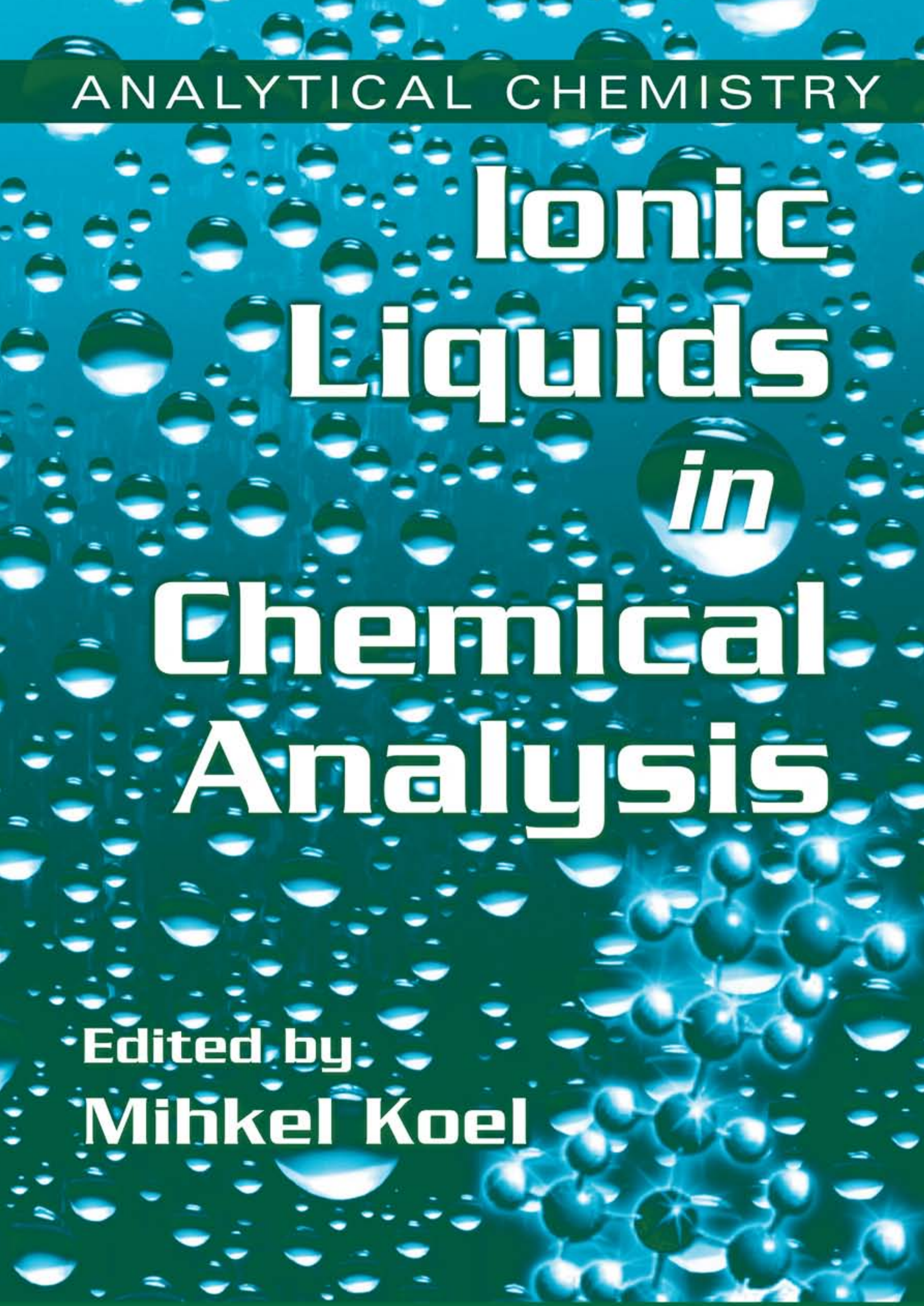
ANALYTICAL CHEMISTRY



Ionic Liquids in Chemical Analysis

Edited by
Mihkel Koel

CRC Press
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Ionic Liquids *in* Chemical Analysis

Analytical Chemistry Series

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Foreword

This excellent book is a well-timed event in a rapidly expanding area within chemistry and within the analytical/measurement community in chemistry. It comes at a time when there is growing pressure for many of us to become familiar with this *new* area and to speculate on the implications for our particular niche in chemical measurement science.

