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Review

Chromatographic and spectroscopic methods for the determination of solvent properties of room temperature ionic liquids

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Abstract

Room temperature ionic liquids are novel solvents with favorable environmental and technical features. Synthetic routes to over 200 room temperature ionic liquids are known but for most ionic liquids physicochemical data are generally lacking or incomplete. Chromatographic and spectroscopic methods afford suitable tools for the study of solvation properties under conditions that approximate infinite dilution. Gas–liquid chromatography is suitable for the determination of gas–liquid partition coefficients and activity coefficients as well as thermodynamic constants derived from either of these parameters and their variation with temperature. The solvation parameter model can be used to define the contribution from individual intermolecular interactions to the gas–liquid partition coefficient. Application of chemometric procedures to a large database of system constants for ionic liquids indicates their unique solvent properties: low cohesion for ionic liquids with weakly associated ions compared with non-ionic liquids of similar polarity; greater hydrogen-bond basicity than typical polar non-ionic solvents; and a range of dipolarity/polarizability that encompasses the same range as occupied by the most polar non-ionic liquids. These properties can be crudely related to ion structures but further work is required to develop a comprehensive approach for the design of ionic liquids for specific applications. Data for liquid–liquid partition coefficients is scarce by comparison with gas–liquid partition coefficients. Preliminary studies indicate the possibility of using the solvation parameter model for interpretation of liquid–liquid partition coefficients determined by shake-flask procedures as well as the feasibility of using liquid–liquid chromatography for the convenient and rapid determination of liquid–liquid partition coefficients. Spectroscopic measurements of solvatochromic and fluorescent probe molecules in room temperature ionic liquids provide insights into solvent intermolecular interactions although interpretation of the different and generally uncorrelated "polarity" scales is sometimes ambiguous. All evidence points to the ionic liquids as a unique class of polar solvents suitable for technical development. In terms of designer solvents, however, further work is needed to fill the gaps in our knowledge of the relationship between ion structures and physicochemical properties.

Keywords: Reviews; Room temperature ionic liquids; Solvent properties; Ionic liquids

Contents

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1. Introduction

Ionic liquids are simply liquids composed entirely of ions. They have garnered increasing interest in the last few years as novel solvents for synthesis, separations, electrochemistry and process chemistry. Organic ionic liquids were known for almost a century, but it was only during the last decade or so that they emerged as important materials with a growing applications base sufficient to sustain interest in their development. Inorganic liquids, also known as molten or fused salts, have an even longer history and are better characterized, but their high melting points, reactivity and poor solvation properties limit applications involving organic compounds. They are not discussed specifically in this article. By comparison, organic ionic liquids generally have lower melting points and favorable solvation properties for supporting a wider range of chemical applications involving organic compounds. It is a subset of these ionic liquids, room temperature ionic liquids, which are discussed here.

There is no agreed nomenclature for the materials referred to as ionic liquids in this report. Ionic liquids are generally defined as organic salts with a melting point below some arbitrary temperature, for example, 150 °C. The melting point limit has nothing to do with any fundamental property of the salts. It merely reflects the convenience of moderate temperatures for laboratory studies while ensuring the availability of a varied pool of materials for study. At temperatures above their melting point, useful organic salts afford stable liquids suitable for a variety of chemical applications where the ionic liquid acts as a solvent, electrolyte or reagent for chemical transformations. Other common terms used to describe ionic liquids (and required for comprehensive information retrieval) include molten salts, fused salts, liquid organic salts and non-aqueous ionic liquids. Although the term ionic liquids fails to distinguish between inorganic and organic salts, this is probably less important than the fact that ionic liquids has become the most widely used keyword to identify the broad range of studies employing liquid (or molten) organic salts in the most recent literature. The description room temperature ionic liquid identifies a subset of the studies of ionic liquids that can be performed at room temperature because the melting point of these materials lies below room temperature. Until recently, there were few known room temperature ionic liquids, which because of their limited number, were treated as chemical curiosities. This picture has changed dramatically in a short time with over 200 room temperature ionic liquids known today. Subsequently, room temperature ionic liquids have entered the main stream of studies of ionic liquids, where they facilitate a wider range of laboratory studies with potential for industrial applications at low and convenient temperatures. In addition, they are considered possible replacements for conventional organic solvents, which more often than not are liquid at room temperature.

The design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances is the main goal of green chemistry [1,2]. The identification of environmentally benign solvents and separation processes is one of the most active research areas in this field today. Most traditional chemical processes use large quantities of organic solvents, which because of their volatility, flammability and toxicity are incompatible with the aims of green chemistry. An ideal solvent for green chemistry should have low volatility, be chemically and physically stable, easy to handle, recyclable and reusable. Possible replacements for traditional solvents that are more compatible with the aims of green chemistry include water, perfluorinated solvents, supercritical fluids and ionic liquids [3–5]. Development of these solvents is occurring in parallel because of their complementary properties. Water, for example, is readily available, inexpensive, has low toxicity and is recyclable but is limited by the low solubility of many organic compounds, its high vapor pressure, and destruction of some products and catalysts. Many useful reactions carried out in organic solvents are ineffective or impossible in water. Cost, toxicity, poor solubility of reactants, the need for specific ligands to solubilize catalysts, thermal stability, and product contamination have so far restricted the use of perfluorinated solvents. Supercritical fluids are limited for many applications by a narrow range of solvating properties, more complex process design and higher energy requirements. Ionic liquids, on the other hand, can conceivably be designed to provide a varied range of properties. Generally favorable properties include virtually no vapor pressure; low flammability; high solubility of organic, inorganic and polymeric materials; high conductivity and large electrochemical windows; low corrosion tendencies; good thermal stability; low viscosity to facilitate mixing; and large density differences compared with other process fluids to hasten phase separation. Low toxicity would be beneficial, but toxicity data for ionic liquids is so far scarce [6]. Their environmental impact also remains to be determined.

Current interest in room temperature ionic liquids is driven by their potential or proven applications as electrolytes for electrochemical devices and processes and as solvents for organic synthesis. Emerging applications include new materials production, solvents for separation and extraction processes and as a medium for enzyme catalysis. These applications are only briefly mentioned here since they have been reviewed often in the last few years [2–5,7–14]. The main benefits of ionic liquids as solvents for organic reactions, including reactions catalyzed by transition metals, are their ability to enhance reaction rates and improve chemo- and regioselectivity relative to traditional organic solvents. This leads to improved product yield and purity as well as allowing the design of processes with favorable green chemistry attributes. In addition, small amounts of ionic liquids insure an efficient absorption of microwave energy for more efficient energy transfer [15]. Ionic liquids with non-coordinating anions dissolve polar transition metal complexes without usually affecting their properties. In a number of cases, ionic liquids were shown to have a beneficial effect on catalytic reactions, which proceed more efficiently than in traditional organic solvents. Products can often be isolated by solvent extraction or more simply by phase separation. In addition, since ionic liquids have no vapor pressure, products can be easily recovered by distillation. Of great interest and practical utility are the increasing number of reaction specific effects that have been discovered as the variety of common reactions tested in ionic liquids increases. Extensively studied processes include Diels–Alder reactions, Fridel–Crafts alkylation, Heck reactions, nucleophilic and electrophilic displacement reactions and hydrogenation reactions. Enzymes, especially lipases, maintain their catalytic activity in ionic liquids affording enhanced (enantio)selectivity, greater operational stability, ease of biocatalyst recycling and simpler product recovery schemes compared with traditional solvents [13,14]. The commercial availability of an increasing number of ionic liquids, some in bulk quantities, has contributed to the rapid expansion of studies in organic synthesis and process design [16].

2. Development of room temperature ionic liquids

2.1. Early history

The first report of a room temperature ionic liquid is probably due to Ray and Rakshit in 1911 [17]. These authors prepared the nitrite salts of ethylamine, dimethylamine and trimethylamine, which, however, spontaneously decompose on standing. The first useful room temperature ionic liquid, ethylammonium nitrate, was described by Walden [18] a few years later. This seems to have created little interest at the time [19] and it was not until the 1980s that the physical and chemical properties of this salt where studied to any significant extent [20]. This revival of interest stemmed from assertions that ethylammonium nitrate exhibited several of the unique solvent properties associated only with water. This water-like behavior was inferred from the heats, entropies and free energies of solution of non-polar gases in ethylammonium nitrate [20] and from a nearly ideal heat of mixing with water as well as the observation of micelle formation by surfactants dissolved in ethylammonium nitrate [21–23]. Mirejovsky and Arnett [24] concluded from the measurement of heats of solution of alcohols in ethylammonium nitrate that the most important characteristic of the ionic liquid was its high cohesive energy, confirmed by retention measurements of different solutes by gas–liquid chromatography [25], and not the formation of a water-like, hydrogen-bonded structure. The interest in ethylammonium nitrate led to the discovery of several analogous alkylammonium nitrate and thiocyannate room temperature ionic liquids summarized in Table 1 [26–28]. Ethylammonium nitrate, and to a lesser extent *n*-propylammonium nitrate, are still widely used today. Contemporary studies, for example, include their use as solvents for organic and enzymatic reactions [12,13,29,30]; as conductive solvents [31–33]; as solvents for cyclodextrins [34]; as solvents and support electrolytes for electrochemical reactions [35]; and in studies of the critical conditions for demixing of mixtures formed with organic solvents [36,37].

Several tetraalkylammonium salts are liquid at room temperature (Table 2). These were discovered by chance while pursuing applications of the more common higher melting point salts. The melting point minimum for quaternary alkylammonium salts usually occurs around tetra-*n*-pentylammonium and tetra-*n*-hexylammonium with a further reduction for tetraalkylammonium cations containing different alkyl groups [38]. Tetra-*n*-hexylammonium benzoate was shown to be a suitable solvent for electrochemical and kinetic studies [39]. Based on the rate of solvolysis of *tert*-butyl chloride in tetra-*n*-hexylammonium benzoate, the polarity of the ionic liquid was estimated to lie between those of ethanol and water. Tetra-*n*-heptylammonium chloride is a viscous, hygroscopic yellow liquid at room temperature with difficult handling characteristics [30,40]. A number of tetraalkylammonium tetraalkylborides are liquid at room temperature with the most widely studied example being *N*-hexyl-*N*,*N*,*N*-triethylammonium triethyl-*n*-hexylboride

Table 1
Physical properties of room temperature alkylammonium nitrate and thiocyanate ionic liquids at 25 °C

Ionic liquid	Melting point (°C)	Refractive index	Density (g/ml)	Viscosity (cP)	Dielectric constant	Temperature limit (°C)[a]	$\mathrm{UV}_{\max}$ (nm)
Ethylammonium nitrate	12.5	1.4537	1.122	32.1	13.4	170 (D), 120 (WL)	292
n-Propylammonium nitrate	4.0	1.4561	1.157	66.6	18.1	120 (D), 110 (WL)	294
Tri-*n*-butylammonium nitrate	21.5	1.4627	0.918	637	127.2	120 (D), 80 (WL)	268
Di-*n*-propylammonium thiocyanate	5.5	1.5062	0.964	85.9	43.3	180 (D), 130 (WL)	275
Butylammonium thiocyanate	20.5	1.5264	0.949	97.1	33.9	190 (D), 120 (WL)	275
sec-Butylammonium thiocyanate	22	1.5262	1.013	196	36.1	200 (D), 120 (WL)	273

[a] D = temperature at which decomposition (e.g. change in the color) is observed; WL = temperature at which weight loss is observed when maintained at this temperature for some time (hours).

[41]. The tetraalkylammonium tetralkylborides are air-stable liquids (although this is disputed [42]) and were used as solvents for spectroscopy, synthesis and electrochemistry as detailed in a number of reports from the 1970s [43–49] and comprehensively reviewed by Hussey [50]. Based on general considerations of reaction rates and electrochemical and spectroscopic properties, these solvents were said to exhibit similar polarity to conventional polar organic solvents. Lewis acid–base interactions were absent. A combination of the difficult multi-step synthesis, lack of a simple purification

Table 2
Physical properties of room temperature tetraalkylammonium ionic liquids at 25 °C

Ionic liquid	Melting point (°C)	Refractive index	Density (g/ml)	Viscosity (cP)	Temperature limit (°C)	$\lambda_{\max}$ (nm)	Reference
Tetra-*n*-heptylammonium							
Bis(trifluoromethylsulfonyl)amide	11.2		1.10	453			[54]
Chloride	−9		0.882 (35)	598	130 (WL)		[30,40]
Tetra-*n*-hexylammonium							
Benzoate	−50		0.938	895	110 (WL)		[39]
Bis(trifluoromethylsulfonyl)amide	−6.8		1.11	435			[54]
Tetra-*n*-pentylammonium							
2-[Bis(2-hydroxyethyl)amino]ethanesulfonate							[56]
Bis(trifluoromethylsulfonyl)amide	25.2		1.16	430			[54]
2-(Cyclohexylamino)ethanesulfonate					170 (WL)	228	[55,56]
2-Hydroxy-4-morpholinopropanesulfonate							[55,56]
Tetra-*n*-butylammonium							
2-(Cyclohexylamino)ethanesulfonate		1.4834		27379	180 (WL)	224	[55,56]
2-Hydroxy-4-morpholinopropanesulfonate		1.4778		4699	170 (WL)	227	[55,56]
4-Morpholinopropanesulfonate					180 (WL)		[56]
2-[Bis(2-hydroxyethyl)amino]ethanesulfonate		1.485		7349	170 (WL)	227	[55,56]
3-(Cyclohexylamino)-1-propanesulfonate					160 (WL)		[56]
3-{[Tris(hydroxymethyl)methyl]amino}-1-propanesulfonate					180 (WL)		[56]
Octanesulfonate					180 (WL)		[57]
Perfluorooctanesulfonate					220 (WL)		[57]
Tetra-*n*-propylammonium							
2-(Cyclohexylamino)ethanesulfonate					160 (WL)	288	[55]
2-Hydroxy-4-morpholinopropanesulfonate							[56]
N-Hexyl-*N*,*N*,*N*-tributylammonium							
Methanesulfonate							[53]
Thiocyanate							[52]
N-Hexyl-*N*,*N*,*N*-triethylammonium							
Triethyl-*n*-hexylboride	<−78		0.847	258	130 (WL)		[41,42]
Dicyanamide	−43				230 (D)		[51]
N-Heptyl-*N*,*N*,*N*-tri-*n*-butylammonium							
Camphorate					170 (WL)		[60]
N-Pentyl-*N*,*N*,*N*-triethylammonium							
Dicyanamide							[51]

Refractive index at the sodium-D line; WL = weight loss determined by evaporation; D = decomposition temperature; $\lambda_{\max}$ = long wavelength absorption maximum for the pure ionic liquid; number in parenthesis is the temperature of the measurement when other than 25 °C.

procedure [42] and high viscosity has diminished interest in these ionic liquids in recent years. Improved performance for electrochemical applications was demonstrated by the recently synthesized *N*-pentyl-*N*,*N*,*N*-tiethylammonium dicyanamide [51], *N*-hexyl-*N*,*N*,*N*-triethylammonium dicyanamide [51] and *N*-hexyl-*N*,*N*,*N*-tributylammonium thiocyanate [52] and methanesulfonate [53] ionic liquids. Similarly, the bis(trifluoromethylsulfonyl)amide salts of the tetra-*n*-pentylammonium, tetra-*n*-hexylammonium and tetra-*n*-heptylammonium cations are probably better candidates for exploitation in electrochemical processes than the tetraalkylammonium tetralkylborides ionic liquids [54].

The synthesis of a range of tetraalkylammonium sulfonate salts containing anions with different polar functional groups for use as stationary phases in gas chromatography lead to the discovery of 15 room temperature ionic liquids [55–58]. The chromatographic properties of these salts, including those that are liquid at room temperature, are reviewed in [59] and their thermodynamic and physicochemical properties in [60]. Salient physical properties are summarized in Table 2. Their spectroscopic and chromatographic properties are discussed later (Sections 3.1 and 3.2).

Haloaluminate and chlorocuprate salts are a well-characterized group of ionic liquids with many applications in organic synthesis and electrochemistry [61–63]. Because of their reactivity with water, oxygen and many functional groups, they are, however, a poor choice as a general solvent, and difficult to handle in the laboratory. A major breakthrough in the chemistry of ionic liquids was realized in 1992, with the report from Wilke and Zaworotko of a series of air-stable imidazolium salts with anions such as tetrafluoroborate and hexafluorophosphate [64]. In contrast to the chloroaluminate salts, these ionic liquids were tolerant to a variety of polar functional groups and opened the door to a wider range of chemical and electrochemical applications. Salts based on the 1,3-dialkylimidazolium cation represent the largest group of room temperature ionic liquids currently available.

2.2. 1,3-Dialkylimidazolium salts

The now lengthy list of 1,3-dialkylimidazolium room temperature ionic liquids is summarized in Table 3 [2,5,51,52,65–87]. In several cases, all that is known about these salts is the method of synthesis and the fact that they are liquid at room temperature, in a few cases, a full range of physical properties are available. Melting points are difficult to correlate with chemical composition. Only modest success was obtained using computer generated molecular descriptors to predict melting points of imidazolium bromides [88]. Ab initio calculations of interaction energies have shown some promise for predicting the melting points of 1-alkyl-3-methylimidazolium halides [89]. The calculated interaction energy was found to increase with decreasing alkyl chain length but no trend was found for the anion radius. Qualitatively, low symmetry, weak intermolecular interactions (such as avoidance of hydrogen-bonding) and effective charge dispersion over the cation and/or anion is likely to result in low melting 1,3-dialkylimidazolium salts [74,90]. These factors reduce the lattice energy of the crystalline form of the salt and hence lower the melting point. The effect of charge delocalization and an irregular shape of the anion has on the melting point is reflected in Table 3 by the high proportion of anions such as tetrafluoroborate, hexafluorophosphate, bis(trifluoromethylsulfonyl)amide, dicyanamide, perfluoroalkanesulfonates and perfluoroalkanecarboxylates among the room temperature ionic liquids. Delocalization of the negative charge within the S–N–S backbone of the bis(trifluoromethylsulfonyl)amide anion, for example, combined with steric protection provided by the sulfonyl oxygen atoms of the trifluoromethylsulfonyl groups presumably decrease ion–ion interactions within the solid thus facilitating ion mobility [91]. The effect of chain length (cation symmetry) on the phase diagram for 1-alkyl-3-methylimidazolium tetrafluoroborates is illustrated in Fig. 1 [83]. The salts with short alkyl chains ($n = 2$–10) are liquid at room temperature forming glasses when cooled below ambient temperature. The cations with longer alkyl chains ($n = 12$–18) are low melting solids forming a smectic mesophase region between the melting and clearing temperatures. Similar results were observed for other ionic liquids [92,93]. Many room temperature ionic liquids exhibit several glass phase transitions possibly derived from a progressive onset of dynamic rotational and/or translational motion of one or more ions from an ordered low-temperature phase [52,72–74,94].

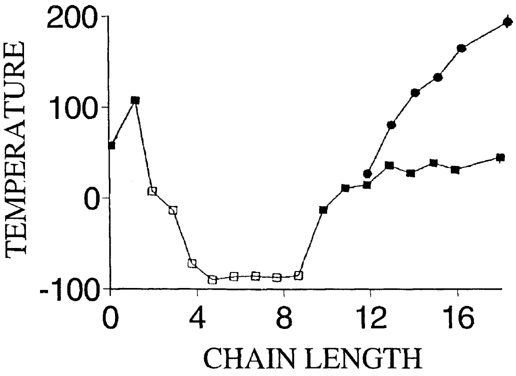

Fig. 1. Phase diagram for 1-alkyl-3-methylimidazolium tetrafluoroborate salts as a function of the alkyl chain length. Melting points are indicated by the filled boxes, glass transition temperatures by the open boxes and the clearing temperatures by the filled circles (data from [83]).

