4.0	3.6	1.37
2,4,6-Trinitrophenol	3.9	3.8	1.33
1-Naphthol	3.8	3.4	2.85
2-Naphthol	3.7	3.2	2.70
Aniline	1.9	1.8	0.90
2-Nitroaniline	2.3	2.3	1.37
4-Methylaniline	2.0	2.0	1.39
Tryptamine	3.5	2.6	1.55

to their small distribution constants, higher cost, and unfavorable viscosity compared with a mixture of xylene and benzyl alcohol.

Room temperature ionic liquids are being considered for the selective extraction of target compounds at finite concentrations from chemical process systems. Contemporary applications fall mainly into three categories: the isolation of alcohols from fermentation liquors [164–166]; the isolation of aromatics from refinery process streams [125,167–173]; and the desulfurization of hydrocarbon fuels [173–182]. Typical of the first two applications ternary diagrams are used to establish operating conditions where the purpose of the ionic liquid is to facilitate phase separation simultaneously with selective extraction of the component of interest in high purity into either of the separated phases. 1-Hexyl-3-methylimidazole was used for the isolation of ethanol or butan-1-ol from water [164]. The addition of ethanol to the room temperature ionic liquid and water mixture increases the solubility of water in the ionic liquid-rich phase, while only slightly increasing the solubility of the ionic liquid in the water-rich phase. The separation of butan-1-ol from a dilute solution of butan-1-ol in water is easily accomplished using 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide with a separation factor of about 100 at 2% (v/v) butan-1-ol while for ethanol the amount of ionic liquid required for practical separations is unfavorable. The phase behavior for 1,3-dialkylimidazolium hexafluorophosphates with aqueous solutions of ethanol is quite complex and includes regions of total miscibility as ethanol functions as a co-solvent assisting the dissolution of water in the ionic liquid [165,166]. Other examples of the extraction of organic compounds by selective interactions with ionic liquids include the separation of tetrahydrofuran from water using 1,3-dialkylimidazolium tetrafluoroborate [183], the separation of ethanol from ethyl acetate using 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate [184], and the separation of octane and ethylbenzene using 1-butyl-3-methylimidazolium hexafluorophosphate in a centrifugal separator [185]. The successful application of centrifugal separators is encouraging for the use of room temperature ionic liquids in large-scale processes [185,189]. The feasibility of extracting aromatic compounds from petroleum products using room temperature ionic liquids was demonstrated by Arce and coworkers [125,168–171]. This group used 1,3-dialkylimidazolium, 1-ethylpyridinium, 2-hydroxyethyltrimethylammonium, and trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide ionic liquids for the separation of benzene from hexane, ethylbenzene from octane, and toluene from heptane as model systems for refinery products. Sulfolane is the most common solvent currently employed for the extraction of aromatics from petroleum products. Except at low aromatic concentrations, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide was superior to sulfolane for the recovery of aromatics from aliphatic compounds in the model systems [171]. The solubility of the aromatics was much higher in the ionic liquids, in general, compared with the alkanes, and for a reasonable range of aromatic concentrations the solubility of the imidazolium-based room temperature ionic liquids with short alkyl chains in the alkane-rich phase was negligible. 2-Hydroxyethylammonium and trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide ionic liquids were not as well-suited as the imidazolium-based ionic liquids for the separation due to the higher solubility of *n*-alkanes in these ionic liquids [171]. The mutual solubility of both *n*-alkanes and the imidazolium-based ionic liquids increases with the alkyl chain length and 1-dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and low molecular mass *n*-alkanes are completely miscible.