Much of the popular reference to ionic fluids seems to be focused on the *green* chemical use of these remarkable substances as more ecologically and environmentally acceptable solvents in analytical procedures. We are a long way from any evidence that every possible use of organic solvents in analytical procedures has an ionic fluid analog. Only time will tell.

I am led to reflect on my early ventures into the chemical literature of the late nineteenth century driven by curiosity and the need in those days of old to meet the foreign language requirements of the typical American doctoral program. One can find articles based purely on the discovery that, for example, acetone is a very useful solvent in organic synthesis! Recall, dear reader, that it took decades to adopt standards for what purity meant for many of the common organic solvents. As late as the 1970s, there was enough variance on the definition of purity that high-performance liquid chromatography methods, which were successful in one area of the world failed in others entirely on the basis of impurities in the components of the mobile phases used. Even pure methanol and pure acetonitrile were not readily available everywhere. My point is that before ionic fluid substitutes can be found for the use of compendial methods, there may be a good deal of work to be done.

Dense ionic fluids are not all that new if one examines the many applications of molten salt use in chemistry to date. A good deal of the work is in electrochemistry where the relatively high temperatures are less of a limitation but the relation between low-temperature molten salts and ionic fluids certainly exists. It would be wise neither to completely depend on nor to completely ignore all that has been learned with molten salts and molten salt chemistry. Some highly reactive, easily oxidized metals are readily purified in molten salt solvent systems without the problems with oxygen or the decomposition of water with release of hydrogen.

How will the microscopic properties of ionic fluids complicate the application of these remarkable substances to new kinds of analysis? If they are used for stationary phases (or mobile phases) in, for example, chromatography, it is likely that the familiar dominant factors in retention—volatility or solubility—will remain. Which of the unique properties of ionic fluids will have significant secondary effects on selectivity may be of concern. Will the *double layer* at the surface favor some sort of Gibbs isotherm with surface sorption competing with bulk dissolution? It is fine to speak of a dense ionic fluid as being electroneutral but how will that dense ionic atmosphere influence solubility for ionic species? Will mixed ionic fluids make analytical use of the common mechanistic organic strategy possible, where different solvents are used to favor by-product production, but, in the case of measurement, favor a more easily measured analyte? One could double the size of this book by speculating on what we will know 30 years hence. Only time will tell and thus there is a lot of work to be done.

Charles H. Lochmüller
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The support of Tallinn University of Technology must be acknowledged in preparation of this book, especially Chair of Analytical Chemistry Prof. Mihkel Kaljurand, whose constant interest and friendly comments helped very much in the development of this project.

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Editor

Mihkel Koel defended his dissertation (Candidate of Chemical Sciences) in analytical chemistry at Leningrad State University (now St Petersburg, Russia) in 1989. He undertook long-term scientific visits to Duke University (United States), Helsinki University (Finland), and USIS Fulbright Fellowship (6 months in Los Alamos National Laboratory, 1999).

Since 1990, he has been a senior research scientist in the Department of Analytical Chemistry in the Institute of Chemistry of Estonian Academy of Sciences. Since 2002 he has been affiliated with the Faculty of Science, Institute of Chemistry, and Chair of Analytical Chemistry at Tallinn University of Technology.

His interests have included such areas of analytical chemistry as separation science, supercritical fluid extraction, chromatography, thermal analysis, and mathematical analysis of the chemical data (chemometrics).