The viscosity of most 1,3-dialkylimidazolium ionic liquids remains substantially greater than typical organic solvents [51]. Higher temperatures or dilution with other solvents can be used to lower the viscosity into a more desirable range for applications restricted by high viscosity. In general, the addition of co-solvent notably reduces the viscosity, with the effect being stronger the higher the dielectric constant of the co-solvent. The viscosity of the ionic liquids is essentially determined by their tendency to form

Table 3
Physical properties of room temperature 1,3-dialkylimidazolium ionic liquids at 25 °C

Ionic liquid	Melting point (°C)	Refractive index	Density (g/ml)	Viscosity (cP)	Temperature limit (°C)	λ_{max} (nm)	References
1-Benzyl-3-methylimidazolium							
Bis(trifluoromethylsulfonyl)amide							[65]
1,3-Bis(3-fluoropropyl)imidazolium							
Bis(trifluoromethylsulfonyl)amide	−80		1.57				[66]
Hexafluorophosphate							[66]
1,3-Bis(3,3,3-trifluoropropyl)imidazolium							
Bis(trifluoromethylsulfonyl)amide	−62		1.85				[66]
1-Butoxymethyl-3-butoxymethyl-2-methylimidazolium							
Tetrafluoroborate							[67]
1-Butoxymethyl-3-decyloxymethyl-2-methylimidazolium							
Tetrafluoroborate							[67]
1-Butoxymethyl-3-dodecyloxymethyl-2-ethylimidazolium							
Tetrafluoroborate							[67]
1-Butoxymethyl-2-ethyl-3-heptyloxymethylimidazolium							
Hexafluorophosphate							[67]
Tetrafluoroborate							[67]
1-Butoxymethyl-2-ethyl-3-hexyloxymethylimidazolium							
Hexafluorophosphate							[67]
Tetrafluoroborate							[67]
1-Butoxymethyl-2-ethyl-3-nonyloxymethylimidazolium							
Hexafluorophosphate							[67]
Tetrafluoroborate							[67]
1-Butoxymethyl-2-ethyl-3-octyloxymethylimidazolium							
Hexafluorophosphate							[67]
Tetrafluoroborate							[67]
1-Butoxymethyl-2-ethyl-3-propyloxymethylimidazolium							
Tetrafluoroborate							[67]
1-Butoxymethyl-3-heptyloxymethyl-2-methylimidazolium							
Hexafluorophosphate							[67]
Tetrafluoroborate							[67]
1-Butoxymethyl-3-hexyloxymethyl-2-methylimidazolium							
Hexafluorophosphate							[67]
Tetrafluoroborate							[67]
1-Butoxymethyl-2-methyl-3-nonyloxymethylimidazolium							
Hexafluorophosphate							[67]
Tetrafluoroborate							[67]
1-Butoxymethyl-2-methyl-3-octyloxymethylimidazolium							
Hexafluorophosphate							[67]
Tetrafluoroborate							[67]
1-Butoxymethyl-2-methyl-3-pentoxymethylimidazolium							
Tetrafluoroborate							[67]
1-Butoxymethyl-2-methyl-3-propyloxymethylimidazolium							
Tetrafluoroborate	5–7						[67]
1-Butyl-2,3-dimethylimidazolium							
Bis(trifluoromethylsulfonyl)amide				97			[68,69]
Chloride[a]							[69,70]
Diethyleneglycolmonomethylethersulfate							[70]
Octylsulfate							[70]
Tetrafluoroborate							[69,70]
1-Butyl-3-ethylimidazolium							
Bis(trifluoromethylsulfonyl)amide		1.4285 (20)	1.404 (19)	48			[71]
Ethylsulfate					387 (D)		[72]
Perfluorobutanesulfonate	21	1.4025 (20)	1.427 (18)	323 (20)			[71]
Trifluoroacetate			1.183	89 (20)			[71]
Trifluoromethanesulfonate	2	1.441 (20)		90 (20)			[71]

Table 3 (*Continued*)

Ionic liquid	Melting point (°C)	Refractive index	Density (g/ml)	Viscosity (cP)	Temperature limit (°C)	λ_{max} (nm)	References
3-Butyl-1-(2-hydroxyethyl)imidazolium							
Hexafluorophosphate				542			[73]
Tetrafluoroborate				204			[73]
3-Butyl-1-{2-[2-(2-hydroxyethoxy)ethoxy]ethyl}imidazolium							
Hexafluorophosphate				923			[73]
1-Butyl-3-methylimidazolium							
Bis(trifluoromethylsulfonyl)amide	−4 (−25, WE)	1.4271 (20)	1.429		69 (27, WE)	439 (D) (349, WE)	[5,68,69,74]
Bromide						212	[70,75]
Chloride[a]							[69,76]
Dibutylphosphate							[77]
Diethyleneglycolmonomethylethersulfate				340			[70]
Heptafluorobutyrate		1.4142 (20)	1.333 (22)	182 (20)			[71]
Hexafluoroantinomate							[69,76]
Hexafluorophosphate	10 (4, WE)		1.373	450 (397, WE), 257, 371 (20), 330 (20)	349 (D) (360, WE)		[2,68,69,74,78]
Iodide	−72			1110	265 (D)		[74]
Methylsulfate	−5				392 (D)		[72]
Nitrate			1.1574	266			[2,79]
Perfluorobutanesulfonate	20	1.4052 (20)	1.473 (18)	373 (20)			[71]
Tetrafluoroborate	−81, −71		1.208	219, 154 (20)	403(D)		[2,5,69,74,79]
Tetra[4-dimethyl(octyl)silylphenyl]borate	−20				170 (D)		[80]
Tetra[4-dimethyl(1,1,2,2-tetrahydro-perfluorodecanyl)silylphenyl]borate	−10				190 (D)		[80]
Trifluoroacetate		1.4487 (20)	1.209 (21)	73 (20)			[71]
Trifluoromethanesulfonate	16	1.4380 (20)	1.290 (20)	90 (20), 99 (20)			[2,69,71]
1-*iso*-Butyl-3-methylimidazolium							
Bis(trifluoromethylsulfonyl)amide		1.4289 (20)	1.428 (20)	83 (20)			[71]
1-*N*-Butylacetylamide-3-methylimidazolium							
Tetrafluoroborate							[81]
1-*N*-Butyl-*N*-methylacetylamide-3-methylimidazolium							
Bis(trifluoromethylsulfonyl)amide							[81]
Bromide							[81]
Dicyanamide							[81]
Tetrafluoroborate							[81]
1-*n*-Decyl-3-methylyimidazolium							
Bis(trifluoromethylsulfonyl)amide							[65]
Hexafluorophosphate							[82]
Tetrafluoroborate	−25		1.072	928 (20)			[2,83]
Trifluoromethanesulfonate				981			[2]
1-*N*,*N*-Diethylacetylamide-3-methylimidazolium							
Tetrafluoroborate							[81]
1,3-Diethylimidazolium							
Bis(trifluoromethylsulfonyl)amide	14	1.4260 (20)	1.452 (22)	35 (20)			[71]
Bromide						190	[75]
Ethylsulfate					389 (D)		[72]
Trifluoroacetate		1.4431 (20)	1.250 (22)	43 (20)			[71]
Trifluoromethanesulfonate	23	1.4367 (20)	1.330 (22)	53 (20)			[71]
1,3-Diethyl-5-methylimidazolium							
Bis(trifluoromethylsulfonyl)amide	−22	1.4300 (20)	1.432 (23)	36 (20)			[71]
1,3-Dimethylimidazolium							
Bis(trifluoromethylsulfonyl)amide	22	1.4220 (20)	1.559 (22)	44 (20)			[71]
Dimethylphosphate							[77]
Methylsulfate							[70]
1-Ethyl-2,3-dimethylimidazolium							
Bis(trifluoromethylsulfonyl)amide	20	1.4305 (20)	1.495 (21)	88 (20)			[71]
4-Methylbenzenesulfonate							[70]
1-Ethyl-3,5-dimethylimidazolium							
Bis(trifluoromethanesulfonyl)amide	−39	1.4275 (20)	1.470 (22)	37			[71]
Trifluoromethanesulfonate	6	1.440 (20)	1.334 (20)	51 (20)			[71]

Table 3 (*Continued*)

Ionic liquid	Melting point (°C)	Refractive index	Density (g/ml)	Viscosity (cP)	Temperature limit (°C)	λ_{max} (nm)	References
L-1-Ethyl-3-(1′-hydroxy-3′-methyl-2′-butanyl)imidazolium							
Bromide	11–12						[84]
L-1-Ethyl-3-(1′-hydroxy-4′-methyl-2′-pentanyl)imidazolium							
Bromide	15–16						[84]
L-1-Ethyl-3-(1′-hydroxy-2′-propanyl)imidazolium							
Bromide	5–6						[84]
1-Ethyl-3-methylimidazolium							
Bis(trifluoromethylsulfonyl)amide	−3	1.4231 (20)	1.520 (22)	34 (20), 28	400 (D)		[61,63]
Bromide							[70]
Dicyanamide	−21		1.06	21 (20)	275 (D)		[51]
Ethylsulfate					408 (D)		[72]
Heptafluorobutyrate			1.450 (22)	105 (20)			[71]
4-Methylbenzenesulfonate							[70]
Methylsulfate					390 (D)		[72]
Tetrafluoroborate	5.8		1.248 (20)	66.5 (20)			[2]
Thiocyanate	−6				237 (WL)		[52]
Trifluoroacetate	−14	1.4405 (20)	1.285 (22)	35 (20)			[71,74]
Trifluoromethanesulfonate	−9	1.4332 (20)	1.390 (22)	45 (20), 50 (20)			[2,71]
1-Ethylacetyl-3-methylimidazolium							
Bis(trifluoromethylsulfonyl)amide							[81]
Bromide							[81]
Dicyanamide							[81]
Hexafluorophosphate							[81]
Tetrafluoroborate							[81]
1-*n*-Heptyl-3-methylimidazolium							
Chloride						190	[75,82]
Tetrafluoroborate	−81						[83]
1-*n*-Hexyl-3-ethylimidazolium							
Chloride						192	[75]
1-*n*-Hexyl-3-methylimidazolium							
Chloride			1.034	18,000			[2,74]
Hexafluorophosphate	−61		1.304	585 (452, WE), 690 (20)	376 (D) (374, WE)		[2,74,82]
Nitrate			1.119	804 (20)			[2]
Tetrafluoroborate	−82		1.208	314			[2,83]
1-*n*-Hexyl-2,3,4,5-tetramethylimidazolium							
Bis(trifluoromethylsulfonyl)amide							[76]
1-*n*-Hexylacetyl-3-methylimidazolium							
Bis(trifluoromethylsulfonyl)amide							[81]
Bromide							[81]
Hexafluorophosphate							[81]
Tetrafluoroborate							[81]
1-(4-Hydroxybutyl)-3-methylimidazolium							
Bromide							[73]
1-[2-(2-Hydroxyethoxyethyl]-3-methylimidazolium							
Bis(trifluoromethylsulfonyl)amide				922			[73]
Hexafluorophosphate				370			[73]
Tetrafluoroborate				201			[73]
1-{2-[2-(2-Hydroxyethoxy)ethoxy]ethyl}-3-methylimidazolium							
Bis(trifluoromethylsulfonyl)amide				2249			[73]
Hexafluorophosphate				864			[73]
Tetrafluoroborate				391			[73]
1-(2-Hydroxyethyl)-3-methylimidazolium							
Bis(trifluoromethylsulfonyl)amide				541			[82,85]
Chloride							[73]
Hexafluorophosphate				336, 149			[73,85]

Table 3 (*Continued*)

Ionic liquid	Melting point (°C)	Refractive index	Density (g/ml)	Viscosity (cP)	Temperature limit (°C)	λ_{max} (nm)	References
Tetrafluoroborate				86, 90			[73,85]
Trifluoroacetate							[73]
1-(3-Hydroxypropyl)-3-methylimidazole							
Chloride							[86]
α-Cyano-4-hydroxycinnamate							[86]
Hexafluorophosphate				538			[85]
1-[2-(2-Methoxyethoxyethyl)]-3-methylimidazolium							
Chloride				613 (20)			[73]
Hexafluorophosphate				426 (20)			[73]
Tetrafluoroborate				377 (20)			[73]
1-(2-Methoxyethyl)-3-methylimidazolium							
Bis(trifluoromethylsulfonyl)amide		1.4293 (20)	1.496 (22)	54 (20)			[71]
Chloride							[73]
Hexafluorophosphate				284			[73]
Tetrafluoroborate				263 (20)			[73]
1-Methylacetyl-3-methylimidazolium							
Bis(trifluoromethylsulfonyl)amide							[81]
Tetrafluoroborate							[81]
1-(4-Methylbenzyl)-3-methylimidazolium							
Chloride							[75]
1-*n*-Nonyl-3-methylimidazolium							
Tetrafluoroborate	−80						[83]
1-*n*-Octyl-3-methylimidazolium							
Bis(trifluoromethylsulfonyl)amide				93			[65]
Chloride			1.012	33070			[2,74]
Diethyleneglycolmonomethylethersulfate				1025			[70]
Hexafluorophosphate			1.235 (20)	691, 866 (20)			[2,68,82,87]
Octylsulfate							[70]
Tetrafluoroborate	−79		1.110	439			[2,83]
Trifluoromethanesulfonate				492			[2]
1-*n*-Octyl-2,3,4,5-tetramethylimidazolium							
Bis(trifluoromethylsulfonyl)amide							[76]
1-*n*-Octylacetyl-3-methylimidazolium							
Bis(trifluoromethylsulfonyl)amide							[81]
Bromide							[81]
Hexafluorophosphate							[81]
Tetrafluoroborate							[81]
1-Pentyl-3-methylimidazolium							
Chloride							[75]
Tetrafluoroborate	−88						[83]
1-(2-Phenylethyl)-3-methylimidazolium							
Chloride						203	[75]
1-Propyl-3-ethylimidazolium							
Bromide						190	[75]
Ethylsulfate					387 (D)		[72]
1-Propyl-3-methylimidazolium							
Bis(trifluoromethylsulfonyl)amide							[65]
Chloride						210	[75]
Methylsulfate					389 (D)		[72]
Tetrafluoroborate	−13.9						[83]
1-*n*-Propylacetyl-3-methylimidazolium							
Bis(trifluoromethylsulfonyl)amide							[81]
Bromide							[81]
Hexafluorophosphate							[81]
Tetrafluoroborate							[81]

Table 3 (*Continued*)

Ionic liquid	Melting point (°C)	Refractive index	Density (g/ml)	Viscosity (cP)	Temperature limit (°C)	λ_{max} (nm)	References
1-(2,2,2-Trifluoroethyl)-3-methylimidazolium Bis(trifluoromethylsulfonyl)amide		1.4090 (20)	1.656 (20)	248 (20)			[71]
1-(3,3,3-Trifluoropropyl)-3-methylimidazolium Bis(trifluoromethylsulfonyl)amide	−70		1.44				[66]

Refractive index at the sodium-D line; WL = weight loss determined by evaporation; D = decomposition temperature; WE = water equilibrated sample; λ_{max} = long wavelength absorption maximum for the pure ionic liquid; number in parenthesis indicated the temperature of the measurement when other than 25 °C.

[a] Reported as a solid or semi-solid in at least one reference.

hydrogen-bonds and by the strength of van der Waals interactions. Delocalization of the charge over the anion seems to favor lower viscosity by weakening hydrogen-bonding with the cation. Longer alkyl chains on the cation result in an increase in viscosity due to stronger van der Waals interactions [71]. For the same cation, viscosity decreases in the order: chloride > hexafluorophosphate > tetrafluoroborate > nitrate >bis(trifluoromethylsulfonyl)amide. These trends are visible in the entries in Table 3. The density of the 1,3-dialkylimidazolium ionic liquids at room temperature is typically greater than water and decreases approximately linearly with an increase in the cation alkyl chain length [2,74]. Many of the 1,3-dialkylimidazolium salts with weak nucleophilic anions show exceptional thermal stability allowing their use for applications at temperatures above 250 °C, and in some cases, above 400 °C, in an inert atmosphere.

2.3. Other heterocyclic cations

The high success rate in the discovery of room temperature ionic liquids based on the 1,3-dialkylimidazolium cation encouraged studies of other asymmetrically substituted heterocyclic cations in the hope of discovering additional ionic liquids with a wider range of physical and chemical properties. This strategy has proven successful (Table 4), and is far from exhausted, with a number of room temperature ionic liquids of the *N*-alkylpryridinium [70,79,95], *N*-alkylimidazolium [96], *N*-alkyl-4-methylpyrrolidinium [51], 1-alkyl-2-methylpyrrolinium [97], *N*-alkylisoquinolinium [98], and 1,4-dialkyl-1,2,4-triazolium [99] cations already reported. The tetrafluoroborate salts of several *N*-heterocyclic cations were shown to be highly conducting room temperature liquids [100]. The same asymmetric and charge-delocalized anions used successfully with 1,3-dialkylimidazolium cations to produce low melting salts were generally used with the above cations. Factors affecting melting points, viscosity, density and thermal stability seem to parallel those discussed for the 1,3-dialkylimidazolium salts, although the database is not as extensive.

2.4. Miscellaneous salts

A number of room temperature ionic liquids not belonging to any of the above groups are summarized in Table 5 [58,76,77,86,95,96,98,99,101,102]. The trialkylalkoxyammonium and alkylammonium sulfonate and carboxylate salts were studied as matrixes for MALDI mass spectrometry [86,101]. For this application, low melting salts were found to be more useful than room temperature ionic liquids. From several tetraalkylphosphonium salts synthesized for use as stationary phases in gas chromatography two were identified as room temperature ionic liquids [58]. Subsequently, several other tetraalkylphosphonium salts have been identified as room temperature ionic liquids [77]. Engel and co-workers [103,104] have described the synthesis of several complex polycationic phosphate, hexafluorophosphate and phosphate ester salts, some of which are liquid at room temperature. The synthesis of a series of trialkylsulfonium bis(trifluoromethylsulfonyl)amide salts resulted in the identification of two room temperature ionic liquids with high electrical conductivity [101]. A number of tetraalkyldimethylguanidinium salts with asymmetrical alkyl substituents and either bis-(trifluoromethylsulfonyl)amide, chloride, hexafluorophosphate or tetrafluoroborate anions were shown to be stable liquids at room temperature [102].

Not of direct interest to this review, a number of polymers with ionic groups are liquid at room temperature, and are used in electrochemical devices and as liquid ion exchangers [105].