A significant amount of work, at least at the feasibility stage for model systems, exists for the desulfurization (and to a lesser extent denitrification) of oil refinery products using room temperature ionic liquids [174–182]. These studies were initiated in response to legislative actions by world governments in support of clean fuel production. Extraction of organosulfur compounds (particularly alkylated benzothiophenes and dibenzothiophenes) and aromatic nitrogen compounds (e.g., pyridine, quinoline, indole, and carbazole) naturally present in refinery products by room temperature ionic liquids is a promising avenue together with other technologies to meeting regulatory requirements. Table 13 summarizes the partition coefficients and percent extracted for dibenzothiophene from dodecane, a model system for fuel products, for 20 room temperature ionic liquids [182]. For the 1-butyl-3-methylimidazolium-based ionic liquids the partition coefficients are clustered into a narrow range of 0.9–1.9. For the seven bis(trifluoromethylsulfonyl)imides the partition coefficients span a wider range of 0.9–4.9. Thus, the general interpretation of Table 13 is that the choice of cation is most important and the choice of anion less so for the selection of a room temperature ionic liquid for the selective extraction of dibenzothiophene from dodecane. The percent dibenzothiophene extracted in a single step rises to about 83% for the *N*-butyl-3-methylpyridinium thiocyanate and *N*-butyl-3,4-dimethylpyridinium bis(trifluoromethylsulfonyl)imide. The ionic liquid 1-butyl-3-methylimidazolium chloride was shown to be suitable for the selective extraction of nitrogen-containing compounds in the presence of aromatic sulfur-containing compounds from straight-run diesel feed [181]. Gao et al. [180] recommended *N*-hexylpyridinium and *N*-octylpyridinium tetrafluoroborates for the selective extraction of aromatic sulfur-containing compounds from diesel fuel (the partition coefficients for dibenzothiophene, however, are generally smaller than those for the *N*-alkylpyridinium-based ionic liquids in Table 13). Mochizuki and Sugawara [179] demonstrated the satisfactory removal of aromatic sulfur-containing compounds from a model fuel by multiple extractions with 1,3-dialkylimidazolium alkylsulfates. Alonso et al. [177] used phase diagrams to determine the efficiency of 1-octyl-3-methylimidazolium tetrafluoroborate for the extraction

Table 13
Recovery (percent extracted) and partition coefficients for dibenzothiophene (500 ppm) from dodecane by liquid–liquid extraction with ionic liquids (phase ratio = 1) at 40 °C [182].

Ionic liquid	Percent extracted	Partition coefficient
1-Butyl-3-methylimidazolium		
Tetrafluoroborate	47	0.9
Octylsulfate	63	1.7
Trifluoromethanesulfonate	50	1.0
Hexafluorophosphate	53	1.2
Bis(trifluoromethylsulfonyl)imide	50	1.0
Thiocyanate	66	1.9
Acetate	61	1.6
N-Butylpyridinium		
Bis(trifluoromethylsulfonyl)imide	55	1.2
Tetrafluoroborate	43	0.8
N-Butyl-4-methylpyridinium		
Bis(trifluoromethylsulfonyl)imide	76	3.3
Tetrafluoroborate	70	2.3
Thiocyanate	79	3.8
Trifluoromethanesulfonate	72	2.6
N-Butyl-3-methylpyridinium		
Bis(trifluoromethylsulfonyl)imide	77	3.4
Tetrafluoroborate	70	2.3
Thiocyanate	83	4.9
Trifluoromethanesulfonate	70	2.3
N-Butyl-3,4-dimethylpyridinium		
Bis(trifluoromethylsulfonyl)imide	83	4.9
N-Butyl-3,5-dimethylpyridinium		
Bis(trifluoromethylsulfonyl)imide	81	4.0
N-Butyl-*N*-methylpyrrolidinium		
Bis(trifluoromethylsulfonyl)imide	47	0.9

of thiophene from both cyclohexane and toluene. These authors demonstrated the possibility of extracting 79% of thiophene and 83% of dibenzothiophene from a model gasoline fuel in a three-step extraction. Eβer et al. [176] demonstrated the feasibility of extracting organosulfur compounds from diesel fuels using 1-alkyl-3-methylimidazolium octylsulfate and ethylsulfate room temperature ionic liquids although the partition coefficients for the aromatic sulfur-containing compounds are not particularly high compared with other room temperature ionic liquids (see Table 13).