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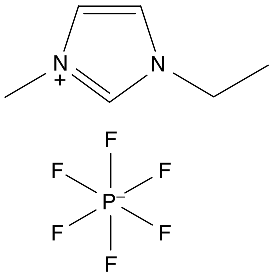
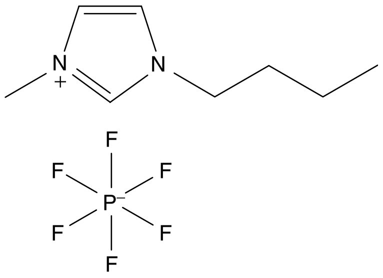
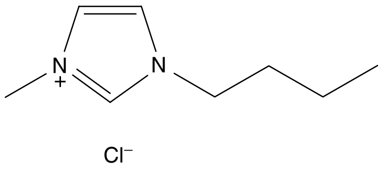
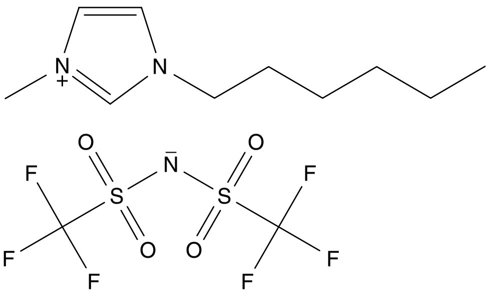
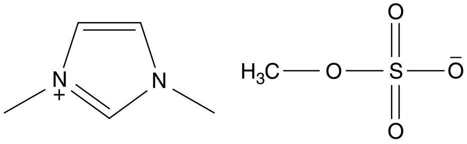
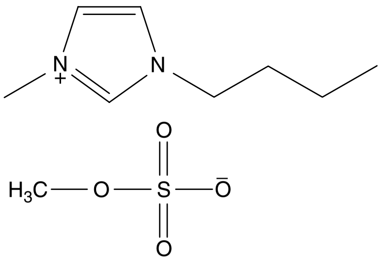
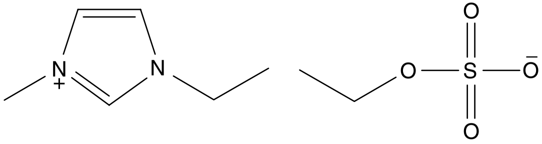
Common ionic liquids—structure, name, and abbreviation

Common ILs include ammonium, phosphonium, sulfonium, guanidinium, pyridinium, imidazolium, and pyrrolidinium cations. However, use of nomenclature vary among researchers. It is prefered to abbreviate throughout this book as $[C_nC_mC_zIm]$, $[C_npy]$, and $[C_nC_mpyr]$ for the alkylimidazolium, pyridinium, and pyrrolidinium cations, respectively, where Im stands for imidazolium, py for pyridinium, and pyr for pyrrolidinium. The number of carbons in the *N*-alkyl chains are expressed by n, m, and z.

The most common anions are Cl^-, Br^-, $[BF_4]^-$, and $[PF_6]^-$. For simplicity, trifluoromethanesulfonyl $[CF_3SO_2]^-$ anion is abbreviated as [TfO], *bis*(trifluo romethanesulfonyl)imide $[(CF_3SO_2)_2N]^-$ anion as $[Tf_2N]^-$ (Tf is a short-hand notation for triflate), and dicyanamide $[N(CN)_2]^-$ anion as [dca]. There are several examples of alkylsulfate anions, which we will abbreviate $[C_nSO_4]^-$, where n is the carbon number of alkyl chain.