2.5. Impurities

A number of room temperature ionic liquids are now commercially available [16,70]. These tend to be marketed as fine chemicals rather than solvents, are relatively expensive compared to traditional solvents, and generally have a lower specified purity compared with organic solvents for chemical applications. The effect of impurities on the properties of ionic liquids appears to be a somewhat neglected issue, especially with regard to trace level contamination. Most organic salts are easy to prepare by either acid–base type neutralization reactions or metathesis of halide salts with silver, sodium or ammonium salts of the desired anion [8–12]. The main advance in the synthesis of ionic liquids of higher purity is the use of microwave irradiation to enhance reaction rates, the extent of reaction and to reduce byproduct production [106–109]. Many of these reactions

Table 4
Physical properties of room temperature ionic liquids at 25 °C with heterocyclic cations other than 1,3-dialkylimidazolium

Ionic liquid	Melting point (°C)	Density (g/ml)	Viscosity (cP)	Temperature limit (°C)	Reference
N-Benzyl-2-ethylimidazolium					
Bis(perfluoroethylsulfonyl)amide			552		[96]
Bis(trifluoromethylsulfonyl)amide			252		[96]
Hexafluorophosphate			>1000		[96]
Perchlorate			>1000		[96]
Tetrafluoroborate			>1000		[96]
Trifluoromethanesulfonate			>1000		[96]
N-Butylisoquinolinium					
Bis(trifluoromethylsulfonamide)	−62	1.23			[98]
N-Butyl-4-methylpyridinium					
Bromide					[70]
Tetrafluoroborate		1.184			[95]
N-Butyl-*N*-methylpyrrolidinium					
Bis(trifluoromethylsulfonyl)amide					[69,76]
Dicyanamide	−55	0.93	50 (20)		[51]
Thiocyanate					[52]
N-Butylpyridinium					
Tetrafluoroborate					[79]
1-Butyl-4-(3,3,3-trifluoropropyl)-1,2,4-triazolium					
Bis(trifluoromethylsulfonyl)amide	−67	1.603 (24)		395 (D)	[99]
N-Decanylisoquinolinium					
Bis(trifluoromethylsulfonyl)amide	−59	1.09			[98]
2,3-Dimethylindolinium					
Tetrafluoroborate					[100]
N-Dodecanylisoquinolinium					
Bis(trifluoromethylsulfonyl)amide	−51	1.08			[98]
1-Decanyl-4-(1-fluoroethyl)-1,2,4-triazolium					
Bis(trifluoromethylsulfonyl)amide	−62			425 (D)	[99]
1-Decanyl-4-(3,3,3-trifluoropropyl)-1,2,4-triazolium					
Bis(trifluoromethylsulfonyl)amide	−68			400 (D)	[99]
N-Ethylcarbazolium					
Tetrafluoroborate					[100]
N-Ethylimidazolium					
Bis(perfluoroethylsulfonyl)amide			133	402 (D)	[96]
Bis(trifluoromethylsulfonyl)amide			54	413 (D)	[96]
Hexafluorophosphate			550		[96]
Perchlorate	21		112		[96]
Tetrafluoroborate			41		[96]
Trifluoromethanesulfonate			58	370 (D)	[96]
N-Ethyl-2-methylimidazolium					
Bis(perfluoroethylsulfonyl)amide	−19		186		[96]
Bis(trifluoromethylsulfonyl)amide			69		[96]
Hexafluorophosphate			>1000		[96]
Perchlorate	7		>1000		[96]
Tetrafluoroborate			100	309 (D)	[96]
N-Ethyl-*N*-methylpyrrolidinium					
Dicyanamide	−10			250 (D)	[51]
1-Ethylpiperidinium					
Tetrafluoroborate	−28				[100]
1-Heptyl-4-(1-fluoroethyl)-1,2,4-triazolium					
Bis(trifluoromethylsulfonyl)amide	−70	1.393 (24)		359 (D)	[99]
1-Heptyl-4-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1,2,4-triazolium					
Bis(trifluoromethylsulfonyl)amide	22			405 (D)	[99]

Table 4 (*Continued*)

Ionic liquid	Melting point (°C)	Density (g/ml)	Viscosity (cP)	Temperature limit (°C)	Reference
1-Heptyl-4-(3,3,3-trifluoropropyl)-1,2,4-triazonium					
Bis(trifluoromethylsulfonyl)amide	−67			402 (D)	[99]
N-Hexadecylisoquinolinium					
Bis(trifluoromethylsulfonyl)amide	−49	1.05			[98]
N-Hexylisoquinolinium					
Bis(trifluoromethylsulfonyl)amide	−77	1.20			[98]
N-Hexyl-*N*-methylpyrrolidinium					
Dicyanamide	−11	0.92	45 (20)		[51]
Thiocyanate					[52]
N-Methylimidazolium					
Bis(perfluoroethylsulfonyl)amide	11		218		[96]
Bis(trifluoromethylsulfonyl)amide	9		81		[96]
N-Methylindolium					
Tetrafluoroborate					[100]
N-Methylpyrazolium					
Tetrafluoroborate	−6				[100]
N-Methylpyrrolidinium					
Tetrafluoroborate	−32				[100]
N-Methylpyrrolium					
Tetrafluoroborate					[100]
N-Methyl-2-methylindolium					
Tetrafluoroborate	24.5				[100]
2-Methylpyrrolium					
Tetrafluoroborate	17.1				[100]
N-Methyl-2-methylimidazolium					
Bis(perfluoroethylsulfonyl)amide	15		>1000		[96]
Bis(trifluoromethylsulfonyl)amide	22		100		[96]
Tetrafluoroborate			100		[96]
1-Methyl-4-(3,3,3-trifluoropropyl)-1,2,4-triazolium					
Bis(trifluoromethylsulfonyl)amide	−58			376 (D)	[99]
2-Methyl-1-propylpyrrolinium					
Bis(trifluoromethylsulfonyl)amide	19	1.46 (20)	57	400 (WL)	[97]
N-Octadecylisoquinolinium					
Bis(trifluoromethylsulfonyl)amide	−47	1.05			[98]
N-Octylisoquinolinium					
Bis(trifluoromethylsulfonyl)amide	−68	1.17			[98]
N-Propyl-*N*-methylpyrrolidinium					
Dicyanamide	−35	0.92	45		[51]
Thiocyanate	7				[74]
Pyrrolium					
Tetrafluoroborate					[100]
N-Tetradecylisoquinolinium					
Bis(trifluoromethylsulfonyl)amide	−50	1.07			[98]

D = weight loss indicated by the onset of decomposition (DSC); WL = weight loss due to evaporation; number in parenthesis is the temperature of the measurement when other than 25 °C.

are solvent-free processes. Since most organic salts are hygroscopic to various extents water is a common contaminant. The concentration of water is determined in a straightforward manner by Karl–Fischer titration. Halide ions are also present in many ionic liquids prepared by metathesis reactions and can be determined by potentiometry using a halide ion selective electrode [110]. Halide ions are known to coordinate to transition metal catalysts, and thus influence (usually negatively) the rate of chemical reactions carried out in contaminated ionic liquids [111]. The presence of 1-alkylimidazole impurities in 1,3-dialkylimidazolium ionic liquids can be assessed using a simple colorimetric reaction

Table 5
Physical properties of miscellaneous room temperature ionic liquids at 25 °C

Ionic liquid	Melting point (°C)	Density (g/ml)	Viscosity (cP)	Temperature limit (°C)	Reference
Bis(*N*-*n*-butyl-*N*-methyl)dimethylguanidinium					
Hexafluorophosphate					[102]
Bis(*N*-ethyl-*N*-*n*-butyl)dimethylguanidinium					
Bis(trifluoromethylsulfonyl)amide		1.36			[102]
Tetrafluoroborate		1.05			[102]
Butylammonium					
α-Cyano-4-hydroxycinnamate					[86]
Diethylmethylammonium					
α-Cyano-4-hydroxycinnamate					[86]
Sinapinate					[86]
Diethylphenylammonium					
α-Cyano-4-hydroxycinnamate					[86]
Dimethylammonium					
2-Pyridinecarboxylate					[76]
Tetra-*n*-butylphosphonium					
Butanesulfate					[77]
2-(Cyclohexylamino)ethanesulfonate				200 (WL)	[58]
4-Morpholinopropanesulfonate				200 (WL)	[58]
Tetrakis(*N*-*n*-hexyl)dimethylguanidinium					
Bis(trifluoromethylsulfonyl)amide		1.20	346		[102]
Chloride		0.90			[102]
Hexafluorophosphate					
Tetrafluoroborate		0.97			[102]
Tetrakis(*N*-octyl)dimethylguanidinium					
Chloride		0.96			[102]
Hexafluorophosphate		0.91			[102]
Tetrafluoroborate		0.97			[102]
Tributylammonium					
Acetate					[76]
α-Cyano-4-hydroxycinnamate					[86]
3-Hydroxypyridine-2-carboxylate					[86]
2-Pyridinecarboxylate					[76]
Sinapinate					[86]
Tri-*n*-butyl(ethyl)phosphonium					
Diethylphosphate					[76]
Ethylsulfate					[76]
Tri-*n*-butyl(methyl)phosphonium					
Dimethylphosphate					[76]
Methylsulfate					[76]
Triethylammonium					
α-Cyano-4-hydroxycinnamate					[86]
2-Pyridinecarboxylate					[76]
Sinapinate					[86]
Triethylammonium$(CH_2CH_2O)_7CH_3$					
Anthraquinone-2-sulfonate					[86]
Sulfobenzoic acid					[86]
Triethylsulfonium					
Bis(trifluoromethylsulfonyl)amide	−35		30		[101]
Trihexyl(tetradecyl)phosphonium					
Bis(2,4,4-trimethylpentyl)phosphinate					[77]
Chloride			18		[77]
Tetrafluoroborate				385 (WL)	[77]
Triisobutyl(ethyl)phosphonium					
Diethylphosphate					[77]

Table 5 (*Continued*)

Ionic liquid	Melting point (°C)	Density (g/ml)	Viscosity (cP)	Temperature limit (°C)	Reference
Triisobutyl(methyl)phosphonium					
Dimethylphosphate					[77]
4-Toluenesulfonate					[77]
Tripropylammonium					
α-Cyano-4-hydroxycinnamate					[86]

D = weight loss indicated by the onset of decomposition (DSC); WL = weight loss due to evaporation; number in parenthesis is the temperature of the measurement when other than 25 °C.

with copper(II) chloride [112]. Reversed-phase liquid chromatography has been used to detect UV-absorbing impurities in 1,3-dialkylimidazolium ionic liquids [113].

Both water and chloride impurities significantly alter physical properties such as melting point, viscosity, density, conductivity and thermal stability. Some examples can be found in Tables 2–4 for the physical properties of dry and water equilibrated (WE) ionic liquids. The presence of chloride contamination commonly increases the viscosity of ionic liquids, whereas the presence of water, or other co-solvents, reduces the viscosity [74,110]. Water in ionic liquids containing the hexafluorophosphate anion results in release of hydrogen fluoride at elevated temperatures (>100 °C) [114].

If room temperature ionic liquids are left open to the atmosphere they can easily absorb water in amounts of 0.2–2 M, depending on the type of ionic liquid, the relative humidity and temperature [114,115]. For a limited, although varied number of ionic liquids, FTIR spectroscopy revealed that most water molecules absorbed from the atmosphere were hydrogen-bonded via both hydrogen atoms of water to two anions of the ionic liquid. For ionic liquids with high anion basicity (e.g. trifluoroacetates) aggregate formation, or perhaps, even droplets of bulk liquid water dispersed throughout the ionic liquid is possible. This dispersed state may prevail at high water concentrations obtained by the intentional addition of water to ionic liquids.

2.6. Thermal stability

An attractive feature of room temperature ionic liquids is their wide temperature operating range with virtually no apparent vapor pressure. Eventually at some temperature, often 300–400 °C above room temperature, a significant vapor pressure is observed using differential scanning calorimetry (weight loss WL in Tables 2–5) or thermal decomposition (D in Tables 2–5). The presence of impurities may considerably influence the fidelity of these measurements, by acting as catalysts for decomposition reactions, for example. In the case of quaternary alkylammonium salts, two general reactions, the reverse Menschukin reaction (Eq. (1)) and Hofmann reaction (Eq. (2)), have been proposed to explain their thermal decomposition [38,59]:

$$R_4N^+X^- \Rightarrow R_3N + RX \qquad (1)$$

$$R_4N^+X^- \Rightarrow R_3NH^+X^- + CH_2{=}CH_2 \qquad (2)$$

There is reasonable evidence to support Eq. (1), which is expected to follow established orders of anion nucleophilicity towards saturated carbon [116]. There is less general support for Eq. (2), as it is not clear whether bases as weak as the anions commonly used for the preparation of room temperature ionic liquids can bring about the elimination depicted. The situation for quaternary phosphonium salts is more complicated and strongly affected by the identity of the anion [117,118].

In this report we have considered ionic liquids as chemically inert solvents exerting their influence on other substances dissolved in them through physical interactions. Of course, ionic liquids can be formulated as chemical reagents for applications in chemical synthesis [12,119]. These applications, important in their own right, are not considered here. The reader should be aware that at elevated temperatures especially, chemical transformations can occur in ionic liquids due to the reactivity of the anion or cation. Some reactions involving nucleophilic displacement of halogens from saturated carbon, degradation of alkanethiols, proton transfer, and oxidation by easily reduced anions (e.g. nitrate) were observed for alkylammonium and tetraalkylammonium salts used as stationary phases in gas chromatography [59,120]. For a wide range of polar compounds with different functional groups, ionic liquids behaved as chemically inert stationary phases.

3. Physicochemical properties

An understanding of the solvent and separation properties of ionic liquids requires that studies are performed to establish core properties using different instrumental techniques. In this section, we will consider techniques that rely upon spectroscopic and chromatographic methods to provide information related to solvation properties of ionic liquids and, in particular, the contribution of intermolecular interactions to solvation behavior.

3.1. Spectroscopy

Solvatochromic and fluorescent probe compounds have been utilized to determine the polarity of solvents, including ionic liquids. Several polarity scales have been devised over the years but all suffer from a lack of a rigorous definition of polarity. While the concept of solvent polarity is easily grasped in a qualitative sense, the provision of an operational definition remains elusive. IUPAC defines solvent polarity as "the sum of all possible, non-specific and specific, intermolecular interactions between the solute ions or molecules and solvent molecules, excluding such interactions leading to definite chemical alterations of the ions or molecules of the solute" [121]. These interactions involve a number of distinct and different intermolecular forces with the consequence that no single probe molecule or macroscopic physical parameter is capable of providing a suitable scale of solvent polarity. On the other hand, studies of solute–solvent interactions by means of solvatochromic probes are both simple and convenient, if only the interpretation is carefully considered. The application of solvatochromic methods to the characterization of solvent properties of room temperature ionic liquids is discussed further.

3.1.1. *Reichardt's betaine dye*

Probably the most widely used empirical scale of solvent polarity is the $E_{T(30)}$ scale, where $E_{T(30)}$ (in kcal/mol) $= 28{,}592/\lambda_{max}$ (in nm) and λ_{max} is the wavelength maximum of the lowest energy, intermolecular charge-transfer π–π^* absorption band of the zwitterionic 2,6-diphenyl-4-(2,4,6-triphenyl-*N*-pyridino)phenolate molecule [122,123]. This compound exhibits one of the largest solvatochromic effects of any known compound. Because of its zwitterionic structure, the solvatochromic properties of Reichardt's dye is strongly affected by the hydrogen-bond acidity of the solvent, since hydrogen-bond-donating solvents stabilize the ground state more than the excited state. Taft and Kamlet calculated that about two-thirds of the shift in the absorbance maximum of Reichardt's dye could be assigned directly to specific interactions involving the phenoxide oxygen [124]. In effect, the $E_{T(30)}$ scale is largely, but not exclusively, a measure of the hydrogen-bond acidity of the solvent system. Reichardt and Harbusch-Gornert [125] also devised a normalized scale of $E_{T(30)}$ polarity, E_T^N, assigning water the value of 1.0 and tetramethylsilane zero.

The $E_{T(30)}$ and E_T^N scales of solvent polarity for ionic liquids are summarized in Table 6 [55,65,69,125–129]. The E_T^N values for the alkylammonium nitrate and thiocyanate salts are much larger than for the tetralkylammonium and 1,3-dialkylimidazolium salts with values similar to those for water (except for tri-*n*-butylammonium nitrate, 0.80). The tetraalkylammonium sulfonate salts have much smaller values, between 0.40 and 0.65, similar to the 1,3-dialkylimidazolium salts, which are more typical of polar solvents such as dimethyl sulfoxide and dimethylacetamide at the lower end of the range and formamide and aliphatic alcohols at the higher end. The E_T^N values for the sulfonates are grouped into narrow ranges characteristic of the anion, and if there is any systematic influence due to the size of the tetraalkylammonium cation, it is that increasing the alkyl chain length leads to a small increase in the E_T^N value. The alkyl chain length for the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ionic liquids has virtually no influence on the E_T^N values, which are similar to ethanol, but the introduction of a polar functional group or a methyl group at C-2 has a significant effect. The introduction of a hydroxyl group, especially, and/or ether group increase the solvent polarity as determined by the E_T^N scale, while a methyl group at C-2 reduces it [65,69]. These changes reflect modification of the hydrogen-bond acidity of the cation in keeping with the presumption that changes in the $E_{T(30)}$ scale are dominated by the hydrogen-bond acidity of the solvent.

The $E_{T(30)}$ value of 1-butyl-3-methylimidazolium hexafluorophosphate is similar to that of ethanol [69,126–128]. The hydrogen-bond basicity of binary mixtures of 1-butyl-3-methylimidazolium hexafluorophosphate and ethanol is significantly lower than that of neat ethanol [129]. This is explained by the fact that ethanol has a higher hydrogen-bond acidity but lower dipolarity/polarizability than 1-butyl-3-methylimidazolium hexafluorophosphate. As the mole fraction of ethanol is increased, the increased hydrogen-bond acidity of the binary solvent system is reflected in the solvatochromic behavior of the indicator probe. There is a linear correlation of the $E_{T(30)}$ scale with temperature for dry 1-butyl-3-methylimidazolium hexafluorophosphate [128]. The negative thermochromism arises from the increased differential stabilization of the highly dipolar zwitterionic betaine ground state relative to the less dipolar excited state at lower temperatures. Intentional addition of water (2%, v/v) alters the hydrogen-bond acidity significantly and the temperature dependence is nearly doubled. This is an indication that $E_{T(30)}$ values are significantly affected by the presence of water as an impurity. Compared with the dry ionic liquid as little as 0.1% (w/w) water could be detected in the ionic liquid by its shift in the long wavelength absorption band for Reichardt's betaine dye [130]. There is no evidence, however, that water selectively solvates the betaine dye in ionic liquids containing a small amount of water.

3.1.2. *Kamlet–Taft solvatochromic parameters*

Kamlet and co-workers [131,133] and de Juan and co-workers [132] have used linear solvation energy relationships and solvatochromic indicator compounds to characterize the properties of numerous solvents used in organic chemistry. Solvents are characterized by their capacity for interactions described as dipolarity/polarizability (π^*), hydrogen-bond acidity (α) and hydrogen-bond basicity (β) determined by absorption measurements for individual or pairs of selected indicator compounds. The experimental protocol and choice of indicator compounds is described elsewhere [28,55,133]. The three scales are normalized so that dimethyl sulfoxide for π^*, methanol for α, and

Table 6
Solvent polarity of room temperature ionic liquids determined by solvatochromic compounds

Ionic liquid	Reichardt's dye		Kamlet–Taft			Reference
	$E_{T(30)}$	E_T^N	π^*	α	β	
1-Benzyl-3-methylimidazolium						
Bis(trifluoromethylsulfonyl)amide	52.4	0.67				[65]
n-Butylammonium						
Thiocyanate	61.4	0.95	1.23	0.92		[55]
sec-Butylammonium						
Thiocyanate	61.6	0.95	1.28	0.91		[55]
1-Butyl-3-methylimidazolium						
Hexafluoroantimonate		0.67	1.04	0.64	0.15	[69]
Hexafluorophosphate	52.3	0.67				[126]
	52.5					[127]
	52.8		0.92	0.75	0.21	[128]
	52.3		1.06	0.64	0.17	[129]
Bis(trifluoromethylsulfonyl)amide	51.5	0.64				[126]
Tetrafluoroborate	52.5	0.67				[126]
Trifluoromethanesulfonate	52.3	0.67				[126]
1-Butyl-2,3-dimethylimidazolium						
Bis(trifluoromethylsulfonyl)amide	48.6	0.55				[126]
Tetrafluoroborate		0.58	1.08	0.40	0.36	[69]
1-Butyl-1-methylpyrrolidinium						
Bis(trifluoromethylsulfonyl)amide		0.54	0.95	0.43	0.25	[69]
1-Decyl-3-methylimidazolium						
Bis(trifluoromethylsulfonyl)amide	51.0	0.63				[65]
Dipropylammonium						
Thiocyanate	63.3	1.01	1.16	0.97	0.39	[55]
Ethylammonium						
Nitrate	61.6	0.95	1.24	0.85	0.46	[55]
1-(2-Hyroxyethyl)-3-methylimidazolium						
Bis(trifluoromethylsulfonyl)amide	60.8	0.93				[65]
1-Methoxyethyl-3-methylimidazolium						
Bis(trifluoromethylsulfonyl)amide	54.1	0.72				[65]
1-Octyl-3-methylimidazolium						
Hexafluorophosphate	51.2	0.63				[126]
Bis(trifluoromethylsulfonyl)amide	51.1	0.63				[126]
Tetrafluoroborate	48.3	0.54				[117]
1-Octyl-2,3-dimethylimidazolium						
Bis(trifluoromethylsulfonyl)amide	47.7	0.53				[126]
n-Propylammonium						
Nitrate	60.6	0.92	1.17	0.88	0.52	[55]
1-*n*-Propyl-3-methylimidazolium						
Bis(trifluoromethylsulfonyl)amide	51.9	0.65				[65]
Tetra-*n*-butylammonium						
2-[Bis(2-hydroxyethyl)amino]ethansulfonate	47.8	0.53	1.07	0.14	0.81	[55]
2-(Cyclohexylamino)ethanesulfonate	50.7	0.62	1.01	0.34	0.98	[55]
2-Hydroxy-4-morpholinopropanesulfonate	46.5	0.49	1.07	0.03	0.74	[55]
Tetra-*n*-hexylammonium						
Benzoate	44.3	0.42				[125]
Tetra-*n*-pentylammonium						
2-(Cyclohexylamino)ethanesulfonate	49.5	0.58	1.00	0.15	0.91	[55]
2-Hydroxy-4-morpholinopropanesulfonate	47.3	0.51	1.02	0.26	0.96	[55]
Tetra-*n*-propylammonium						
2-[Bis(2-hydroxyethyl)amino]ethansulfonate	49.0	0.56	0.99	0.35	1.00	[55]
2-(Cyclohexylamino)ethanesulfonate	50.9	0.62	1.08	0.34	0.80	[55]