3.4. Liquid-phase microextraction

Liquid-phase microextraction encompasses several solvent-based extraction techniques with the goal of miniaturizing the sample preparation process to simplify laboratory operations, reduce solvent waste, and improve sample utilization. Miniaturized systems should be easier to automate and some have the potential for use in field sampling. Those techniques that employ room temperature ionic liquids include dispersive liquid-phase microextraction, single-drop liquid-phase microextraction (both headspace and immersion), hollow-fiber based liquid-phase microextraction, and solid-phase microextraction using supported liquid films.

Dispersive liquid-phase microextraction takes advantage of the low solubility of the extraction solvent, in this case a room temperature ionic liquid such as 1-hexyl-3-methylimidazolium hexafluorophosphate, to be dispersed throughout a larger sample (aqueous) volume assisted by a disperser solvent, and subsequently recovered from solution as a discrete drop [186–189]. The advantage of dispersive methods compared with single-drop microextraction is the greater surface area provided by the dispersed or dissolved extraction solvent, which enhances the rate of analyte transfer to the extraction solvent. Initially an increase in temperature was used to fully dissolve the room temperature ionic liquid in the sample solution followed by cooling and centrifugation to recover the ionic liquid as a single drop [186]. Subsequently, ultrasonication was shown to be more efficient and convenient for dispersing the room temperature ionic liquid throughout the sample. A small amount of organic solvent, such as acetonitrile, can be added to the sample to improve the extraction efficiency for poorly soluble compounds and to minimize the adsorption of these compounds to the container walls [188]. In situ formation of the extraction phase by adding a small amount of sodium hexafluorophosphate to a sample solution containing 1-hexyl-3-methylimidazolium tetrafluoroborate afforded a convenient method of forming a dispersive phase within the sample solution [189]. Using liquid chromatography and UV detection for analysis allowed detection limits of 0.2–0.6 $\mu g\,L^{-1}$ for various pesticides and aromatic amines in a 10 mL sample [186–188].

Single-drop liquid-phase microextraction involves suspending a drop of solvent at the tip of a microsyringe needle, usually, located in the headspace above a thermostated sample (headspace liquid-phase microextraction) or immersed in an agitated and thermostated solution (immersion liquid-phase microextraction). The extraction efficiency depends on the relative affinity of the analytes for the extraction solvent, the diffusion coefficient of the analyte in the sample solution and extraction solvent, the viscosity of the sample solution and extraction solvent, the solubility of the extracting solvent in the sample solution, and the volume of sample solution and extraction solvent. Extraction generally occurs under non-equilibrium conditions with enrichment factors that depend on the extraction time. For practical sampling conditions with 1,3-dialkylimidazolium-based ionic liquids enrichment factors of 5–200 are typical for low molecular mass compounds [190]. Higher enrichment factors and shorter sampling times are generally observed for headspace liquid-phase microextraction because of its better mass transfer characteristics. In the headspace mode the analyte does not need to be transported across a liquid–liquid interface, which is the rate determining step for the direct-immersion method. Conventional organic solvents, which dominate the practice of liquid-phase microextraction, are limited by drop instability, limited drop size, and solvent evaporation or solubility in the sample solvent. The low vapor pressure and high viscosity of ionic liquids can address these problems facilitating the suspension of larger drop volumes, allowing the use of longer extraction times, and eliminating evaporation losses. When gas chromatography is used for the determination step, however, a major disadvantage of ionic liquids is that they contaminate sample inlets and columns resulting in distorted chromatograms of little practical utility. To circumvent this problem a novel sample inlet with a removable insert was developed for the direct injection of room temperature ionic liquids containing volatile organic compounds [191–194]. More generally, however, for the analysis of ionic liquid extracts reversed-phase liquid chromatography with UV detection has been used. Ionic liquids are compatible with columns and aqueous organic mobile phases used in reversed-phase liquid chromatography, and apart from interference in the detection of some analytes by the large ionic liquid peak close to the column hold-up time, there is usually no problem with direct introduction of the small volumes of ionic liquids used in liquid-phase microextraction. The dominance of liquid chromatography as the analysis tool does mean that the typical applications described for liquid-phase microextraction using room temperature ionic liquids are often different to those proposed for conventional organic solvents where gas chromatography is the dominant separation method. With the use of the special inlet discussed above halomethanes and alkyl aromatic compounds (BTEX) in water were determined by headspace liquid-phase microextraction using 1-octyl-3-methylimidazolium hexafluorophosphate as the extraction solvent [191–194]. Other applications of headspace liquid-phase microextraction include the