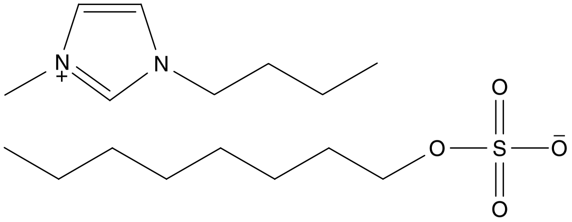
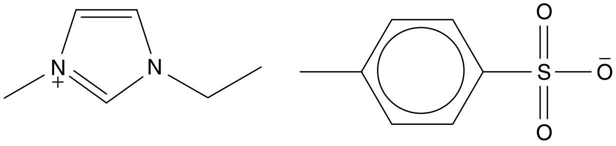
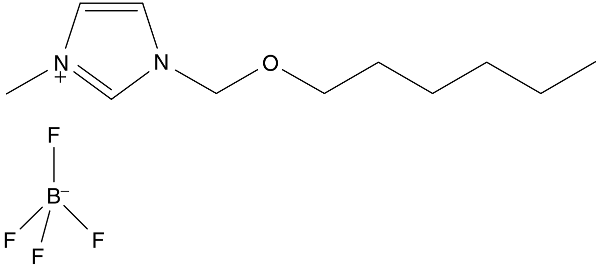
Some Examples of Names, Structural Formulas, and Abbreviations Used

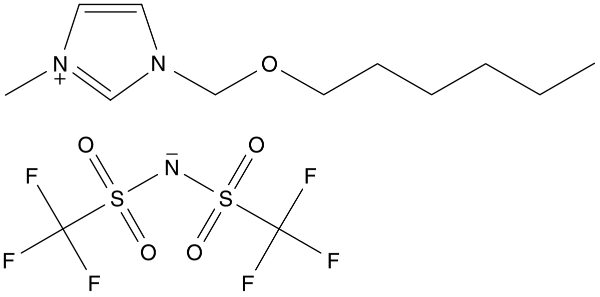
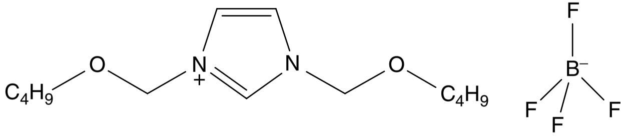
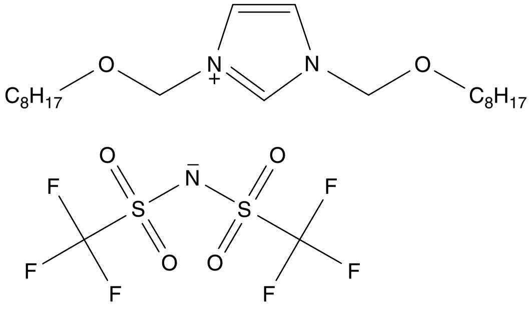
Ionic Liquid	Structural Formula	Abbreviation
1-Ethyl-3-methylimidazolium hexafluorophosphate		$[C_2C_1Im][PF_6]$
1-Butyl-3-methylimidazolium hexafluorophosphate		$[C_4C_1Im][PF_6]$
1-Butyl-3-methylimidazolium chloride		$[C_4C_1Im]Cl$

1-Hexyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide		$[C_6C_1Im][Tf_2N]$
1,3-Dimethylimidazolium methylsulfate		$[C_1C_1Im][C_1SO_4]$
1-Butyl-3-methylimidazolium methylsulfate		$[C_4C_1Im][C_1SO_4]$
1-Ethyl-3-methylimidazolium ethylsulfate		$[C_2C_1Im][C_2SO_4]$

(*continued*)