Table 6 (*Continued*)

Ionic liquid	Reichardt's dye		Kamlet–Taft			Reference
	$E_{T(30)}$	E_T^N	π^*	α	β	
2-Hydroxy-4-morpholinopropanesulfonate	45.5	0.46	1.05	0.03	0.83	[55]
Tributylammonium						
Nitrate	56.7	0.80	0.97	0.84		[55]
Non-ionic solvents						
Water	63.1	1.00	1.09	1.17	0.18	
Methanol	55.5	0.77	0.60	0.93	0.62	
Ethanol	51.9	0.65	0.54	0.83	0.77	
Acetonitrile	46.0	0.47	0.75	0.19	0.31	
Dimethyl sulfoxide	45.0	0.44	1.00	0	0.76	
Dimethylformamide	43.8	0.40	0.88	0	0.69	
Acetone	42.2	0.36	0.71	0.08	0.48	
Ethyl acetate			0.55	0	0.45	
Methylene chloride	41.1	0.32	0.82	0.30	0	
n-Heptane	32.3	0.05	−0.08	0	0	

hexamethylphosphoramide for β have values of one. The $E_{T(30)}$ scale is related to the Kamlet–Taft solvatochromic parameters by the general expression [55,134]:

$$E_T(30) = 30.31 + 14.6\pi^* + 16.53\alpha \tag{3}$$

The alkylammonium nitrate and thiocyanate salts in Table 6 are all more dipolar/polarizable than dimethyl sulfoxide and water with $\pi^* > 1$ (except for tri-*n*-butylammonium nitrate $\pi^* = 0.97$) [28]. These solvents are all strong hydrogen-bond acids ($\alpha = 0.84$–0.97) and moderate hydrogen-bond bases ($\beta = 0.39$–0.52 for salts with available values). These results are similar in character and magnitude to water ($\pi^* = 1.09$, $\alpha = 1.17$ and $\beta = 0.18$) although selectivity differences between the ionic liquids and water is also indicated. The eight tetraalkylammonium sulfonate salts in Table 6 all have π^* values close to 1.0 with no obvious trends in the values related to the structure of the anions or cations [55]. None of the tetraalkylammonium sulfonate ionic liquids are strong hydrogen-bond acids ($\alpha = 0.03$–0.35). A larger α value closer to that of methanol was anticipated for the salts containing the 2-hydroxy-4-morpholinopropanesulfonate and 2-[bis(2-hydroxyethyl)amino]ethanesulfonate anions. In this case, the hydroxyl groups of the anions are probably involved in the formation of association complexes and are unavailable for interaction with the solvatochromic probe molecules. The larger α values for the tetra-*n*-pentylammonium sulfonates is probably a consequence of a weakening of the anion/anion interactions resulting from the accommodation of the larger cation into the structured solvent. In contrast to the alkylammonium nitrate and thiocyanate salts, the tetraalkylammonium sulfonate salts are much stronger hydrogen-bond bases ($\beta = 0.74$–1.00). The most likely site for solvent hydrogen-bond acceptor interactions is the sulfonate group, with secondary interactions at the oxygen and nitrogen electron-donor sites of the anions. On the other hand, there is no simple relationship between the β values and anion (or cation) structure. 1-Butyl-3-methylimidazolium hexafluorophosphate has π^* values slightly lower than for water and dimethyl sulfoxide but much higher than the short chain alcohols. Its hydrogen-bond basicity, β value, is much lower than that for the short chain alcohols, while α values are similar to short chain alcohols [69,127,129]. These results demonstrate that 1-butyl-3-methylimidazolium hexafluorophosphate is a remarkable amphoteric solvent with no peer among conventional organic solvents. Most solvents possessing such low nucleophilicity are generally regarded as non-polar. However, the dipolarity/polarizability of 1-butyl-3-methylimidazolium hexafluorophosphate at ambient conditions is 55–95% higher than the short chain alcohols and only 10–15% below that of water or dimethyl sulfoxide.

3.1.3. Nile red

The visible absorption band for Nile red displays one of the largest positive solvatochromic shifts known [135]. It is most likely sensitive to changes in solvent dipolarity/polarizability, although exactly which factors dominate shifts in its absorption maximum is unclear. Values for the electronic transition energy (E_{NR}) are available for a number of 1-alkyl-3-methylimidazolium ionic liquids (Table 7) [65,80,127,136]. Perhaps what is most striking of these results is the narrow range of values indicating that neither the structure of the anion or cation have a large affect on solvent polarity determined by Nile red. Conflict should be noted between the value indicated in Table 7 for 1-butyl-3-methylimidazolium hexafluorophosphate [136] and the value reported in [127] of 580.2 nm. The former value is in broad agreement with the other ionic liquids indicating a similar polarity to short chain alcohols, the latter value would place the polarity of 1-butyl-3-methylimidazolium hexafluorophosphate much higher indicating a solvent polarity similar to water. For the 1-butyl-2-methylimidazolium ionic liquids, the polarity decreases, albeit slightly, through the anion series of nitrite,

Table 7
Solvent polarity of ionic liquids determined by the solvatochromic indicator Nile red and the square planar copper complex acetylacetonatotetramethylethyldiaminecopper(II) tetraphenylborate

Ionic liquid	Nile red		$[Cu(acac)(tmen)][BPh_4]$ λ_{max} (nm)
	λ_{max} (nm)	E_{NR} (kcal/mol)	
1-Benzyl-3-methylimidazolium			
Bis(trifluoromethylsulfonyl)amide	546.0	51.8	
1-Butyl-2,3-dimethylimidazolium			
Bis(trifluoromethylsulfonyl)amide			547.5
1-Butyl-3-methylimidazolium			
Nitrite	556.0	51.4	
Nitrate	555.7	51.5	
Tetrafluoroborate	550.8	51.9	
Hexafluorophosphate	547.5, 580.2	52.2	516.5
Bis(trifluoromethylsulfonyl)amide	548.7	52.1	546.0
Trifluoromethanesulfonate			601.5
Tetra[4-dimethyl(octyl)silylphenyl]borate	534		
Tetra[4-dimethyl(1,1,2,2-tetrahydro-perfluorodecanyl)silylphenyl]borate	542		
1-Decyl-3-methylimidazolium			
Bis(trifluoromethylsulfonyl)amide	560.5	52.2	
Tetrafluoroborate	545.7	52.4	
1-Hexyl-3-methylimidazolium			
Hexafluorophosphate	551.7	51.8	
Nitrate	552.9	51.7	
Tetrafluoroborate	551.9	51.8	
1-(2-Hyroxyethyl)-3-methylimidazolium			
Bis(trifluoromethylsulfonyl)amide	470.0	50.6	
1-Methoxyethyl-3-methylimidazolium			
Bis(trifluoromethylsulfonyl)amide	528.0	51.0	
1-Octyl-2,3-dimethylimidazolium			
Bis(trifluoromethylsulfonyl)amide			549.5
1-Octyl-3-methylimidazolium			
Bis(trifluoromethylsulfonyl)amide			548.5
Hexafluorophosphate	549.8	52.0	516.5
Nitrate	550.1	52.0	
Tetrafluoroborate	549.5	52.0	
1-Propyl-3-methylimidazolium			
Bis(trifluoromethylsulfonyl)amide	550.3	52.3	
Non-ionic solvents			
Water	584.5	48.2	
Methanol	542.9	52.0	
Ethanol	539.8	52.2	
Acetonitrile	520.7	53.8	
Dimethyl sulfoxide	544.8	52.0	
Methylene chloride	523.4	53.4	
Hexane		59.0	

nitrate, tetrafluoroborate, bis(trifluoromethylsulfonyl)amide and hexafluorophosphate. This decrease in polarity correlates with increasing anion size, hence a reduction in the effective charge density. The slightly anomalous behavior of the bis(trifluoromethylsulfonyl)amide anion was explained by partial charge delocalization within the anion. The effect of chain length on polarity for the 1-alkyl-3-methylimidazolium salts with a common anion is more complex with a maximum for the observed solvent polarity observed for the cation with a 1-hexyl group. Compared with conventional solvents the E_{NR} values for the 1-alkyl-3-methylimidazolium ionic liquids positions them in the upper half of the solvent polarity table with the short chain alcohols as nearest neighbors.

3.1.4. Acetylacetonatotetramethylethyldiaminecopper(II) tetraphenylborate

The absorption maximum for the lowest energy d–d band arising from changes in the splitting of the d-orbitals as the solvent coordinates at the axial sites on the metal center for the square planar Cu(II) salt is said to provide a good estimate of the donor number for ions in solution [8,126,137]. For the limited data available for 1-alkyl-3-methylimidazolium ionic liquids (Table 7), two conclusions can be made. Firstly, for a given anion, the absorption maximum exhibits virtually no dependence on the cation present. Thus, the cation plays no part in the nucleophilicity of the ionic liquid. Secondly, the order of nucleophilicity for the anions studied is hexafluorophosphate > bis(trifluoromethylsulfonyl)amide > trifloromethylsulfonate. The 1-alkyl-3-methylimidazolium hexafluorophosphate is effectively a non-coordinating solvent with the salts of the other two anions weakly coordinating solvents.

3.1.5. *Polycyclic aromatic hydrocarbons*

The neutral fluorescent molecule pyrene, and to a lesser extent other polycyclic aromatic hydrocarbons such as benzo[*g*,*h*,*i*]perylene and ovalene, have been used to characterize the polarity of numerous solvents [138,139]. The solvent polarity scale is defined as the I_1/I_3 emission intensity ratio, where band I_1 corresponds to an $S_1\,(\nu = 0) \Rightarrow S_0\,(\nu = 1)$ transition and band I_3 is an $S_1\,(\nu = 0) \Rightarrow S_0\,(\nu = 1)$ transition. The I_1/I_3 ratio increases with increasing solvent polarity. The solvatochromic behavior was rationalized as a difference in vibronic coupling between the weakly allowed first electronic singlet state and the strongly allowed second electronic singlet state. Solvent classification methods require that the experimentally determined ratio of emission intensities be free of both chemical and instrumental artifacts (such as inner filtering, slit width, etc.) that may lead to erroneous values [139,140]. This applies to the alkylammonium nitrate [141] and thiocyanate [142] ionic liquids where inner filtering effects and inadequate spectral resolution limit the usefulness of the pyrene (Py) scale. The benzo[*g*,*h*,*i*]perylene (BPe) and ovalene (Ov) scales afford a more reliable estimate of solvent polarity for these ionic liquids. The different polarity scales (Py, Bpe and Ov) are strongly correlated, at least for non-ionic liquids, although by no means linear [139]. The BPe scale indicates that tri-*n*-butylammonium nitrate is the most polar of the alkylammonium ionic liquids and that the nitrate salts are more polar than the thiocyanate ionic liquids (Table 8) [71,127,129,130,140–153]. Ethylammonium and *n*-propylammonium nitrate have similar polarity to polar non-ionic solvents like acetonitrile. The alkylammonium thiocyanate and tetra-*n*-butylammonium sulfonate ionic liquids and have solvent polarity comparable to cyclohexanone. The two solvent polarity values for 1-butyl-3-methylimidazolium hexafluorophosphate in Table 8 are significantly different. Baker et al. [143] determined a solvent polarity greater than water and similar to dimethyl sulfoxide. Fletcher and Pandey [129] determined a value similar to acetonitrile and less than water and dimethyl sulfoxide. The reason for this difference is not obvious. Addition of ethanol or water to 1-butyl-3-methylimidazolium hexafluorophosphate hardly changes the I_1/I_3 emission ratio indicating a strong preference for selective solvation of pyrene by the ionic liquid [130]. 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide has a solvent polarity close to that of ethanol [71]. In general, there is only a weak correlation between the solvatochromic scales discussed earlier and the polycyclic aromatic hydrocarbon scales. Some similarity to the Kamlet–Taft π^* scale is expected but this is not the case for the ionic liquids.

Table 8
Polarity of ionic liquids determined by the ratio of I_1/I_3 fluorescence vibronic bands for polycyclic aromatic hydrocarbons

Ionic liquid	Solvent polarity scale		
	Py	BPe	Ov
n-Butylammonium			
Thiocyanate	1.18	1.06	1.66
sec-Butylammonium			
Thiocyanate	1.01	0.96	1.70
1-Butyl-3-methylimidazolium			
Hexafluorophosphate[a]	2.08 1.84		
Di-*n*-propylammonium			
Thiocyanate	1.23	1.04	1.70
Ethylammonium			
Nitrate		1.20	
1-Ethyl-3-methylimidazolium			
Bis(trifluoromethylsulfonyl)amide	0.85		
n-Propylammonium			
Nitrate		1.20	
Tetra-*n*-butylammonium			
2-[Bis(2-hydroxyethyl)amino]ethansulfonate	1.51	1.45	2.81
2-(Cyclohexylamino)ethanesulfonate	1.32	1.41	2.71
2-Hydroxy-4-morpholinopropanesulfonate	1.52	1.35	2.63
Tri-*n*-butylammonium			
Nitrate		1.36	
Non-ionic solvents			
Methanol	1.35	1.00	1.37
Acetonitrile	1.79	1.23	1.75
Dimethyl sulfoxide	1.95	1.36	2.38
Acetone	1.64	1.19	1.80
Heptane	0.58	0.39	0.30

Py = pyrene; BPe = benzo[*g*,*h*,*i*]perylene; Ov = ovalene.

[a] Poor agreement between literature values (see text for details).

3.1.6. *Polar fluorescent probe molecules*

The fluorescence emission of 1-pyrenecarboxaldehyde is known to depend on the static dielectric constant of the cybotactic region [71,127,129,130]. The fluorescence maximum red shifts with an increase in the static dielectric constant of the surrounding medium. The fluorescence emission spectra of 1-pyrenecarboxaldehyde indicated a solvent polarity similar to acetonitrile and dimethyl sulfoxide for 1-butyl-3-methylimidazolium hexafluorophosphate [127]. The emission spectra of 1-pyrenecarboxaldehyde in 1-ethyl-3-

methylimidazolium bis(trifluoromethylsulfonyl)amide was typical of a solvent of low dielectric constant, such as hexane [71]. The 1-pyrenecarboxaldehyde emission maximum in 1-butyl-3-methylimidazolium hexafluorophosphate is red shifted by the intentional addition of water or ethanol to the ionic liquid [129,130]. As little as 0.1% (w/w) water in 1-butyl-3-methylimidazolium hexafluorophosphate could be detected using 1-pyrenecarboxaldehyde as a solvatochromic probe. This behavior is due to selective enrichment of the solvation sphere for 1-pyrenecarboxaldehyde by ethanol or water related to the presence of the aldehyde group on the probe molecule.

The fluorescence spectrum of 6-propionyl-2-(*N*,*N*-dimethylamino)naphthalene was used to indicate that the solvent polarity of 1-butyl-3-methylimidazolium hexafluorophosphate lies between that of chloroform and dimethylformamide and acetone [143]. The fluorescence emission maximum of 3-aminophthalamide and 3-dimethylaminophthalamide was used to demonstrate that the ionic liquids 1-butyl-3-methylimidazolium hexafluorophosphate, 1-octyl-3-methylimidazolium hexafluorophosphate, 1-butyl-3-methylimidazolium nitrate and *N*-butylpyridinium tetrafluoroborate were more polar than acetonitrile and less polar than methanol [79]. Replacing the hexafluorophosphate anion by nitrate for the 1-butyl-3-methylimidazolium cation had little affect on the observed polarity.

3.2. *Gas–liquid partition coefficients*

Gas chromatography is a widely used method for determining thermodynamic properties of pure substances or solvent properties of binary mixtures in which one component, the sample, is generally present at infinite dilution and the other, the stationary phase, is most commonly a non-volatile liquid [144–146]. From retention measurements the gas–liquid partition coefficient and the free energy, enthalpy and entropy of mixing or solution and the infinite dilution solute activity coefficient are easily obtained. Using these parameters and appropriate models allows and understanding of the intermolecular interactions responsible for solvation in the stationary phase [147,148]. From studies of band broadening, liquid diffusion coefficients and reaction rate data (for on column reactions) can be obtained. Studies of the variation of retention with phase loading and/or temperature allow elucidation of phase transitions and wetting characteristics. Early results of the application of gas chromatography to studies of liquid organic salts (including some data for room temperature ionic liquids) are summarized elsewhere [38,59,60]. In this section, we will deal exclusively with the properties of room temperature ionic liquids and their solvation properties derived from measurements by gas chromatography. Where needed additional information is included for comparison and to aid interpretation. The popularity of gas chromatography for physicochemical measurements is due to its simplicity when compared with static methods, small sample size requirements, accuracy and the ease with which temperature can be controlled and varied as an experimental parameter.

3.2.1. *Measurement*

Retention in gas chromatography is a complex process involving partition and adsorption with different liquid film types and interfaces co-existing in the column. A comprehensive retention model would have to consider contributions to retention from gas–liquid partitioning with the bulk liquid phase and with a structured layer close to the support surface, by gas–liquid adsorption at the bulk liquid and structured liquid interfaces, and by adsorption at the gas–solid support interface [146,149–152]. When the goal is to determine bulk liquid properties the retention mechanism can be simplified by using supports of low surface area and high liquid phase loadings. For these conditions, the contributions to retention from the structured layer close to the support surface can usually be neglected. This allows a general retention model to be written as:

$$V_N^* = V_L K_L + A_L K_A + A_S K_S \tag{4}$$

where V_N^* is the net retention volume per gram of column packing, V_L the volume of liquid phase per gram of packing, K_L the gas–liquid partition coefficient, A_L the liquid surface area per gram of packing, K_A the coefficient for adsorption at the bulk liquid–gas interface, A_S the solid-gas interfacial area per gram of packing, and K_S the coefficient for adsorption at the support interface. For operational purposes Eq. (4) is rearranged to:

$$\frac{V_N^*}{V_L} = K_L + \frac{A_L K_A + A_S K_S}{V_L} \tag{5}$$

A plot of V_N^*/V_L against $1/V_L$ reveals both the retention mechanism for the solute and the intercept corresponding to $1/V_L = 0$ provides the gas–liquid partition coefficient for the solute at the measurement temperature. If interfacial adsorption does not contribute to the retention mechanism, there is no slope to the plot, since $V_N^* = V_L K_L$ and K_L is computed as the average of the experimental values. If there is a slope, then it is advantageous to avoid conditions resulting in a non-linear extrapolation to determine K_L. Ionic liquids are excellent support-deactivating agents and at high phase loadings it is reasonable to assume that $A_S K_S \approx 0$.