extraction of chlorobenzenes [195] and chloroanilines [196] from water by 1-butyl-3-methylimidazolium hexafluorophosphate with separation by reversed-phase chromatography. Applications using immersion liquid-phase microextraction include the analysis of polycyclic aromatic hydrocarbons [197], alkylphenols [198], and benzophenone (from urine) [199] using 1,3-dialkylimidazolium hexafluorophosphates as the extraction solvent and reversed-phase chromatography for separation. Formaldehyde (as a 2,4-dinitrophenylhydrazone derivative) was extracted from a filtered suspension of shiitake mushrooms by immersion liquid-phase microextraction using 1-octyl-3-methylimidazolium hexafluorophosphate as the extraction solvent and reversed-phase chromatography for separation [200]. Although an adequate linear range and detection limits of 0.3–5 $\mu g\,L^{-1}$ conforming to requirements for regulatory analyses were demonstrated in the above studies, there is no indication that any of these methods have moved from the proof of concept phase, or replaced conventional methods for monitoring these analytes.

A general approach used to overcome the problems of drop instability in liquid-phase microextraction is the use of hollow fibers as a support for the extraction solvent. The extraction solvent is immobilized within the pores of the membrane and forms a liquid barrier between the donor phase (sample solution) and acceptor phase (injection solvent). Typically about 1 cm of a porous poly(propylene) hollow-fiber membrane (internal diameter 0.6 mm) is sealed at one end and the other end is attached to a microsyringe to facilitate moving the acceptor solvent into and out of the fiber. This arrangements acts as the sampling device and is immersed in a stirred solution (donor phase) for extraction. The requirements for the barrier solvent are low volatility and immiscibility with the donor and acceptor phases as well as good extraction efficiency and suitable mass transfer properties for the analytes. Rather few organic solvents (e.g., toluene and 1-octanol) are currently used as solvent barriers and this restricts the range of possible applications for this technique. For aqueous donor phases the room temperature ionic liquids 1-octyl-3-methylimidazolium hexafluorophosphate [201] and 1-butyl-3-methylimidazolium hexafluorophosphate [202] were shown to be suitable barrier solvents for the extraction of chlorophenols into a basic buffer and aliphatic and aromatic hydrocarbons into toluene, respectively. The use of toluene as an acceptor phase is notable in the extraction of aliphatic and aromatic hydrocarbons, since it allows direct transfer of the sample into a gas chromatograph, a major problem when ionic liquids are used as the acceptor phase, for example, in single-drop liquid-phase microextraction. Limits of detection for the chlorophenols were in the range of 0.5–1 $\mu g\,L^{-1}$ and aliphatic and aromatic hydrocarbons 1–7 $ng\,L^{-1}$, which are suitable for analysis of typical environmental samples. For the aliphatic and aromatic hydrocarbons enrichment factors were 53–210 and recoveries 77–100% for an extraction time of 40 min using a 10 mL donor phase with an analyte concentration of 5 $ng\,L^{-1}$.