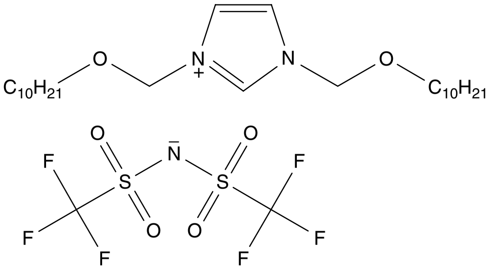
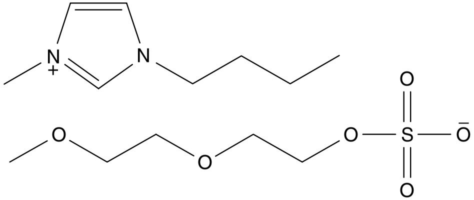
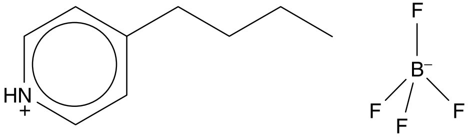
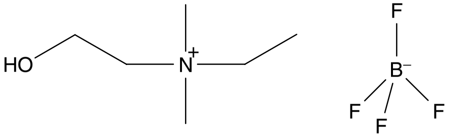
(Continued)

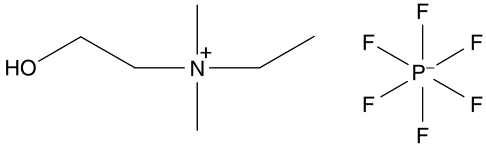
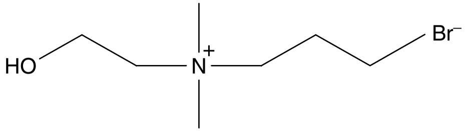
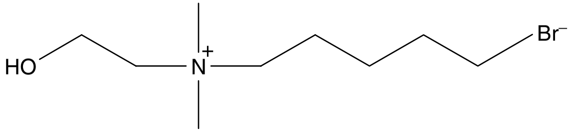
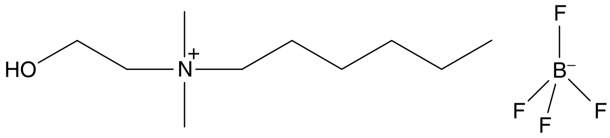
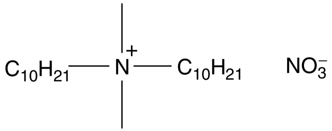
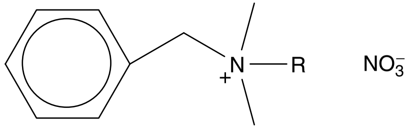
Ionic Liquid	Structural Formula	Abbreviation
1-Butyl-3-methylimidazolium octylsulfate		$[C_4C_1Im][C_8SO_4]$
1-Ethyl-3-methylimidazolium tosylate		$[C_2C_1Im][TOS]$
1-Hexyloxymethyl-3-methylimidazolium tetrafluoroborate		$[C_6H_{13}OCH_2\text{–}C_1Im][BF_4]$

1-Hexyloxymethyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide		$[C_6H_{13}OCH_2–C_1Im][Tf_2N]$
1,3-Dibutyloxymethylimidazolium tetrafluoroborate		$[(C_4H_9OCH_2)_2Im][BF_4]$
1,3-Dioctyloxymethylimidazolium *bis*(trifluoromethylsulfonyl)imide		$[(C_8H_{17}OCH_2)_2Im][Tf_2N]$

(*continued*)

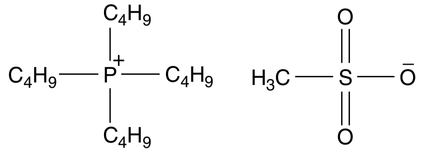
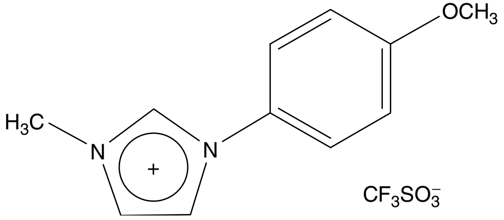
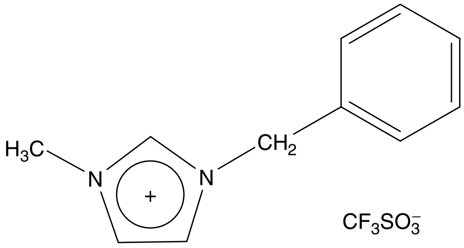
(Continued)