The derivation of Eq. (5) requires that the individual contributions to the retention mechanism are independent and additive. For this to be true the solute must be at infinite dilution with respect to the partition mechanism and at zero surface coverage for the adsorption mechanism. Recommended experimental conditions for determining K_L values for ionic liquids are summarized in Table 9 together with their acceptable uncertainty. Typical uncertainty in K_L values from gas–liquid chromatography are about 3–5% R.S.D. for K_L values between 10 and 100 and 2–3% for values between 100 and 10,000 [153]. These results do not include an estimate of the systematic uncertainty arising from non-ideal

Table 9

Summary of experimental parameters for the determination of gas–liquid partition coefficients

Parameter	Acceptable uncertainty	Comments
Support		Low surface area diatomaceous earth type W-AW. Particle size 60–80 mesh
Packings	$w = 0.0002$ g 0.15%	Four packings with a liquid phase loading evenly spaced between 8 and 18% (w/w) Exact phase loading determined by Soxhlet extraction or thermal evaporation
Column length		1–2 m
Column hold-up time	$t_R \gg t_M$	Retention time for methane in most cases
Sample size		0.1–10 μg (solids), 0.0001–0.01 μl (liquids), 5–50 μl (headspace vapors)
Flow rate	0.2 ml/min	20 ml/min
Pressure	1 mmHg	Column inlet and outlet (using a Hg manometer or electronic sensor)
Temperature	0.2 °C	Check set point of column oven and temperature gradients over the column volume
Density	0.0008 g/ml	Pycnometer (Lipkin bicapillary pycnometer is a suitable device to determine density over a temperature range)
Time	0.02 min	

behavior of the gas phase. The latter is usually small for simple gases like hydrogen and helium, and to a lesser extent nitrogen, when the experimental conditions are arranged to minimize the average column pressure. Estimating corrections for non-ideal behavior of the gas phase is often difficult. The required virial coefficients are rarely available and calculation methods based on the use of corresponding states contain an unknown uncertainty.

The use of Eq. (5) requires an accurate value for the volume of ionic liquid for several column packings. In turn, this requires an accurate determination of the phase loading for each packing as well as a determination of the density of the ionic liquid at (usually) several temperatures corresponding to those used for the gas chromatographic measurements. An accurate value of the phase loading can be obtained by thermal evaporation [154] or Soxhlet extraction (usually the preferred method for ionic liquids) [60,155]. The packing, ca. 0.5–1.0 g, accurately weighed into a fine porosity glass sintered crucible with a small piece of filter paper on the top, is placed in a standard Soxhlet apparatus. Glass beads are used to raise the level of the crucible above that of the siphon arm. The packing is then extracted at a rate of about 10–15 cycles/h with, generally, the same (good) solvent used for coating. Extractions can be expected to take from 4 to 6 h but overnight extraction is generally used to ensure completion. After extraction, the packing is oven-dried to constant weight, cooled, and accurately weighed. This step should be performed carefully, since it is usually the main source of error in the partition coefficients. For hygroscopic ionic liquids it may be necessary to use a glove box to minimize contact with atmospheric moisture.

Densities can be determined with a standard pycnometer in the usual way. The Lipkin bicapillary pycnometer is useful for small volumes of ionic liquids [60,156]. Poor density values can result from measurements on ionic liquids containing a significant amount of water as an impurity. Since the ionic liquids are dried during column conditioning the ionic liquid will be in a different state of hydration for the column and density measurements.

Packed columns are more suitable than open-tubular columns for the determination of gas–liquid partition coefficients with ionic liquids. Ionic liquids do not form stable films on glass surfaces and their low viscosity results in poor film stability as the column temperature is varied. Improved coating performance and stability is obtained using whisker-walled [157,158], sodium chloride deposition [159,160] or barium carbonate deposition [161] wall surface treatments. However, it is almost impossible to control film thickness and prepare columns with different film thickness to evaluate the contribution of interfacial adsorption to retention. Packed columns can be handled without difficulty and the larger liquid volumes typical of packed columns minimize errors in the calculation of gas–liquid partition coefficients.

The retention mechanism for ionic liquids has largely been studied at temperatures above room temperature to allow comparison with non-ionic liquids at temperatures typical for analytical separations. Arancibia et al. [162] determined partition and adsorption coefficients for a small number of alkanes and halocarbon compounds at room temperature on ethylammonium nitrate and *n*-propylammonium nitrate ionic liquids. The probe compounds were retained by a mixed retention mechanism with the hydrocarbon compounds exhibiting low solubility in the ionic liquids. For the same ionic liquids a wider range of compounds were studied at 80.8 °C [150]. Plots of V_N^* against the phase loading revealed a wetting transition between 5 and 6% (w/w) of the ionic liquids. The broad hump observed in the plots is due to coalescence of the ionic liquid from droplets to a continuous film, subsequently followed by pore filling of the support (Fig. 2). The *n*-alkanes shown in the plot are retained largely by gas–liquid interfacial adsorption. Plots of V_N^*/V_L against $1/V_L$ for polar compounds on ethylammonium nitrate reveals that partitioning is the dominant retention mechanism with a small contribution from interfacial adsorption (Fig. 3). For compounds of low polarity, particularly *n*-alkanes, the dominant retention mechanism is interfacial adsorption. Similar results were observed for *n*-propylammonium nitrate.

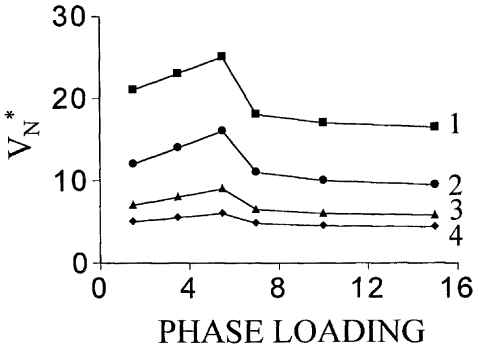

Fig. 2. Plot of the net retention volume per gram of packing (corrected to 25°), V_N^*, against phase loading measured at 80.8 °C for *n*-alkanes on Chromosorb W-AW coated with ethylammonium nitrate. Identification: 1 = *n*-hexadecane; 2 = *n*-pentadecane; 3 = *n*-tetradecane; 4 = *n*-tridecane.

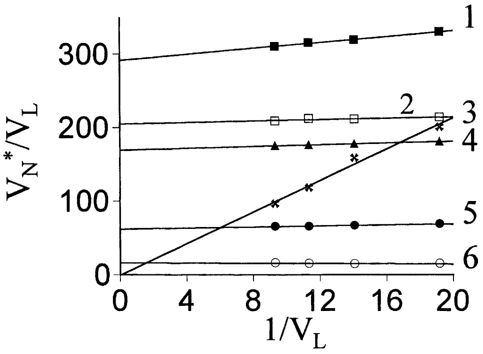

Fig. 3. Plot of V_N^*/V_L against $1/V_L$ for ethylammonium nitrate coated on Chromosorb W-AW at 80.8 °C. Identification: 1 = *n*-butanol; 2 = dioxane; 3 = *n*-pentadecane; 4 = 1-nitropropane; 5 = 2-pentanone; 6 = benzene.

The retention of polar compounds on the alkylammonium thiocyanate salts occurs largely by partitioning with a small contribution from interfacial adsorption, except for *n*-alkanes, where interfacial adsorption makes a significant contribution to the retention mechanism (Fig. 4) [150,163,164]. Interestingly, although not explained, it was observed that *n*-alkanes are significantly more soluble in *sec*-butylammonium thiocyanate compared with *n*-butylammonium thiocyante ionic liquids. For the tetra-*n*-alkylammonium sulfonate ionic liquids, a mixed retention mechanism was observed for most compound types at 90 °C [55–57]. In addition, a mixed retention mechanism was observed for a group of varied compounds on tetra-*n*-butylphosphonium 2-(cyclohexylamino)ethanesulfonate and 4-morpholinepropanesulfonate ionic liquids [58]. 1-Methyl-3-ethylimidazolium chloride was shown to retain most compounds by interfacial adsorption with partitioning as a minor retention mechanism at temperatures between 60 and 140 °C [150].

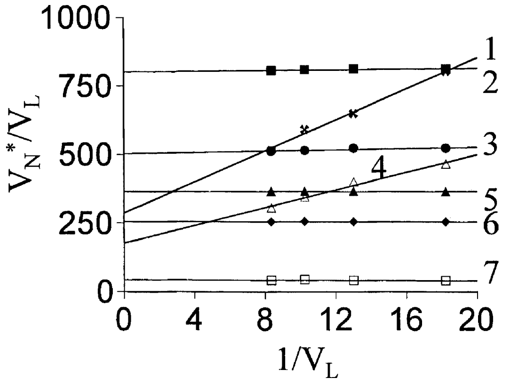

Fig. 4. Plot of V_N^*/V_L against $1/V_L$ for *sec*-butylammonium thiocyanate coated on Chromosorb W-AW at 80.8 °C. Identification: 1 = *n*-hexadecane; 2 = *n*-butanol; 3 = dioxane; 4 = *n*-pentadecane; 5 = 1-nitropropane; 6 = 2-pentanone; 7 = benzene.

Table 10
Relative percent contribution of gas–liquid partitioning and gas–liquid interfacial adsorption to retention on *n*-propylammonium nitrate (6% w/w) and di-*n*-propylammonium thiocyanate (11.8%, w/w) at 80.8 °C

Solute	*n*-Propylammonium nitrate		Di-*n*-propylammonium thiocyanate	
	Partitioning	Adsorption	Partitioning	Adsorption
Benzene	89.4	10.6	100	0
n-Butanol	99.4	0.6	97.2	2.8
Dioxane	96.0	4.0	96.2	3.8
n-Dodecane	23.3	76.7	82.7	17.3
2-Hexanone	95.2	4.8	96.6	3.4
1-Iodobutane	88.9	11.1	97.6	2.4
1-Nitropropane	96.6	3.4	100	0
2-Octanone	90.0	10.0	96.1	3.9
n-Pentadecane	14.9	85.1	76.2	23.8

Support Chromosorb W-AW with a surface area of 1–3 m^2/g.

The relative contribution of interfacial adsorption to the retention mechanism depends on system properties as well as the identity of the ionic liquid and solute. The surface area of the ionic liquid is determined by physical properties of the support while its volume is a bulk solvent property. There is no simple method to determine the surface area of a column packing [146], and consequently, coefficients for gas–liquid interfacial adsorption are virtually unknown [162]. An indication of the contribution from interfacial adsorption for a particular column can be obtained from the measured value for V_N^* and the calculated value of V_N^* from the gas–liquid partition coefficient (Table 10). The message here is that the accuracy of solvation properties determined from a single retention measurement depends on the absence of interfacial adsorption. Unless methods are used to confirm the absence of interfacial adsorption the calculated partition coefficients cannot be considered reliable. In general, for mixed retention mechanisms, an increase in temperature tends to favor partitioning over interfacial adsorption and vice versa.

3.2.2. Solvation parameter model

The solvation parameter model provides a general tool to assign the contributions of cavity formation and individual intermolecular interactions to equilibrium processes such as retention in chromatography. For the gas–liquid partition coefficient the model takes the form [146–149]:

$$\log K_{\mathrm{L}} = c + eE + sS + aA + bB + lL \qquad (6)$$

where the lower case letters (*l*, *e*, *s*, *a*, *b*) are the system constants representing contributions from the ionic liquid to the solvation process, and the capital letters (*L*, *E*, *S*, *A*, *B*) are the solute descriptors for the complementary solute interactions with the system constants of the ionic liquid. The solute descriptors are: *L* the gas–liquid distribution constant on hexadecane at 298 K; *E* the excess molar refraction; *S* the ability of the solute to stabilize a neighboring dipole by virtue of its capacity for orientation and induction interactions; *A* the solute's effective hydrogen-bond acidity; and *B* the solute's effective hydrogen-bond basicity. Solute descriptors are available for over 4000 compounds with others available by experiment or calculation methods [147,148,165,166]. The solute descriptors do not concern us here, since all information concerning the contribution of intermolecular interactions to the gas–liquid partition coefficients for the ionic liquids is contained in the system constants. These are identified as cavity formation and dispersion interactions, *l*, the contribution from interactions with solute n- or π-electrons, *e*, the contribution from dipole-type interactions, *s*, the contribution from hydrogen-bond basicity (because a basic solvent will interact with an acidic solute), *a*, and *b* the contribution from hydrogen-bond acidity. The *c* term is the model constant. The system constants are calculated from the experimental gas–liquid partition coefficient for a number of solutes. These solutes are selected to be sufficient in number and variety to meet the chemical and statistical demands for calculation of the system constants by multiple linear regression analysis. The requirements for solute selection are detailed elsewhere [147,148,167,168], and must be adhered to if the system constants are to take meaningful values.

The system constants for the alkylammonium nitrate and thiocyanate ionic liquids at 80.8 °C are summarized in Table 11. For perspective, the system constants for four non-ionic liquids of different polarity are included as well. To asses the effect of cohesion of the ionic liquids on solute transfer from the gas phase the sum term $\sum(c + lL)$ for *n*-decane is given in Table 12 [169]. The ionic liquids are cohesive solvents. The alkylammonium thiocyanate ionic liquids are more cohesive that the poly(ethylene glycol) solvent (Carbowax 20M) but less cohesive than 1,2,3-tris(2-cyanoethoxypropane). This places them in the range of normal polar solvents for the measurement temperature. The alkylammonium nitrate ionic liquids are considerably more cohesive than 1,2,3-tris(2-cyanoethoxypropane) and are more cohesive than typical non-ionic polar solvents with the exception of water. This is a major distinguishing feature of the alkylammonium thiocyanate and alkylammonium nitrate ionic liquids and between the ionic liquids and non-ionic polar solvents.

Table 12
The contribution of the cavity and dispersion interaction term to the transfer of decane from the gas to liquid phase at 80.8 °C

Solvent	System constants		$\sum(c + lL)$
	c	*l*	
Squalane	−0.192	0.725	3.205
OV-17	−0.311	0.639	2.683
Carbowax 20M	−0.416	0.526	2.049
Di-*n*-propylammonium thiocyanate	−0.597	0.474	1.624
n-Butylammonium thiocyanate	−0.747	0.454	1.380
sec-Butylammonium thiocyanate	−0.602	0.399	1.268
1,2,3-Tris(2-cyanoethoxypropane)	−0.479	0.360	1.208
n-Propylammonium nitrate	−0.974	0.356	0.694
Ethylammonium nitrate	−0.869	0.210	0.115

Electron lone pair interactions (*e* system constant) are favorable for solute transfer from the gas phase to the ionic liquids (Table 11). These interactions, however, are weak and not much different to other polar non-ionic liquids. The dipolarity/polarizability (*s* system constants) of the alkylammonium nitrate ionic liquids are similar to

Table 11
System constants for alkylammonium ionic liquids at 80.8 °C

	System constants						Statistics[a]			
	e	*s*	*a*	*b*	*l*	*c*	*r*	S.E.	*F*	*n*
Ionic liquid										
n-Butylammonium thiocyanate	0.14 (0.09)	1.65 (0.09)	2.76 (0.16)	1.32 (0.11)	0.45 (0.02)	−0.75 (0.10)	0.995	0.058	326	23
sec-Butylammonium thiocyanate	0.14 (0.10)	1.65 (0.11)	2.63 (0.18)	1.50 (0.12)	0.40 (0.02)	−0.60 (0.12)	0.994	0.065	306	23
Di-*n*-propylammonium thiocyanate	0.30 (0.05)	1.73 (0.06)	2.66 (0.10)	0.68 (0.07)	0.47 (0.01)	−0.60 (0.06)	0.998	0.032	663	21
Ethylammonium nitrate	0.47 (0.16)	2.21 (0.16)	3.38 (0.28)	1.03 (0.17)	0.21 (0.04)	−0.87 (0.20)	0.994	0.089	175	17
n-Propylammonium nitrate	0.25 (0.06)	2.02 (0.06)	3.50 (0.10)	0.90 (0.07)	0.36 (0.01)	−0.97 (0.07)	0.998	0.037	1032	23
Non-ionic liquids										
Squalane	0.07 (0.03)	0	0	0	0.73 (0.006)	−0.19 (0.02)	0.999	0.025	7638	22
OV-17	0.08 (0.05)	0.80 (0.03)	0.40 (0.07)	0	0.64 (0.009)	−0.31 (0.04)	0.998	0.036	1462	23
Carbowax 20M	0.27 (0.08)	1.52 (0.07)	2.16 (0.13)	0	0.53 (0.02)	−0.42 (0.10)	0.994	0.053	311	21
1,2,3-Tris(2-cyanoethoxy)propane	0.29 (0.10)	2.17 (0.10)	1.99 (0.18)	0.28 (0.11)	0.36 (0.02)	−0.48 (0.12)	0.993	0.062	213	22

Dependent variable $\log K_{\mathrm{L}}$ corrected for interfacial adsorption.

[a] r = multiple correlation coefficient; S.E. = standard error in the estimate; F = Fischer's statistic; n = number of solutes; the numbers in parenthesis are the standard deviation for the system constants.

1,2,3-tris(2-cyanoethoxy)propane and the alkylammonium thiocyanates bracketed between the poly(ethylene glycol) and 1,2,3-tris(2-cyanoethoxy)propane non-ionic liquids. In this respect, they are highly polar and polarizable solvents with properties similar to polar non-ionic solvents. The hydrogen-bond basicity of the ionic liquids (a system constants) is considerably larger than poly(ethylene glycol), a general solvent of high hydrogen-bond basicity. This is a further defining feature of the alkylammonium ionic liquids. They are stronger hydrogen-bond bases than typical non-ionic polar solvents. The alkylammonium ionic liquids are also strong hydrogen-bond acids (b system constants), which is not a common property of typical non-ionic stationary phases [170]. The hydrogen-bond acidity must be a property of the cations, since the anions do not contain hydrogen atoms to participate in hydrogen-bond formation.

The system constants for the tetra-*n*-butylammonium and tetra-*n*-butylphosphonium sulfonate ionic liquids at 121.4 °C are summarized in Table 13. These values are part of a larger database of 48 low-melting-point salts, some of which are room temperature ionic liquids [171,172]. A similar database is available for 23 non-ionic stationary phases widely used in gas chromatography [146–148,169,170]. The sulfonate ionic liquids show similar selectivity for electron lone pair interactions to polar non-ionic stationary phases. The sulfonate ionic liquids have a similar capacity for dipole-type interactions as the most dipolar/polarizable non-ionic stationary phases, with the exception of the octanesulfonate and perfluorooctanesulfonate ionic liquids. The latter have more in common with non-ionic stationary phases of intermediate polarity in terms of their capacity for dipole-type interactions. The general range of hydrogen-bond basicity for non-ionic phases ($a = 0$–2.1) is considerably lower than for the sulfonate ionic liquids ($a = 3.06$–3.71). The exception is the perfluorooctanesulfonate ionic liquid where the inductive effect of fluorine is responsible for lowering the hydrogen-bond basicity into the same range as the polar non-ionic stationary phases [171]. None of the sulfonate ionic liquids are hydrogen-bond acids. Several of the anions in Table 13 possess hydroxyl and amine functional groups selected to introduce hydrogen-bond acidity to the ionic liquids. To explain this behavior it was assumed that these anions preferentially form hydrogen-bonded inter-ion association complexes to the exclusion of significant interactions with dissolved hydrogen-bond bases. The formation of hydrogen-bond association complexes is also responsible for an increase in the cohesion of these ionic liquids resulting in a less favorable cavity term. The tetra-*n*-butylammonium and tetra-*n*-butylphosphonium ionic liquids with non-associated anions have surprisingly large l system constants, compared with non-ionic polar solvents, and are unique among polar solvents in their ability to separate members of a homologous series by gas–liquid chromatography. Although the spacing between members of a homologous series are similar for non-associated ionic liquids and low polarity non-ionic solvents, the absolute retention for compounds such as n-alkanes is lower for the ionic liquids. This is due to the generally larger and negative c term for the ionic liquids. For anions assumed to be associated as hydrogen-bond complexes the l system constants are significantly smaller and similar to the values observed for the most polar of the non-ionic stationary phases.