Solid-phase microextraction is a widely used sampling technique employing an immobilized liquid film supported on a fused silica fiber as a sampling device. The fiber can be retracted into a syringe needle facilitating handling in the extraction phase (exposure to the sample) and recovery phase (thermal desorption in a gas chromatograph injection port or solvent rinse for liquid chromatography). Room temperature ionic liquids were used as the extraction solvent in solid-phase microextraction initially as a physically adsorbed film on a fused silica fiber or stainless steel wire [203]. The higher surface area and improved mass transfer properties of thin films compared with a drop suggest that this format could have significant advantages. Although physically adsorbed films of 1-octyl-3-methylimidazolium hexafluorophosphate were shown to be successful for the headspace extraction of volatile aromatic hydrocarbons from paint samples detection limits were rather poor compared with commercially available polymer-coated fibers due to the relatively thin films of ionic liquid that could be coated on the fiber. In addition, physically adsorbed films lack mechanical stability as the coated fiber is moved in and out of its housing and during thermal desorption for release of the analytes into the gas chromatograph [204]. The coating could be renewed for each use but the film thickness is not easily controlled using dipping as the film loading process. To increase the film loading and uniformity fused silica fibers were precoated with a Nafion polymer (a perfluorinated polymer with side chains terminated in sulfonic acid groups) [204] or etched with a solution of ammonium hydrogen difluoride [205] prior to dip coating with a solution of 1-octyl-3-methylimidazolium trifluoromethanesulfonate. Etching was more effective than precoating with Nafion at increasing the loading of the ionic liquid and resulted in lower detection limits for polycyclic aromatic hydrocarbons in headspace solid-phase microextraction. None of these studies demonstrate that the ionic liquid film-coated fibers are a better alternative for solid-phase microextraction than fibers coated with immobilized organic polymers that are normally used. 1-Vinyl-3-alkyl imidazolium-based ionic liquids can be immobilized by crosslinking using free radical initiators [206] or by trapping in a crosslinkable silicone elastomer [207]. These methods provide mechanically stable ionic liquid films suitable for solid-phase microextraction. Both approaches resulted in fiber coatings with favorable physical properties and a reasonable lifetime for repeated use in headspace sampling. The 1-vinyl-3-alkylimidazolium-based polymerized films (film thickness of 12–18 μm) demonstrated similar extraction properties to poly(dimethylsiloxane) and poly(acrylic)-coated fibers with small selectivity differences for some compounds [206]. The fibers coated with 20% (w/w) 1-ethoxyethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide trapped in a silicone matrix had a film thickness of 50 μm and were evaluated for the headspace extraction of amphetamine and methamphetamine from urine [207]. A comparison with poly(dimethylsiloxane)-coated fibers indicated an extraction efficiency that fell between those of a 7 μm and a 100 μm film thickness fiber for the extraction of the two drugs.

3.5. Supported liquid membranes

Supported liquid membranes are prepared from a thin porous polymer or ceramic material in which the pores are filled by a solvent, in this case a room temperature ionic liquid. The membrane is used to create a permeable barrier between the feed (sample solution) and a receiving phase. Sample components that dissolve in the solvent-filled pores can cross the membrane barrier by diffusion. Selectivity results from differences in membrane permeability, resulting in enrichment of compounds of higher permeability in the receiving phase compared with the sample solution. The rate of mass transfer depends on the solubility of the analyte in the solvent-filled pores as well as the solvent viscosity. The main problems when conventional organic solvents are used in supported liquid membranes are instability and poor long-term performance, leading to a reduction of solute flux and membrane selectivity. These effects are attributed to loss of solvent from the supporting membrane, either by evaporation or dissolution/displacement into the adjacent phases. Since room temperature ionic liquids have virtually no vapor pressure loss by evaporation can be effectively suppressed [208,209]. The high viscosity and high surface tension of ionic liquids provide mechanically stable membranes more tolerant of mechanical forces, pressure drops, and temperature changes. Thin membranes with short diffusion paths compensate for the slow mass transfer due to the high viscosity of the room temperature ionic liquids. Room temperature ionic liquids immiscible

with the sample and receiving solvents should be suitable for condensed phase separations, but in reality, it is quite likely that the high mutual solubility of water and organic solvents in many room temperature ionic liquids will restrict their use for some applications [210–214]. For supported liquid membranes containing 1,3-dialkylimidazolium-based ionic liquids the selectivity observed for organic compounds in aqueous samples is lost quite quickly. In the course of the extraction, water microenvironments (reversed micelles) are formed in the ionic liquid by absorption of water from the sample or receiving phases [213,214]. Transport through these water microenvironments eventually dominates the transport mechanism initiating a non-selective transport process. These conditions are not favorable for selective enrichment of sample components. In most studies polymeric or ceramic materials with micron-sized pores have been used as supports. Recent studies have demonstrated that membranes prepared with nanometer-sized supports are superior at immobilizing liquids in the porous structure [215,216]. Supported liquid membranes containing 1-butyl-3-methylimidazolium hexafluorophosphate demonstrated remarkable selectivity for the separation of secondary and tertiary amines [208]. The high permeability for the secondary amines arises from preferential interaction of the secondary amines with the imidazole ring, mainly due to the formation of hydrogen-bonds with the protons at the C-2 position. The selectivity is largely lost in room temperature ionic liquids with an alkyl group at the C-2 position. The observed selectivity for morpholine over methylmorpholine was 83:1 for the hexafluorophosphate salt but only 44:1 for the bis(trifluoromethylsulfonyl)imide salt. Thus, although the cation plays a dominant role in establishing the selectivity the choice of anion cannot be ignored entirely.