A general illustration of the unique gas–liquid partitioning properties of the ionic liquids is provided by the score plot of

Table 13
System constants for tetra-*n*-alkylammonium sulfonate ionic liquids at 121.4 °C

Ionic liquid	System constants						Statistics[a]		
	e	s	a	b	l	c	r	S.E.	n
Tetra-*n*-butylammonium salts									
2-Bis(2-hydroxyethyl)amino]ethanesulfonate	0.27	1.96	3.06	0	0.32	−0.80	0.996	0.048	27
2-(Cyclohexylamino)ethanesulfonate	0.07	1.57	3.67	0	0.51	−0.83	0.996	0.060	18
3-(Cyclohexylamino)-1-propanesulfonate	0	1.58	3.71	0	0.54	−0.93	0.995	0.066	18
2-Hydroxy-4-morpholinepropanesulfonate	0	1.76	3.20	0	0.49	−0.91	0.994	0.053	18
4-Morpholinepropanesulfonate	0	1.60	3.41	0	0.44	−0.94	0.990	0.097	34
Octanesulfonate	0.27	1.14	3.53	0	0.50	−0.59	0.997	0.077	32
Perfluorooctanesulfonate	0	1.09	1.62	0	0.40	−0.26	0.992	0.098	32
3-[Tris(hydroxymethyl)methyl]amino-2-hydroxy-1-propanesulfonate	0.27	1.96	3.06	0	0.32	−0.86	0.996	0.048	27
Tetra-*n*-butylphosphonium									
2-(Cyclohexylamino)ethanesulfonate	0.11	1.58	3.63	0	0.49	−0.82	0.995	0.059	26
4-Morpholinepropanesulfonate	0.13	1.68	3.66	0	0.49	−0.77	0.995	0.054	27
Non-ionic liquids									
Squalane	0.14	0	0	0	0.58	−0.22			
OV-17	0.07	0.65	0.26	0	0.52	−0.37			
Carbowax 20M	0.32	1.26	1.88	0	0.45	−0.56			
1,2,3-Tris(2-cyanoethoxypropane)	0.12	2.09	2.10	0.26	0.37	−0.74			

Dependent variable $\log K_{\mathrm{L}}$ corrected for interfacial adsorption.

[a] r = multiple correlation coefficient; S.E. = standard error in the estimate; and n = number of solutes.

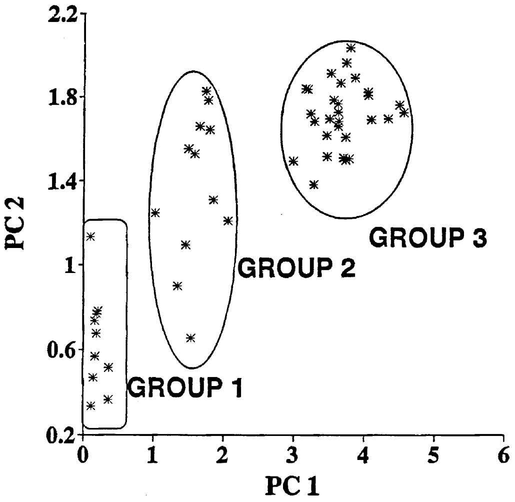

Fig. 5. Score plot for 55 solvents obtained by principal component analysis. Group 1 contains non-ionic solvents of low and intermediate polarity (weak hydrogen-bond bases of low and intermediate cohesion that differ in their dipolarity/polarizability); group 2 contains mainly polar non-ionic solvents and a few ionic liquids with a delocalized charge on at least one ion; group 3 contains ionic liquids (data from [172]).

Fig. 5 [172]. The input data are the system constants for 34 ionic liquids and 21 non-ionic stationary phases at 121.4 °C. The first two principal components account for 95.6% of the total variance. Principal component 1 is heavily weighted towards solvent hydrogen-bond basicity (*a* system constant) while component 2 is weighted more towards dipole-type interactions (*s* system constant) with a smaller contribution from the cavity/dispersion term (*l* system constant). The score plot of principal component 1 against component 2 show three clusters. Group 1 contains phases with weak polar interactions. Group 2 contains all the polar non-ionic solvents and a few ionic liquids with a highly dispersed charge on the anion. Group 3 contains all the remaining ionic liquids. This group is well separated from groups 1 and 2 and is an indication of the unique solvent characteristics of the ionic liquids.

System constants at two or three temperatures for several ionic liquids were reported by Anderson et al. [76] (Table 14). These results are single-column values with the retention factor as the dependent variable. The system constants, therefore, are uncorrected for contributions from interfacial adsorption, and their interpretation is suspect [173]. Open-tubular columns coated with thin films have an unfavorable surface area to volume ratio that tends to favor adsorption over partition [174]. In addition, the low viscosity of ionic liquids tends to result in film disruption as the column temperature is varied, exposing the sample to interactions with the column wall. The *c* term, when the retention factor is used as the dependent variable, contains the column phase ratio. It is usual to observe smooth changes in the *c* term, becoming increasingly negative at higher temperatures, which is not always the case for the results in Table 14. This indicates a significant lack of fit for some models. There is no statistical information (standard error for the estimate, standard deviation of the system constants) provided in [76] to judge the quality of the models in explaining the individual contributions to the retention mechanism. The negative *b* system constant for some ionic liquids in Table 14 is an indication that some models are erroneous. The interpretation in this case is that the gas phase is more hydrogen-bond acidic than the ionic liquid, which is clearly untenable. Although it is likely that some of the results in Table 14 will undergo revision in time, at least in qualitative terms the main trends provide a reasonable picture of the intermolecular interactions promoting partition from the gas phase into a variety of ionic liquids that have not been characterized previously. The strong hydrogen-bond basicity of the ionic liquids and its relationship to the chemistry of the anion; the capacity for dipole-type interactions equivalent to polar non-ionic liquids; exceptional ability to separate members of a homologous series compared with non-ionic liquids of similar polarity; weak or absent electron lone pair and hydrogen-bond acid interactions. These general characteristics represent the hallmark of ionic liquids characterized so far.

3.2.3. *Activity coefficients*

Since ionic liquids have a negligible vapor pressure, the most suitable method for measuring limiting activity coefficients of volatile solutes in ionic liquids is by gas chromatography using the ionic liquid as the stationary phase. Retention data should be corrected for contributions from interfacial adsorption and gas phase interactions. The activity coefficients at infinite dilution provides information about solute–solvent intermolecular interactions and are used, in particular, for the selection of solvents for extraction and extractive distillation. Unfortunately, the information currently available is quite limited. Kersten and Poole determined infinite dilution activity coefficients for benzene, *n*-butanol, 2-pentanone, 1-nitropropane and dioxane in ethylammonium and *n*-propylammonium nitrates and *n*-butylammonium, *sec*-butylammonium and di-*n*-propylammonium thiocyanates at 80.8 °C [150]. The limited information indicated strong interactions with solutes containing polar functional groups. Arancibia et al. [162] determined infinite dilution activity coefficients for 17 alkane, alkene, alkylbenzene and haloalkanes at 25 °C in ethylammonium and *n*-propylammonium nitrate ionic liquids. Heintz and co-workers [95,175,176] determined infinite dilution activity coefficients, partial molar excess enthalpies and Henry's coefficients at room temperature (298 K) for 38 varied solutes (alkanes, alkenes, alkylbenzenes, alcohols and several polar organic compounds) in the ionic liquids 4-methyl-*n*-butylpyridinium tetrafluoroborate and 1-methyl-3-ethylimidazolium and 1,2-dimethyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)amide. Alkene and aromatic hydrocarbons with polarizable electrons showed stronger interactions with the ionic liquids than alkanes, probably due to the increasing strength of ion-induced dipole interactions. Solutes with polar functional groups

Table 14
System constants for miscellaneous room temperature ionic liquids determined at several temperatures

Ionic liquids	Temperature (°C)	System constants					
		e	*s*	*a*	*b*	*l*	*c*
1-Butyl-2,3-dimethylimidazolium							
Bis(trifluoromethylsulfonyl)amide	40	0.07	1.96	2.03	0.13	0.64	−2.93
	70	0.08	1.75	1.79	0.16	0.57	−3.14
	100	0.09	1.58	1.57	0.11	0.48	−3.15
1-Butyl-3-methylimidazolium							
Hexafluoroantimonate	40	0	1.88	3.09	−0.33	0.59	−2.44
	70	0	1.81	2.70	−0.37	0.51	−2.69
	100	0	1.66	2.28	−0.33	0.46	−2.85
Bis(trifluoromethylsulfonyl)amide	40	0	1.89	2.02	0.36	0.63	−2.87
	70	0	1.67	1.75	0.38	0.56	−3.03
	100	0	1.60	1.55	0.24	0.49	−3.13
Chloride	40	0.24	2.25	7.03	−0.36	0.63	−3.10
	70	0.29	2.01	5.23	−0.32	0.45	−2.84
	100	0.41	1.83	4.86	−0.12	0.39	−3.10
Hexafluorophosphate	40	0	1.91	1.89	0	0.62	−2.61
	70	0	1.70	1.58	0	0.52	−2.62
	100	0	1.54	1.37	0	0.44	−2.68
Tetrafluoroborate	40	0	1.65	2.22	−0.10	0.64	−2.66
	70	0	1.46	1.97	−0.13	0.57	−2.74
	100	−0.14	1.37	1.66	−0.28	0.47	−2.72
Trifluoromethanesulfonate	40	0	1.86	3.02	0	0.61	−2.43
	70	0	1.73	2.71	0	0.52	−2.64
	100	0	1.39	2.35	0	0.49	−2.76
N-Butyl-*N*-methylpyrrolidinium							
Bis(trifluoromethylsulfonyl)amide	40	0	1.69	2.08	0.16	0.68	−2.78
	70	0	1.53	1.78	0	0.56	−2.80
	100	0	1.44	1.55	0	0.48	−2.92
Dimethylammonium							
2-Pyridinecarboxylate	40	−0.24	0.78	1.17	0	0.76	−3.61
	70	−0.23	0.78	0.80	0	0.61	−3.53
1-Hexyl-2,3,4,5-tetramethylimidazolium							
Bis(trifluoromethylsulfonyl)amide	40	0.21	1.72	1.97	0	0.70	−2.80
	70	0.17	1.58	1.85	0	0.61	−2.91
	100	0.24	1.40	1.57	0	0.50	−2.90
1-Octyl-2,3,4,5-tetramethylimidazolium							
Bis(trifluoromethylsulfonyl)amide	40	0.22	1.68	1.94	0	0.72	−2.89
	70	0.17	1.53	1.83	0	0.63	−3.02
	100	0.13	1.40	1.56	0	0.55	−3.09
Tributylammonium							
Acetate	40	−0.25	0.73	1.34	−0.22	0.83	−3.41
	70	−0.24	0.65	1.05	−0.21	0.74	−3.63
2-Pyridinecarboxylate	40	−0.13	0.59	1.51	−0.22	0.74	−2.65
	70	0	0.50	1.51	−0.37	0.62	−2.70
3-Hydroxypyridine-2-carboxylate	40	−0.13	0.48	1.08	−0.16	0.75	−2.90
	70	0	0.37	0.94	−0.15	0.64	−3.01
α-Cyano-4-hydroxycinnamate	60	0.32	1.37	2.21	1.09	0.68	−3.83
	70	0.26	1.34	2.18	1.04	0.55	−3.35
Sinapinate	60	0.16	1.88	2.85	1.38	0.77	−4.28
	70	0.24	1.74	2.69	1.13	0.67	−4.08
Triethylammonium							
2-Pyridinecarboxylate	40	0	0.52	1.35	0	0.71	−3.14
	70	−0.10	0.58	0.84	0	0.49	−2.70

Dependent variable $\log k$ uncorrected for interfacial adsorption.

had higher solubility due to attractive interactions with ions of the ionic liquids. Activity coefficients were generally larger in the tetrafluoroborate ionic liquid compared with the bis(trifluoromethylsulfonyl)amides. This was explained by the smaller size of the tetrafluoroborate anion, which gives rise to a stronger Coulombic interaction with the ionic liquid. Dissolution in the tetrafluoroborate ionic liquid requires more energy to overcome solvent–solvent interactions than the ionic liquids containing the larger bis(trifluoromethylsulfonyl)amide ion. Diedenhofen et al. [177] demonstrated that the activity coefficients determined by Heintz and co-workers could be adequately predicted by COSMOS-RS software based on quantum chemical calculations. Letcher et al. [178] determined infinite dilution activity coefficients at temperatures close to room temperature for hydrocarbons of different types and methanol in the ionic liquid 1-hexyl-3-methylimidazolium hexafluorophosphate. The activity coefficients for methanol, benzene and alkynes were much smaller than the values for alkanes and alkenes owing to more favorable interactions between the more polar solutes and the ionic liquid. David et al. [179] assessed the possibility of separating benzene from hydrocarbons of different structure on 1-methyl-3-octylimidazolium chloride using experimental infinite dilution activity coefficients. Anthony et al. [87,180] determined the solubility, Henry's constant and enthalpy and entropy of solution for nine gases and water in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate at three temperatures and different pressures. Water and carbon dioxide exhibited the strongest interactions and the highest solubility in the ionic liquid, followed by ethylene, ethane and methane. Argon and oxygen both had very low solubility and essentially no interaction with the ionic liquid. The solubility of hydrogen and carbon monoxide was very low and less than typical values for non-ionic solvents used in synthetic organic chemistry for reactions employing these gases. Similar results for oxygen and carbon dioxide were obtained by Husson-Borg et al. [181] for the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate. Krummen et al. [182] determined activity coefficients for 20 solutes (alkanes, alkenes, aromatic hydrocarbons, ketones, alcohols and water) in the ionic liquids 1-methyl-3-methylimidazolium, 1-ethyl-3-methylimidazolium and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide and 1-butyl-3-methylimidazolium ethanesulfate at 293.15–333.15 K. These data were used to show that the ionic liquids possessed distinct advantages for the separation of aromatic and aliphatic hydrocarbons by extractive distillation and extraction.

3.3. Liquid–liquid partition coefficients

The ionic liquids are cohesive solvents of high density some of which form biphasic systems with water and traditional organic solvents. The density difference between ionic liquids and traditional organic solvents promotes rapid phase separation, a favorable property for applications employing liquid–liquid separation systems, and a key component for the industrial development of ionic liquids. Physicochemical data to support these developments is incomplete and was largely assembled over the last few years. Further development in both methods and archiving of primary information is required to support expanded use of ionic liquids outside the laboratory.

3.3.1. Phase behavior

The 1,3-dialkylimidazolium salts with halide, nitrate, trifluoroacetate anions are generally miscible with water [110]. The 1,3-dialkylimidazolium hexafluorophosphate and bis(trifluoromethylsulfonyl)amide are generally immiscible with water, while the tetrafluoroborate and trifluoromethanesulfonate salts are either miscible or immiscible depending on the substituents on the cation [110]. 1-Ethyl-3-methylimidazolium tetrafluoroborate is totally soluble in water while 1-hexyl-3-methylimidazolium tetrafluoroborate is essentially insoluble in water, although water is soluble in the ionic liquid at up to about 30 g/l [83]. All 1,3-dialkylimidazolium tetrafluoroborate ionic liquids are generally miscible with acetone and dichloromethane. 1-Ethyl-3-methylimidazolium, *N*,*N*-dialkylpyrrolidinium, and tetraalkylammonium dicyanamide ionic liquids are completely miscible with water and most common laboratory solvents except for hexane and toluene [51]. The 1,3-dialkylimidazolium methanesulfate and ethanesulfate ionic liquids are miscible with water and most common organic solvents of intermediate polarity [72]. The alkylammonium nitrate and thiocyanate room temperature ionic liquids are insoluble in hexane [27]. Their solubility increases with the polarity of the organic solvent, and most salts are miscible with a wide range of common solvents including water. However, increasing the alkyl chain length of the cation decreases the solubility of the nitrate and thiocyanate ionic liquids in water. Miscibility data for room temperature ionic liquids with different organic solvents and water are summarized in Table 15. These basic data are available for only a few ionic liquids. In most cases, these data are based on simple physical observations of phase separation. There is even less information concerning the mutual solubility of solvents in biphasic systems. Brennecke and co-workers [87,183] have determined the mutual solubility of components in the biphasic systems 1-butyl-3-methylimidazolium hexafluorophosphate–water (2 wt.% of ionic liquid in the water rich phase and 2.3 wt.% water in the ionic liquid rich phase), 1-octyl-3-methylimidazolium hexafluorophosphate–water (0.7 wt.% of ionic liquid in the water rich phase and 1.3 wt.% water in the ionic liquid rich phase), and 1-octyl-3-methylimidazolium tetrafluoroborate (1.8 wt.% of ionic liquid in the water rich phase and 10.8 wt % water in the ionic liquid rich phase). Supercritical fluid carbon dioxide was shown to be soluble in 1-butyl-3-methylimidazolium hexafluorophosphate but the ionic liquid was insoluble in carbon dioxide [87]. This allows supercritical fluid

Table 15
Solvent miscibility of ionic liquids

Ionic liquid	Solvent[a]									
	Water	MOH	ACN	THF	MCl_2	HEX	EtOAc	Acet	Tol	MCl_3
n-Butylammonium thiocyanate	M	M	M	M	M	I				
sec-Butylammonium thiocyanate	M	M	M	M	M	I				
1-Butyl-3-ethylimidazolium										
Ethanesulfate	M		M		M			M		
1-Butyl-3-methylimidazolium										
Chloride	M									
Heptafluorobutyrate				M	M		M		I	
Hexafluorophosphate	I	M				I		M	I	M
Iodide	M									
Methanesulfate	M		M		M			M		
Tetrafluoroborate	M	M			I		M	I	M	
Trifluoroacetate				M	M		M		I	
1-Butyl-4-(3,3,3-trifluoropropyl)-1,2,4-triazolium										
Bis(trifluoromethylsulfonyl)amide	PM			M	M	I	M	M		
1-Decanyl-4-(1-fluoroethyl)-1,2,4-triazolium										
Bis(trifluoromethylsulfonyl)amide	PM			M	PM	I	M	M		
1-Decanyl-4-(3,3,3-trifluoropropyl)-1,2,4-triazolium										
Bis(trifluoromethylsulfonyl)amide	PM			M	M	I	M	M		
1,3-Diethylimidazolium										
Ethanesulfate	M		M		M			M		
Di-*n*-propylammonium thiocyanate	M	M	M	M	M	I				
Ethylammonium nitrate	M	M	M	M	I	I				
1-Ethyl-3-methylimidazolium										
Heptafluorobutyrate				M	M		PM		I	
Hexafluorophosphate	M	M				I		M	I	M
Methanesulfate	M		M		M			M		
Trifluoroacetate				M	M		PM		I	
Trifluoromethanesulfonate				M	M		M		I	
1-Heptyl-4-(1-fluoroethyl)-1,2,4-triazolium										
Bis(trifluoromethylsulfonyl)amide	PM			M	PM	I	M	M		
1-Heptyl-4-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1,2,4-triazolium										
Bis(trifluoromethylsulfonyl)amide	PM			M	PM	I	M	M		
1-Heptyl-4-(3,3,3-trifluoropropyl)-1,2,4-triazonium										
Bis(trifluoromethylsulfonyl)amide	PM			M	M	I	M	M		
1-Methyl-3-ethylimidazolium										
Ethanesulfate	M		M		M			M		
1-Methyl-4-(3,3,3-trifluoropropyl)-1,2,4-triazolium										
Bis(trifluoromethylsulfonyl)amide	PM			M	M	I	M	M		
n-Propylammonium nitrate	M	M	M	M	60%	I				
1-Propyl-3-ethylimidazolium										
Ethanesulfate	M		M		M			M		
1-Propyl-3-methylimidazolium										
Methanesulfate	M		M		M			M		
Tri-*n*-butylammonium nitrate	40%	M	M	M	M	I				
N-(3,3,3-trifluoropropyl)-1,2,4-triazolium Bis(trifluoromethylsulfonyl)amide	PM			M	M	I	M	M		

M = miscible; PM = partially miscible; I = immiscible.

[a] MOH = methanol; ACN = acetonitrile; THF = tetrahydrofuran; MCl_2 = methylene chloride; HEX = *n*-hexane; EtOAc = ethyl acetate; Acet = acetone; Tol = toluene; MCl_3 = chloroform.

carbon dioxide to be exploited for the extraction of organic compounds from ionic liquids without contamination of the extracted products with the ionic liquid [4,87]. The phase diagram for a binary mixture of fluoroform and 1-ethyl-3-methylimidazolium hexafluorophosphate (vapor–liquid and solid–liquid boundaries) has been determined over a wide pressure and temperature range [184].