Some of the problems discussed above for condensed phase sampling are avoided by using vapor permeation [217]. The absence of a liquid phase in direct contact with the room temperature ionic liquid mitigates against the loss of ionic liquid by dissolution, and evaporation losses are not important because of the absence of a significant vapor pressure for ionic liquids. The insignificant vapor pressure and high viscosity of ionic liquids facilitates the use of higher temperatures without loss of membrane integrity as well as enhancing mass transfer properties. A supported liquid membrane containing 1-butyl-3-methylimidazolium hexafluorophosphate showed good long-term stability and a selectivity (15–25 depending on sample feed rate) for the separation of toluene and cyclohexane with a transmembrane pressure of about 1 bar [217]. The same membrane when used to dehydrate water–alcohol mixtures had a selectivity of only 4–6 in which water was selectively extracted by the membrane. Supported ionic liquid membranes are particularly promising for the separation of carbon dioxide from industrial gas mixtures [215,216,218–220]. The high solubility of carbon dioxide in room temperature ionic liquids results from weak Lewis acid/base complex formation with carbon dioxide acting as an electron-pair acceptor and the anion of the ionic liquid as the electron-pair donor. The free volume within different ionic liquids is also said to affect the solubility of carbon dioxide. Membranes prepared with 1-ethyl-3-methylimidazolium dicyanamide provided a selectivity ratio of 20–61 for carbon dioxide over nitrogen and 11–20 for carbon dioxide over methane with good mass transfer kinetics [219]. For membranes prepared with 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide a selectivity of 8.6 was obtained for carbon dioxide over helium [219]. Task-specific room temperature ionic liquids with a free amine group, 1-(3-aminopropyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide or trifluoromethylsulfonate, were shown to facilitate the transport of carbon dioxide through liquid supported membranes resulting in selectivity values > 100 for the separation of carbon dioxide and methane and >15 for carbon dioxide and hydrogen [220,221]. These preliminary results are quite favorable in terms of selectivity, membrane stability, and throughput compared with non-porous membranes and waits testing in a process environment.

3.6. Miscellaneous

In static headspace analysis a matrix solvent is commonly used to dissolve the sample and facilitate the release of volatile compounds into the headspace. The volatility of the matrix solvent limits the sensitivity and range of compounds that can be determined by this method by restricting the maximum temperature that can be used for sampling. At temperatures approaching the boiling point of the matrix solvent excessive pressure build up in the headspace vials can be a problem. In addition, separating the large matrix solvent peak in the chromatogram from compounds of interest may also be a problem. For compounds of low volatility high sampling temperatures are desirable to increase the concentration of analyte in the vapor phase allowing favorable detection limits. Common matrix solvents such as water, dimethyl sulfoxide, *N*-methyl-2-pyrrolidinone are suitable choices for volatile solvents but limit applications to less volatile solvents, monomers, and general impurities. Room temperature ionic liquids can potentially expand the volatility range of compounds that can be analyzed by static headspace gas chromatography. They have enabled the analysis of such low volatility solvents as *N*,*N*-dimethylformamide, dimethyl sulfoxide, tri-*n*-butylamine, etc. in pharmaceutical products using 1,3-dialkylimidazolium-based ionic liquids as matrix solvents at temperatures up to 200 °C [222–225]. Equilibrium is fast at higher temperatures, usually less than 15 min, and detection limits for compounds with atmospheric boiling points > 200 °C are very good, on the order of 1–10 ng g^{-1}. 1-Butyl-3-methylimidazolium dimethyl phosphate was shown to be particularly useful for analyzing pharmaceutical products because of its ability to dissolve carbohydrate and cellulosic excipients (e.g., starch, guar, cellulose derivatives, salts of fatty acids, etc.) commonly used in formulating pharmaceutical products [225]. Von Wald et al. [224] identified the common volatile impurities in six room temperature ionic liquids considered suitable for use as matrix solvents. These were mainly contaminants carried through the production process. After heating while sparging the average concentration of contaminants could be reduced to acceptable levels. Headspace analysis was used to study the equilibria for ionic liquids with products and reactants of esterification reactions [226], ethanol produced from the hydrolysis of biomass [227], and the separation of hexene isomers in an ionic liquid saturated with silver tetrafluoroborate [228]. In the case of the ethanol determination the concentration of water in the ionic liquid was shown to affect the partition of ethanol into the vapor phase. To develop a quantitative method it was necessary to establish the hydration level of the room temperature ionic liquid in a separate experiment.