Phase diagrams for binary mixtures of 1-alkyl-3-methylimidazolium hexafluorophosphate with butan-1-ol [185] and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) amide with propan-1-ol, butan-1-ol and pentan-1-ol [186] have been described. The binodal co-existence curves of the mixtures were found to have an upper critical solution temperature at a defined concentration of the alcohol that depends on the identity of the cation and the alcohol for each ionic liquid. The relatively hydrophobic ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate forms a single-phase ternary system with ethanol and water [187,188]. The ionic liquid is only partially miscible with either pure water or absolute ethanol. The single-phase region is formed from mixtures containing 0.5–0.9 mole fraction of ethanol. Approximate ternary phase diagrams for 1-butyl-3-methylimidazolium hexafluorophosphate and water with acetonitrile, methanol, ethanol, 1-propanol and 2-propanol were described by Berthod and Carda-Broch in their search for suitable biphasic systems of low viscosity containing ionic liquids for separations by countercurrent chromatography [189]. The phase diagram for ternary mixtures of 1-octyl-3-methylimidazolium chloride and benzene with heptane, dodecane and hexadecane was used to predict the effectiveness of the ionic liquid in extracting benzene from hydrocarbon fuels [190]. Ternary phase systems extend the range of partitioning properties for the ionic liquids and will probably find practical applications in the future as new systems are characterized.

3.3.2. *Shake-flask methods*

Rogers and co-workers [191,192] used radiolabeled compounds to determine the partition coefficients for several compounds in biphasic systems containing 1,3-dialkylimidazolium ionic liquids and water by the shake-flask method. Carda-Broch and co-workers [78,189] determined partition coefficients for ionized and neutral compounds at several pH values in the biphasic system containing 1-butyl-3-methylimidazolium hexafluorophosphate and water by the shake-flask method. In addition, Carda-Broch and co-workers [78,189] determined partition coefficients for several neutral compounds in the biphasic system containing 1-butyl-3-methylimidazolium hexafluorophosphate and heptane [78,189]. The partitioning of charged and neutral aromatic compounds between 1-butyl-3-methylimidazolium hexafluorophosphate and water conformed to expectations based on observations for traditional organic solvent–water systems. Acids were extracted more efficiently by the ionic liquid in their neutral form after adjusting pH. A rough correlation was found between the partition coefficients for the ionic liquid–water system and the octanol–water partition coefficient for the same compounds, although partition coefficients for the ionic liquid–water system were generally an order of magnitude smaller [192]. Polar compounds, particularly those with hydrogen-bonding functional groups, were extracted more efficiently by the ionic liquid than non-polar solutes. The *N*-octylisoquinolinium and *N*-tetradecylisoquinolinium bis(perfluoroethylsulfonyl)amide ionic liquids provided higher extraction efficiency than 1-butyl-3-methylimidazolium hexafluorophosphate for the extraction of compounds of low polarity and for aromatic compounds in particular [98]. The ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium hexafluorophosphate and 1-butyl-3-methylimidazolium tetrafluoroborate were found to be effective for the selective removal of sulfur-containing compounds from hydrocarbon fuels at room temperature [193]. Sulfur-containing compounds with a C-5 aromatic ring are selectively absorbed over C-6 aromatics, while sulfur-containing non-aromatic compounds were poorly absorbed. 1-Butyl-3-methylimidazolium hexafluorophosphate was demonstrated to be an effective solvent for the extraction of heavy metals as dithizone complexes from water [194].

Partition coefficients for a range of compounds were reported for the biphasic systems formed between ethylammonium nitrate, *n*-propylammonium nitrate or di-*n*-propylammonium thiocyanate and hexane, benzene, toluene, octanol, dichloromethane and methyl *tert*-butyl ether [28,195]. The partition coefficients of non-polar and dipolar solutes generally favor distribution to the organic solvent. The ionic liquids, however, selectively extract compounds with hydrogen-bonding functional groups. Di-*n*-propylammonium thiocyanate extracts a larger portion of all compounds than ethylammonium nitrate and *n*-propylammonium nitrate from hexane.

A single report offers a reliable interpretation of the partition coefficients for ionic liquid–water systems using the appropriate form of the solvation parameter model [196]:

$$\log P = c + eE + sS + aA + bB + vV \qquad (7)$$

where P is the liquid–liquid partition coefficient and V the McGowan's characteristic volume. Compared with Eq. (6), the L solute descriptor is replaced by V because transfer of a solute between two condensed phases occurs with cancellation of dispersion interactions [146–148]. Other aspects of the interpretation remain the same. It should be noted, however, that solvation properties of ionic liquids determined by gas–liquid chromatography, are likely to be a poor guide to the properties of biphasic ionic liquid–water systems, because, in the latter case, the ionic liquids are saturated with water. System constants are available for the biphasic 1-butyl-3-methylimidazolium hexafluorophosphate–water system ($c = -0.17$, $e = 0.45$, $s = 0.23$, $a = -1.76$, $b = -1.83$ and $v = 2.15$) and 1-hexyl-3-methylimidazolium hexafluorophosphate–water system ($c = -0.13$, $e = 0.05$, $s = 0.40$, $a = -1.48$, $b = -2.11$ and $v = 2.30$). These results can be compared with a database of organic solvent–water systems determined in the same way [197]. The unusual feature of both ionic liquids is the small positive *s* system constant indicating that the dipolarity/polarizability of the wet ionic liquids is slightly greater than water itself, while for conventional organic solvents the *s* system constant is always negative. The two ionic liquids have a rather average *a* system constant, which indicates that the ionic liquids are less basic than water and about as basic as a typical ester. The basicity of the ionic liquids is probably determined mainly by the properties of the anion. The *b* system constant for the wet ionic liquids lies between those calculated for the hypothetical ethylene glycol–water and 2,2,2-trifluoroethanol–water systems, and is larger than values for traditional biphasic organic solvent–water systems. This is an indication that the ionic liquids are strong hydrogen-bond acids, largely a property of the cation, which has three acidic hydrogen atoms. The relatively small *v* system constant for the ionic liquids is an indication that the ionic liquids are more cohesive than traditional organic solvents.

3.3.3. *Liquid–liquid chromatography*

The ionic liquid phase of a biphasic system is usually selected as the stationary phase and the organic or aqueous solvent portion as the mobile phase. The stationary phase is coated on a prepacked porous silica column of an appropriate particle size. Solvent generated stationary phases allow more stable and reproducible systems to be prepared compared with conventional dynamic coating and equilibration with the mobile phase after displacement of the coating solvent [198–200]. To adjust the phase ratio of the column, a support with a different surface area and specific pore volume is selected. Long-time operation usually requires presaturation of the mobile phase with the stationary phase and thermostating of the mobile phase and column to avoid fluctuations in the phase ratio and displacement of the ionic liquid from the column. To minimize erosion of the ionic liquid, the sample solvent should have a similar composition to the mobile phase.

In the absence of adsorption by the support, which is typically the case for ionic liquids, retention in liquid–liquid chromatography is described by:

$$V_R = V_M + PV_S \tag{8}$$

where V_R is the retention volume, V_M the column hold-up volume, P the liquid–liquid partition coefficient and V_S the volume of ionic liquid saturated with the mobile phase. The column hold-up volume and stationary phase volumes are calculated from the intercept and slope, respectively, of the plot of the retention volume against the partition coefficient for several calibration compounds determined in a separate shake-flask experiment. Once values for the column hold-up and stationary phase volumes have been determined, partition coefficients for other solutes are simply obtained from their retention volume in the same chromatographic system.

The use of liquid–liquid chromatography for the determination of partition coefficients for ionic liquids is limited so far [195]. The method, however, has a number of favorable features that include speed, accuracy and minimal consumption of samples and ionic liquid. In addition, the method was effective for identifying suitable biphasic systems for liquid–liquid extraction of complex mixtures. Biphasic systems were prepared using ethylammonium and *n*-propylammonium nitrate and mixtures of hexane with methyl *tert*-butyl ether, chloroform or dichloromethane containing up to 75% (v/v) of the polar organic solvent as the mobile phase. By varying the composition of the mobile phase, the relationship between the partition coefficient and the composition of the mobile phase was used to optimize the selectivity of the extraction procedure for sample preparation. Some examples of partition coefficients determined with hexane-methyl *tert*-butyl ether as a counter solvent are presented in Table 16.

Table 16
Partition coefficients determined by liquid–liquid chromatography for *n*-propylammonium nitrate (stationary phase) and hexane containing different volume fractions of methyl *tert*-butyl ether (mobile phase)

Compound	Partition coefficient			
	0.76[a]	0.6[a]	0.4[a]	0.2[a]
Aniline	3.26	4.69	7.31	9.47
N,*N*-Diethyl-3-nitroaniline	0.06	0.06	0.11	0.46
N,*N*-Diethyl-4-nitroaniline	0.41	1.14	1.66	2.74
N,*N*-Dimethyl-4-nitroaniline	1.43	2.17	3.49	5.60
Diphenylamine	0	0.40	0.86	1.60
N-Methyl-2-nitroaniline	0.80	0.97	1.49	2.17
N-Methyl-4-nitroaniline	4.75	7.31	12.40	16.44
1-Naphthol	1.03	1.31	2.23	2.83
2-Naphthol	1.60	2.06	3.42	4.35
4-Nitroaniline	10.57	16.40	33.26	44.78
4-Nitroanisole	0.69	0.80	1.66	3.29
3-Nitrobenzaldehyde	0.54	2.97	4.51	8.17
1-Nitronaphthalene	0.19	0.51	0.80	1.26
2-Nitrophenol	0.51	0.63	0.80	0.96
4-Nitrophenol	3.66	5.43	10.11	13.42

[a] Volume fraction of methyl *tert*-butyl ether (v/v).

4. Separation media

For completeness, mention is made of the use of room temperature ionic liquids as a separation medium in chromatography and electrophoresis. Few real applications have emerged so far and curiosity rather than design was responsible for most activity. Now that a large number of ionic liquids have emerged with a wider range of properties than was available just a few years ago, the possibility of finding useful applications in separation science has increased significantly. A large number of papers demonstrate the separation of standard mixtures by packed column gas chromatography with ionic liquids as the stationary phase [59]. Probably the only real application described so far that relies on a specific property of an ionic liquid is the separation of benzene and alkylbenzenes after dodecane for the analysis of aromatic compounds in gasoline and similar fuel oils [201]. The development of fused silica columns with immobilized stationary phases revolutionized the practice of gas chromatography and essentially replaced packed columns for general analytical applications. This somewhat ended interest in ionic liquids as stationary phases since no method was found to prepare stable and immobilized films with ionic liquids on fused silica surfaces [157–160]. Interest may return to this area as the need for new stationary phases with complementary selectivity to the widely used poly(siloxanes) gathers momentum in attempts to expand the application range of gas chromatography. Room temperature ionic liquids were demonstrated to be good solvents for chiral selectors (e.g. cyclodextrins and their derivatives) for the separation of enantiomers by gas chromatography [160,202]. The complexing ability of cyclodextrins dissolved in 1-butyl-3-methylimidazolium chloride has been studied by near-infrared spectroscopy [203].

Alkylammonium nitrate and thiocyanate ionic liquids have been used as mobile phase components in reversed-phase liquid chromatography [27,28,195]. The ionic liquids showed limited ability to modify retention being weak solvents similar to water. A greater fundamental limitation was the relatively high viscosity of the mobile phase. The larger number of ionic liquids now available should provide a wider range of physicochemical properties better suited to separations by liquid chromatography. The development of chemically bonded phases just about terminated interest in liquid–liquid chromatography for separations. Ionic liquids, however, are well suited to separations of this kind and could rekindle some interest for special applications [195]. 1-Alkyl-3-methylimidazolium ionic liquids at low concentrations were shown to be suitable additives for improving the separation properties of basic compounds in reversed-phase liquid chromatography [204].

Applications of liquid–liquid extraction using shake-flask methods were discussed in Section 3.3.2. This is an application area that is easy to develop and a necessary stepping stone to the development of isolation schemes as a component of integrated industrial processes. Further information will likely appear as the use of ionic liquids in organic synthesis progresses. Branco et al. [205] have already demonstrated the successful use of ionic liquids in supported liquid membranes for analytical extractions, which should prove to be fruitful area for new applications.

Ionic liquids have been used as background electrolytes in aqueous and non-aqueous capillary electrophoresis and as wall coatings in aqueous capillary electrophoresis [206–211]. As wall coating agent, their primary use was to reverse the direction of electroosmotic flow independent of the buffer pH. A number of different sample types (DNA fragments, metal ions, ionic dyes, phenols, etc.), have been separated using 1,3-dialkylimidazolium-based ionic liquids as a major component of the background electrolyte without significant operational difficulties. These results demonstrate the feasibility of using ionic liquids in capillary electrophoresis without demonstrating that an ionic liquid is necessary to obtain a suitable separation that could not be obtained with conventional support electrolytes.

5. Conclusions

There are few aspects of solution chemistry which have generated the same interest as ionic liquids in the last few years. This has resulted in more hype than substance, but not without reason. To establish ionic liquids as “unique”, “selective” or “designer” solvents requires a larger database of physicochemical properties so that speculation can be transformed into reality. Chromatography is in many ways the preferred tool for the construction of databases of solvation properties at infinite dilution required to underpin current technical developments. In this report, I have tried to summarize what is known at this time without any pretence that this is a satisfactory story. My own feeling is that what we need to know far exceeds what is known, but that is what research is for, and explains the current hype and interest in ionic liquids.

References

[1] P.T. Anasias, M.M. Kirchhoff, Acc. Chem. Res. 35 (2002) 686.
[2] M.A. Abraham, L. Moens, Clean Solvents. Alternative Media for Chemical Reactions and Processing, American Chemical Society, Washington, DC, 2002.
[3] P. Wasserscheid, W. Keim, Angew. Chem. Int. Ed. 39 (2000) 3773.
[4] C.C. Tzschucke, C. Markert, W. Bannwarth, S. Roller, A. Hebel, R. Haag, Angew. Chem. Int. Ed. 41 (2002) 3964.
[5] S.V. Dzyuba, R.A. Bartsch, Angew. Chem. Int. Ed. 42 (2003) 148.
[6] B. Jastorff, R. Stormann, J. Ranke, K. Molter, F. Stock, B. Oberheitmann, W. Hoffmann, J. Hoffmann, M. Nuchter, B. Ondruschka, J. Filser, Green Chem. 5 (2003) 136.
[7] J. Dupont, R.F. de Souza, P.A.Z. Suarez, Chem. Rev. 102 (2002) 3667.
[8] C.M. Gordon, Appl. Catal. 222 (2001) 101.
[9] T. Welton, Chem. Rev. 99 (1999) 2071.
[10] D. Zhao, M. Wu, Y. Kou, E. Min, Catal. Today 74 (2002) 157.
[11] H. Olivier-Bourbigon, L. Magna, J. Mol. Catal. A 182 (2002) 419.
[12] P. Wasserscheid, T.E. Welton (Eds.), Ionic Liquids in Synthesis, VCH–Wiley, Weinheim, Germany, 2002.
[13] U. Kragel, M. Eckstein, N. Kaftzik, Curr. Opin. Biotechnol. 13 (2002) 565.
[14] F. van Rantwijk, R.M. Lau, R.A. Sheldon, Trends Biotechnol. 21 (2003) 131.
[15] J. Hoffmann, M. Nuchter, B. Ondruschka, P. Wasserscheid, Green Chem. 5 (2003) 296.
[16] J.H. Davis, P.A. Fox, J. Chem. Soc., Chem. Commun. (2003) 1209.
[17] P.C. Ray, J.N. Rakshit, J. Chem. Soc. (1911) 1470.
[18] P. Walden, Bull. Acad. Imper. Sci. (St. Petersberg) (1914) 1800.
[19] S. Sugden, H. Wilkins, J. Chem. Soc. (1929) 1291.
[20] D.F. Evans, S.-H. Chen, G.W. Schriver, E.M. Arnett, J. Am. Chem. Soc. 103 (1981) 481.

[21] D.F. Evans, E.W. Kaler, W.J. Benton, J. Phys. Chem. 87 (1983) 533.

[22] D.F. Evans, A. Yamauchi, R. Roman, E.Z. Cassassa, J. Colloid Interface Sci. 88 (1982) 89.

[23] D.F. Evans, A. Yamauchi, G.J. Wel, V.A. Bloomfield, J. Phys. Chem. 89 (1983) 3537.

[24] D. Mirejovsky, E.M. Arnett, J. Am. Chem. Soc. 105 (1983) 1112.

[25] F. Pacholec, H.T. Butler, C.F. Poole, Anal. Chem. 54 (1982) 1938.

[26] R.A. Mathes, F.D. Stewart, F. Swedish, J. Am. Chem. Soc. 70 (1948) 3455.

[27] C.F. Poole, B.R. Kersten, S.S.J. Ho, M.E. Coddens, K.G. Furton, J. Chromatogr. 352 (1986) 407.

[28] P.H. Shetty, P.J. Youngberg, B.R. Kersten, C.F. Poole, J. Chromatogr. 411 (1987) 61.

[29] R.V. Hangarge, D.V. Jarikote, M.S. Shingare, Green Chem. 4 (2002) 266.

[30] A. Kumar, Chem. Rev. 101 (2001) 1.

[31] J.B. Shotwell, B.A. Flowers, Electroanalysis 12 (2000) 223.

[32] G. Perron, A. Hardy, J.C. Justice, J.E. Desnoyers, J. Solution Chem. 22 (1993) 1159.

[33] H. Weingartner, A. Knocks, W. Schrader, U. Kaatze, J. Phys. Chem. A 105 (2001) 8646.

[34] S. Duvivier, M. Turmine, P. Letellier, Can. J. Chem. 76 (1998) 1210.

[35] N. Benhlima, M. Turmine, P. Letellier, R. Naejus, P. Lemordant, J. Chem. Phys. Phys. Chim. Biol. 95 (1998) 25.

[36] A. Oleinikova, M. Bonetti, J. Solution Chem. 31 (2002) 397.

[37] H. Weingartner, W. Schroer, J. Mol. Liq. 65 (1995) 107.

[38] J.E. Gordon, in: D.B. Denney (Ed.), Techniques and Methods of Organic and Organometallic Chemistry, vol. 1, Dekker, New York, 1969, pp. 51–188.

[39] C.G. Swain, A. Ohno, D.K. Roe, R. Brown, T. Maugh, J. Am. Chem. Soc. 89 (1967) 2648.

[40] T.G. Coker, J. Abrose, G.J. Janz, J. Am. Chem. Soc. 92 (1970) 5293.

[41] W.T. Ford, R.J. Hauri, D.J. Hart, J. Org. Chem. 38 (1973) 3916.

[42] K.G. Furton, S.K. Poole, C.F. Poole, Anal. Chim. Acta 192 (1987) 49.

[43] W.T. Ford, R.J. Hauri, J. Am. Chem. Soc. 95 (1973) 7381.

[44] D.J. Hart, W.T. Ford, J. Org. Chem. 39 (1974) 363.

[45] W.T. Ford, D.J. Hart, J. Am. Chem. Soc. 96 (1974) 3261.

[46] W.T. Ford, R.J. Hauri, S.G. Smith, J. Am. Chem. Soc. 96 (1974) 4316.

[47] W.T. Ford, Anal. Chem. 47 (1975) 1125.

[48] W.T. Ford, J. Am. Chem. Soc. 98 (1976) 2727.

[49] W.T. Ford, D.J. Hart, J. Phys. Chem. 80 (1976) 1002.

[50] C.L. Hussey, Adv. Molten Salt Chem. 5 (1983) 185.

[51] D.R. MacFarlane, S.A. Forsyth, J. Golding, G.B. Deacon, Green Chem. 4 (2002) 444.

[52] J.M. Pringle, J. Golding, C.M. Forsyth, G.B. Deacon, M. Forsyth, D.R. MacFarlane, J. Mater. Chem. 12 (2002) 3475.

[53] J. Golding, S. Forsyth, D.R. MacFarlane, M. Forsyth, G.B. Deacon, Green Chem. 4 (2002) 223.

[54] H. Matsumoto, H. Kageyama, Y. Miyazaki, Chem. Lett. (2001) 182.

[55] S.K. Poole, P.H. Shetty, C.F. Poole, Anal. Chim Acta 218 (1989) 241.

[56] R.M. Pomaville, C.F. Poole, Anal. Chem. 60 (1988) 1103.

[57] R.M. Pomaville, C.F. Poole, J. Chromatogr. 468 (1989) 261.

[58] R.M. Pomaville, S.K. Poole, L.J. Davis, C.F. Poole, J. Chromatogr. 438 (1988) 1.

[59] C.F. Poole, K.G. Furton, B.R. Kersten, J. Chromatogr. Sci. 24 (1986) 400.

[60] C.F. Poole, K.G. Furton, R.M. Pomaville, S.K. Poole, B.R. Kersten, Molten Salt Tech. 4 (1991) 41.

[61] R.M. Pagni, Adv. Molten Salt Chem. 6 (1987) 211.

[62] K.R. Seddon, J. Chem. Technol. Biotechnol. 68 (1997) 351.

[63] S. Geetha, D.C. Trivedi, Bull. Electrochem. 19 (2003) 37.

[64] J.S. Wilkes, M.J. Zaworotko, J. Chem. Soc., Chem. Commun. (1992) 965.

[65] S.V. Dzyuba, R.A. Bartsch, Tetrahedron Lett. 43 (2002) 4657.

[66] R.P. Singh, S. Manandhar, J.M. Shreeve, Tetrahedron Lett. 43 (2002) 9497.

[67] J. Pernak, A. Olszowka, R. Olszewski, Pol. J. Chem. 77 (2003) 179.

[68] A.J. McLean, M.J. Muldoon, C.M. Gordon, I.R. Dunkin, J. Chem. Soc., Chem. Commun. (2002) 1880.

[69] L. Crowhurst, P.R. Mawdsley, J.M. Perez-Arlandis, P.A. Salter, T. Welton, Phys. Chem. Chem. Phys. 5 (2003) 2790.

[70] Solvent-Innovation, http://www.solvent-innovation.de.

[71] P. Bonhote, A.-P. Dias, M. Papageorgiou, K. Kalyanasundaram, M. Gratzel, Inorg. Chem. 35 (1996) 1168.

[72] J.D. Holbrey, W.M. Reichert, R.P. Swaitoski, G.A. Broker, W.R. Pimer, K.R. Seddon, R.D. Rogers, Green Chem. 4 (2002) 407.

[73] L.C. Branco, J.N. Rosa, J.J.M. Ramos, C.A.M. Afonso, Chem. Eur. J. 8 (2002) 3671.

[74] J.C. Huddlestone, A.E. Visser, W.M. Reichert, H.D. Willauer, G.A. Broker, R.D. Rogers, Green Chem. 3 (2001) 156.

[75] P. Stepnowski, A. Muller, P. Behrend, J. Ranke, J. Hoffmann, B. Jastorff, J. Chromatogr. A 993 (2003) 173.

[76] J.L. Anderson, J. Ding, T. Welton, D.W. Armstrong, J. Am. Chem. Soc. 124 (2002) 14247.

[77] C.J. Bradaric, A. Downard, C. Kennedy, A.J. Robertson, Y.H. Zhou, Green Chem. 5 (2003) 143.

[78] S. Carda-Broch, A. Berthod, D.W. Armstrong, Anal. Bional. Chem. 375 (2003) 191.

[79] N.V.K.A. Sudhir, J.F. Brennecke, A. Samanta, J. Chem. Soc., Chem. Commun. (2001) 413.

[80] J. van den Broeke, M. Stam, M. Lutz, H. Kooijman, A.L. Spek, B.-J. Deelman, G. van Koten, Eur. J. Inorg. Chem. (2003) 2798.

[81] N. Gathergood, P.J. Scammells, Aust. J. Chem. 55 (2002) 557.

[82] A.E. Visser, R.P. Swatloski, R.D. Rogers, Green Chem. 2 (2000) 1.

[83] J.D. Holbrey, K.R. Seddon, J. Chem. Soc., Dalton Trans. (1999) 2133.

[84] W.L. Bao, Z.M. Wang, Y.X. Li, J. Org. Chem. 68 (2003) 591.

[85] J. Fraga-Dubreuil, M.H. Famelart, J.P. Bazureau, Org. Process Res. Dev. 6 (2002) 374.

[86] D.W. Armstrong, L.-K. Zhang, L. He, M.L. Gross, Anal. Chem. 73 (2001) 3679.

[87] J.L. Anthony, E.J. Maginn, J.F. Brennecke, J. Phys. Chem. B 105 (2001) 10942.

[88] A.R. Katritzky, J.R. Lomaka, R. Petrkhin, M. Karelson, A.E. Visser, R.D. Rogers, J. Chem. Inf. Comput. Sci. 42 (2002) 225.

[89] E.A. Turner, C.C. Pye, R.D. Singer, J. Phys. Chem. A 107 (2003) 2277.

[90] H.L. Ngo, K. LeCompte, L. Hargens, A.B. McEwen, Thermochim. Acta 357 (2000) 97.

[91] C.M. Forsyth, D.R. MacFarlane, J.J. Golding, J. Haung, J. Sun, M. Forsyth, Chem. Mater. 14 (2002) 2103.

[92] C.M. Gordon, J.D. Holbrey, A.R. Kennedy, K.R. Seddon, J. Mater. Chem. 8 (1998) 2627.

[93] H. Chen, D.C. Kwait, Z.S. Gonen, B.T. Weslowski, D.J. Abdallah, R.G. Weiss, Chem. Mater. 14 (2002) 4063.

[94] J.J.M. Ramos, C.A.M. Afonso, L.C. Branco, J. Therm. Anal. Calorim. 71 (2003) 659.

[95] A. Heintz, D.V. Kulikov, S.P. Verevkin, J. Chem. Thermodyn. 34 (2002) 1341.

[96] H. Ohno, M. Yoshizawa, Solid State Ionics 154 (2002) 303.

[97] J. Sun, D.R. MacFarlane, M. Forsyth, Electrochim. Acta 48 (2003) 1707.

[98] A.E. Visser, J.R. Holbrey, R.D. Rogers, J. Chem. Soc., Chem. Commun. (2001) 2484.

[99] Y.R. Mirzaei, B. Twamley, J.M. Shreeve, J. Org. Chem. 67 (2002) 9340.

[100] M. Hirao, H. Sugimoto, H. Ohno, J. Electrochem. Soc. 147 (2000) 4168.

[101] S. Carda-Broch, A. Berthod, D.W. Armstrong, Rapid Commun. Mass Spectrom. 17 (2003) 553.

[102] N.M.M. Mateus, L.C. Branco, N.M.T. Loureneo, C.A.M. Afonso, Green Chem. 5 (2003) 347.

[103] S. Lall, V. Behaj, D. Mancheno, R. Casiano, M. Thomas, A. Rikin, J. Gaillard, R. Raju, A. Scumpia, S. Castro, R. Engel, J.L. Cohen, Synthesis (2002) 1530.

[104] R. Engel, J.L. Cohen, S.I. Lall, Phosphorus Sulfur Silicon Relat. Elem. 177 (2002) 1441.

[105] M. Yoshizawa, W. Ogihara, H. Ohno, Polym. Adv. Technol. 13 (2002) 589.

[106] M. Deetlefs, K.R. Seddon, Green Chem. 5 (2003) 181.

[107] J.M. Leveque, J.L. Luche, C. Petrier, R. Roux, W. Bonrath, Green Chem. 4 (2002) 357.

[108] V.V. Namboodin, R.S. Varma, Org. Lett. 4 (2002) 3161.

[109] V.V. Namboodin, R.S. Varma, Tetrahedron Lett. 43 (2002) 5381.

[110] K.R. Seddon, A. Stark, M.J. Torres, Pure Appl. Chem. 72 (2000) 2275.

[111] P. Stepnowski, A. Muller, P. Behrend, J. Ranke, J. Hoffmann, B. Jastorff, J. Chromatogr. A 993 (2003) 173.

[112] J.D. Holbrey, K.R. Seddon, R. Wareing, Green Chem. 3 (2001) 33.

[113] V. Gallo, P. Mastrorilli, C.F. Nobile, G. Romanazzi, G.P. Suranna, J. Chem. Soc., Dalton Trans. (2002) 4342.

[114] L. Cammarata, S.G. Kazarian, P.A. Salter, T. Welton, Phys. Chem. Chem. Phys. 3 (2001) 5192.

[115] R.M. Lynden-Bell, N.A. Atamas, A. Vasilyuk, C.G. Hanke, Mol. Phys. 100 (2002) 3225.

[116] W.J. Criddle, J. Thomas, J. Anal. Appl. Pyrolysis 2 (1980) 361.

[117] S.J. Abraham, W.J. Criddle, J. Anal. Appl. Pyrolysis 9 (1985) 65.

[118] S.J. Abraham, W.J. Criddle, J. Anal. Appl. Pyrolysis 7 (1985) 337.

[119] H.S. Kim, Y.J. Kim, H. Lee, K.Y. Park, C. Lee, C.S. Chin, Angew. Chem. Int. Ed. 41 (2002) 4300.

[120] S.K. Poole, C.F. Poole, J. Chromatogr. 435 (1988) 17.

[121] P. Muller, Pure Appl. Chem. 66 (1994) 1077.

[122] C. Reichardt, Chem. Rev. 94 (1994) 409.

[123] C. Reichardt, Solvents and Solvent Effects in Organic Chemistry, VCH–Wiley, Weinheim, Germany, 1988.

[124] R.W. Taft, M.J. Kamlet, J. Am. Chem. Soc. 98 (1976) 2886.

[125] C. Reichardt, E. Harbusch-Gornert, Justus Liebigs Ann. Chem. (1983) 721.

[126] M.J. Muldoon, C.M. Gordon, I.R. Dunkin, J. Chem. Soc., Perkin Trans. 2 (2001) 433.

[127] K.A. Fletcher, I.A. Storey, A.E. Hendricks, S. Pandey, S. Pandey, Green Chem. 3 (2001) 210.

[128] S.N. Baker, G.A. Baker, F.V. Bright, Green Chem. 4 (2002) 165.

[129] K.A. Fletcher, S. Pandey, Appl. Spectrosc. 56 (2002) 1498.

[130] K.A. Fletcher, S. Pandey, Appl. Spectrosc. 56 (2002) 266.

[131] R.W. Taft, J.L.M. Abboud, M.J. Kamlet, M.H. Abraham, J. Solution Chem. 14 (1985) 153.

[132] A. de Juan, G. Fonrodona, E. Casassas, Trends Anal. Chem. 16 (1997) 52.

[133] M.J. Kamlet, J.L.M. Abboud, R.W. Taft, Prog. Phys. Org. Chem. 13 (1981) 485.

[134] M.J. Kamlet, J.L.M. Abboud, M.H. Abraham, R.W. Taft, J. Org. Chem. 48 (1983) 2877.

[135] J.F. Deye, T.A. Berger, A.G. Anderson, Anal. Chem. 62 (1990) 615.

[136] A.J. Carmichael, K.R. Seddon, J. Phys. Org. Chem. 13 (2000) 591.

[137] W. Linert, R.F. Jameson, A. Taha, J. Chem. Soc., Dalton Trans. (1993) 3181.

[138] D.S. Karpovich, G.J. Blanchard, J. Phys. Chem. 99 (1995) 3951.

[139] R. Waris, M.A. Rembert, D.M. Sellers, W.E. Acree, K.W. Street, C.F. Poole, P.H. Shetty, J.C. Fetzer, Appl. Spectrosc. 42 (1988) 1525.

[140] K.W. Street, W.E. Acree, Analyst 111 (1986) 1197.

[141] K.W. Street, W.E. Acree, C.F. Poole, P.H. Shetty, Analyst 113 (1988) 1869.

[142] K.W. Street, W.E. Acree, J.C. Fetzer, P.H. Shetty, C.F. Poole, Appl. Spectrosc. 43 (1989) 1149.

[143] S.N. Baker, G.A. Baker, M.A. Kane, F.V. Bright, J. Phys. Chem. B 105 (2001) 9663.

[144] R.J. Laub, R.L. Pecsok, Physicochemical Applications of Gas Chromatography, Wiley, New York, 1979.

[145] J.R. Conder, C.L. Young, Physicochemical Measurements by Gas Chromatography, Wiley, New York, 1979.

[146] C.F. Poole, The Essence of Chromatography, Elsevier, Amsterdam, 2003.

[147] C.F. Poole, S.K. Poole, J. Chromatogr. A 965 (2002) 263.

[148] M.H. Abraham, C.F. Poole, S.K. Poole, J. Chromatogr. A 842 (1999) 79.

[149] C.F. Poole, T.O. Kollie, S.K. Poole, Chromatographia 34 (1992) 281.

[150] B.R. Kersten, C.F. Poole, J. Chromatogr. 399 (1987) 1.

[151] S.K. Poole, T.O. Kollie, C.F. Poole, J. Chromatogr. A 664 (1994) 229.

[152] R.N. Nikolov, J. Chromatogr. 241 (1982) 237.

[153] S.K. Poole, C.F. Poole, J. Chromatogr. 500 (1990) 329.

[154] R.J. Laub, J.H. Purnell, P.S. Williams, M.W.P. Harbison, D.E. Martire, J. Chromatogr. 155 (1978) 233.

[155] E.F. Sanchez, J.A.G. Dominguez, J.G. Munoz, M.J. Molera, J. Chromatogr. 299 (1984) 151.

[156] K.G. Furton, C.F. Poole, J. Chromatogr. 399 (1987) 47.

[157] S.C. Dhanesar, C.F. Poole, Anal. Chem. 56 (1984) 2509.

[158] S.C. Dhanesar, M.E. Coddens, C.F. Poole, J. Chromatogr. 324 (1985) 415.

[159] S.C. Dhanesar, M.E. Coddens, C.F. Poole, J. Chromatogr. Sci. 23 (1985) 320.

[160] D.W. Armstrong, L. He, Y.-S. Liu, Anal. Chem. 71 (1999) 3873.

[161] S.C. Dhanesar, M.E. Coddens, C.F. Poole, J. Chromatogr. 349 (1985) 249.

[162] E.L. Arancibia, R.C. Castells, A.M. Nardillo, J. Chromatogr. 398 (1987) 21.

[163] B.R. Kersten, C.F. Poole, K.G. Furton, J. Chromatogr. 411 (1987) 43.

[164] B.R. Kersten, C.F. Poole, J. Chromatogr. 452 (1988) 191.

[165] J.A. Platts, B. Butina, M.H. Abraham, A. Hersey, J. Chem. Inf. Comput. Sci. 39 (1999) 835.

[166] M.H. Abraham, Chem. Soc. Rev. 22 (1993) 73.

[167] C.F. Poole, S.K. Poole, M.H. Abraham, J. Chromatogr. A 798 (1998) 207.

[168] M.D. Trone, M.G. Khaledi, J. Chromatogr. A 886 (2000) 245.

[169] S.K. Poole, C.F. Poole, J. Chromatogr. A 697 (1995) 415.

[170] S.D. Martin, C.F. Poole, M.H. Abraham, J. Chromatogr. A 805 (1998) 217.

[171] T.O. Kollie, C.F. Poole, Chromatographia 33 (1992) 551.

[172] S.K. Poole, C.F. Poole, Analyst 120 (1995) 289.

[173] Q. Li, C.F. Poole, Chromatographia 52 (2000) 639.

[174] M.H. Abraham, J. Andonian-Haftvan, C.M. Du, J.P. Osei-Owsusu, P. Sakellariou, W.J. Shuley, C.F. Poole, S.K. Poole, J. Chromatogr. A 688 (1994) 125.

[175] A. Heintz, D.V. Kulikov, S.P. Verevkin, J. Chem. Eng. Data 46 (2001) 1526.

[176] A. Heintz, D.V. Kulilov, S.P. Verevkin, J. Chem. Eng. Data 47 (2002) 894.

[177] M. Diedenhofen, F. Eckert, A. Klamt, J. Chem. Eng. Data 48 (2003) 475.

[178] T.M. Letcher, B. Soko, D. Ramjugernath, N. Deenadayalu, A. Nevines, P.K. Naicker, J. Chem. Eng. Data 48 (2003) 708.

[179] W. David, T.M. Letcher, D. Ramjugernath, J.D. Raal, J. Chem. Thermodyn. 35 (2003) 1335.

[180] J.L. Anthony, E.J. Maginn, J.F. Brennecke, J. Phys. Chem. B 106 (2002) 7315.

[181] P. Husson-Borg, V. Majer, M.F.C. Gomes, J. Chem. Eng. Data 48 (2003) 480.

[182] M. Krummen, P. Wasserscheid, J. Gmehling, J. Chem. Eng. Data 47 (2002) 1411.

[183] L.A. Blanchard, J.F. Brennecke, Ind. Eng. Chem. Res. 40 (2001) 287.
[184] A. Shariati, C.J. Peters, J. Supercrit. Fluids 25 (2003) 109.
[185] C.-T. Wu, K.N. Marsh, A.V. Deev, J.R. Boxall, J. Chem. Eng. Data 48 (2003) 486.
[186] A. Heintz, J.R. Lehmann, C. Wertz, J. Chem. Eng. Data 48 (2003) 472.
[187] R.P. Swatloski, A.E. Visser, W.M. Reichert, G.A. Broker, L.M. Farina, J.D. Holbrey, R.D. Rogers, J. Chem. Soc., Chem. Commun. (2001) 2070.
[188] V. Najdanovic-Visak, J.M.S.S. Esperanca, L.P.N. Rebelo, M. Nunes da Ponte, H.J.R. Guedes, K.R. Seddon, J. Szydlowski, Phys. Chem. Chem. Phys. 4 (2002) 1701.
[189] A. Berthod, S. Carda-Broch, J. Liq. Chromatogr. Relat. Technol. 26 (2003) 1493.
[190] T.M. Letcher, N. Deenadayalu, J. Chem. Thermodyn. 35 (2003) 67.
[191] J.G. Huddleston, H.D. Willauer, R.P. Swatloski, A.E. Visser, R.D. Rogers, J. Chem. Soc., Chem. Commun. (1998) 1765.
[192] A.E. Visser, R.P. Swatloski, R.D. Rogers, Green Chem. 2 (2000) 1.
[193] S.G. Zhang, Z.C. Zhang, Green Chem. 4 (2002) 376.
[194] G.T. Wei, Z.S. Yang, C.J. Chen, Anal. Chim. Acta 488 (2003) 183.
[195] P.H. Shetty, S.K. Poole, C.F. Poole, Anal. Chim. Acta 236 (1990) 51.
[196] M.H. Abraham, A.M. Zissimos, J.G. Huddleston, H.D. Willauer, R.D. Rogers, W.E. Acree, Ind. Eng. Chem. Res. 42 (2003) 413.
[197] A. Zissimos, M.H. Abraham, M.C. Barker, R.J. Box, K.Y. Tam, J. Chem. Soc., Perkin Trans. 2 (2002) 470.
[198] M. Cichna, P. Markl, J.F.K. Huber, J. Pharm. Biomed. Anal. 13 (1995) 339.
[199] J.P. Crombeen, S. Heemstra, J.C. Kraak, J. Chromatogr. 286 (1984) 119.
[200] J.P. Crombeen, S. Heemstra, J.C. Kraak, Chromatographia 19 (1985) 219.
[201] S.K. Poole, K.G. Furton, C.F. Poole, J. Chromatogr. Sci. 26 (1988) 67.
[202] A. Berthod, L. He, D.W. Armstrong, Chromatographia 53 (2001) 63.
[203] C.D. Tran, S.H.D. Lacerda, Anal. Chem. 74 (2002) 5337.
[204] L. He, W. Zhang, L. Zhao, X. Liu, S. Jiang, J. Chromatogr. A 1007 (2003) 39.
[205] L.C. Branco, J.G. Crespo, C.A.M. Afonso, Chem. Eur. J. 8 (2002) 3865.
[206] E.G. Yanes, S.R. Gratz, M.J. Baldwin, S.E. Robinson, A.M. Stalcup, Anal. Chem. 73 (2001) 3838.
[207] B. Cabovska, G.P. Kreishman, D.F. Wassell, A.M. Stalcup, J. Chromatogr. A 1007 (2003) 179.
[208] M. Vaher, M. Koel, M. Kaljurand, J. Chromatogr. A 979 (2002) 27.
[209] M. Vaher, M. Koel, M. Kalijurand, Chromatographia 53 (2001) 302.
[210] W. Qin, H. Wei, S.F.Y. Li, J. Chromatogr. A 985 (2003) 447.
[211] W. Qin, S.F.Y. Li, Analyst 128 (2003) 37.