The use of room temperature ionic liquids for leaching solid samples has been little explored. Ionic liquids have good solvation properties and are expected to be less hazardous than volatile organic solvents in common use because of their negligible vapor pressure and (assumed) lower toxicity. A significant disadvantage, however, is their high viscosity, which restricts their ability to permeate porous materials. Their negligible vapor pressure renders them unsuitable for Soxhlet and similar extraction methods. Fan et al. [229] compared 1-butyl-3-methylimidazolium and 1-octyl-3-methylimidazolium hexafluorophosphates for the extraction of Sudan dyes and para red from chilli powder and oil. The 1-octyl-3-methylimidazolium-containing ionic liquid provided higher extraction efficiency and was a suitable replacement for acetonitrile, commonly used for this extraction. Several 1,3-dialkylimidazolium-based room temperature ionic liquids were evaluated for the ultrasonic-assisted extraction of piperine from

white pepper [230]. The ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate was the most successful at extracting piperine. Under optimized conditions the ionic liquid was shown to provide a higher recovery of piperine in a shorter extraction time than standard methods employing extraction with refluxing methanol–water (3:1, v/v). The extraction efficiency remained significantly higher for the room temperature ionic liquid when compared with ultrasonic-assisted extraction with methanol–water. 1-Butyl-3-methylimidazolium hexafluorophosphate and chloride were evaluated for the extraction of a limited number of organochlorine pesticides from two types of soil with different organic carbon compositions [231]. For the spiked aged soil samples recoveries by shaking with the room temperature ionic liquids were in most cases equivalent to those obtained with ethanol or acetone, but in some cases were lower. The results depended on the type of soil and there was no obvious advantage to using the ionic liquids in this application.

About 20 or so ionic liquids are known to self-aggregate in aqueous solution with the formation of micelles [232]. The 1,3-dialkylimidazolium-based ionic liquid micelles preferentially extract hydrophobic compounds from water, just like conventional surfactants, and often with a similar range of partition coefficients [233]. 1-Hexadecyl-3-methylimidazolium bromide micelles were used for the focused microwave-assisted extraction of polycyclic aromatic hydrocarbons from sediments suspended in water [234]. For a certified reference material the concentration of six polycyclic aromatic hydrocarbons determined by extraction with the ionic liquid micelles showed good agreement with the known values. The recoveries of individual compounds exceeded 90% and were higher than those obtained with hexadecyltrimethylammonium bromide. A sorbent prepared by coating silica with the ionic liquid 1-dodecyl-3-methylimidazolium bromide was used for the mixed hemimicelles-based solid-phase extraction of phthalate esters from water [235]. Recovery measurements for spiked samples exceeded 85% with detection limits of 0.1–0.2 $\mu g\,L^{-1}$ by liquid chromatography with UV detection.

4. Conclusions

Room temperature ionic liquids have yet to loose their status as "novel solvents with potential" to become conventional solvents for extraction and sample preparation. This slow pace is not unusual as much of the curiosity based research and hype resides in academia while most application-driven work is performed elsewhere. The academicians are often overtly optimistic while laboratory analysts have a long tradition of conservativism. What is clear is that the proof of concept and feasibility studies completed in academia has not obtained sufficient weight so far to establish the use of room temperature ionic liquids in routine laboratory practice. The green shoots of development seem closer to fruition in process chemistry driven mainly by the unique physical properties of ionic liquids that allow them to be used as economic and environmentally friendly replacements for conventional organic solvents at a time when such actions are seen as being politically correct.

Some general issues need attention before room temperature ionic liquids will likely become common place in analytical laboratories. There are an increasing number of ionic liquids commercially available but these are generally sold as fine chemicals. This keeps their relative cost high and purity below what would be typically specified for laboratory solvents. Since room temperature ionic liquids are not easily purified by crystallization or distillation there are no easy routes to adjust their purity. In addition, most room temperature ionic liquids are hygroscopic to some degree, and water tends to be a ubiquitous contaminant, difficult to remove completely, and subject to readjustment during laboratory manipulations if exposed to the atmosphere. The purity of room temperature ionic liquids and its affect on their solution and physicochemical properties often gets too little attention and can spoil some otherwise reliable work.

Ionic liquids have a simple structure made up of an anion and a cation. An attractive feature of such an arrangement is the comparative ease of adjusting the properties of ionic liquids by bringing different ions together to match the needs of specific applications. The global benefits of this approach remain largely a goal, as apart from ion-specific system constants for use in the solvation parameter model, no suitable methods for predicting the properties of ionic liquids yet to be synthesized or characterized has emerged to solidify the field. Thus, the selection of a room temperature ionic liquid for a specific task is more often than not an empirical process, or simply advantageous, in that the ionic liquid to hand is the ionic liquid used. Even a casual glance at the current literature will indicate that only a few of the known room temperature ionic liquids are used to any considerable extent in laboratory studies. This has the effect that the global properties of room temperature ionic liquids are continuously assessed and reassessed based on the performance of these few ionic liquids. Opportunities may be missed and false conclusions reached unless a broader view of the spectrum of room temperature ionic liquids is pressed into practice. A persistent problem of room temperature ionic liquids for several applications is their high viscosity with respect to conventional solvents. For sample preparation procedures it is necessary to pump the solvent, or there is a requirement for rapid mass transfer, then room temperature ionic liquids are generally found wanting. Room temperature ionic liquids with viscosities closer to those of conventional organic solvents would certainly have an impact on their range of applications. We should not loose sight of the fact that the high viscosity of room temperature ionic liquids was indicated as an advantage for some applications in this report. This again highlights the issue of the need to identify and include a wider range of room temperature ionic liquids in laboratory studies and the need to develop a reliable approach to predict their key physicochemical and solution properties from structure.

A positive feature of several room temperature ionic liquids is their stability over a wide temperature range and their negligible vapor pressure at comparatively high temperatures. These are two of the properties that stand out in defining the most useful applications of room temperature ionic liquids and in distinguishing the room temperature ionic liquids from conventional organic solvents. In themselves, these properties may contribute to the development of new laboratory uses for room temperature ionic liquids in sample preparation. These features come at a price, since they account for the fact that room temperature ionic liquids are incompatible with common sample introduction techniques for gas chromatography. As discussed earlier (Section 3.4), this limitation can be overcome by redesign of the sample inlet, but there are no commercially available products for this purpose at present.

We will know a lot more about room temperature ionic liquids in a decade time than we know today. For now we simply do not know enough to determine how important room temperature ionic liquids will prove to be for laboratory-scale sample preparation procedures. We do know sufficient to be optimistic and to expect further reports of advances in those areas that need to be addressed. The key feature to drive the field forward is to evoke a change in the mindset that room temperature ionic liquids are unique solvents because of their solvation properties, for which there is little in the way of supporting evidence (see Section 2) to the view that unique possibilities exist for room temperature ionic liquids because of the way they are able to blend physical and solution properties in a way that distinguishes them from polar organic solvents and, indeed, water.

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