Ionic Liquid	Structural Formula	Abbreviation
1,3-Didecyloxymethylimidazolium *bis*(trifluoro-methylsulfonyl)imide		$[(C_{10}H_{21}OCH_2)_2Im][Tf_2N]$
1-Butyl-3-methylimidazolium 2-(2-methoxyethoxy)-ethysulfate		$[C_4C_1Im][MDEGSO_4]$
4-Butyl-pyridinium tetrafluoroborate		$[4\text{-}C_4py][BF_4]$
Ethyl-(2-hydroxyethyl)-dimethyl-ammonium tetrafluoroborate		$[(C_1)_2C_2\ HOC_2N][BF_4]$

Ethyl-(2-hydroxyethyl)-dimethyl-ammonium hexafluoroborate		$[(C_1)_2C_2\,HOC_2N][PF_6]$
Butyl-(2-hydroxyethyl)-dimethyl-ammonium bromide		$[(C_1)_2C_4\,HOC_2N]Br$
Hexyl(2-hydroxyethyl)dimethyl-ammonium bromide		$[(C_1)_2C_6\,HOC_2N]Br$
Hexyl(2-hydroxyethyl)dimethyl-ammonium tetrafluoroborate		$[(C_1)_2C_6\,HOC_2N][BF_4]$
Didecyldimethylammonium nitrate		$[(C_{10})_2(C_1)_2N][NO_3]$
(Benzyl)dimethylalkylammonium nitrate		$[Be(C_1)_2C_nN][NO_3]$

(*continued*)

(Continued)

Ionic Liquid	Structural Formula	Abbreviation
Tetrabutylphosphonium methanesulfonate	 C_4H_9 C_4H_9 P + C_4H_9 C_4H_9 H_3C S O O $\bar{O}$	$[(C_4)_4P][C_1SO_3]$
1-(4-Methoxyphenyl)imidazolium trifluoromethanesulfonate	 OCH_3 H_3C N + N $CF_3SO_3^-$	$[CH_3O–PhC_1Im][TfO]$
1-Benzyl-3-methylimidazolium trifluoromethanesulfonate	 H_3C N + N CH_2 $CF_3SO_3^-$	$[BeC_1Im][TfO]$

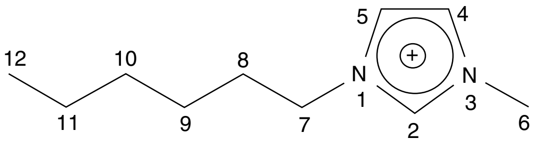
Note: The less common ionic liquids not seen in this list are described in the text.

List of abbreviations

2,5-Dihydroxybenzoic acid	DHB
α-Cyano-4-hydroxycinnamic acid	HCCA
β-Cyclodextrin	β-CD or HP-β-CD
Acetonitrile	ACN
Aqueous two-phase liquid system	ATPS
Atmospheric pressure chemical ionization	APCI
Background electrolyte	BGE
Calcium binding proteins	CALB
Calix[4]arene-*bis*(*tert*-octylbenzo-crown-6)	BOBCalixC6
Capillary electrochromatography	CEC
Capillary electrophoresis	CE
Capillary gel electrophoresis	CGE
Capillary zone electrophoresis	CZE
Charge transfer	CT
Chiral stationary phases	CSP
Circular dichroism	CD
Collision-induced decomposition	CID
Conductor-like screening model for real solvents	COSMO-RS
Countercurrent chromatography	CCC
Critical micelle concentration	CMC
Crown ether dicyclohexano-15-crown-5	DC15C5
Crown ether dicyclohexano-18-crown-6	DC18C6
Cytochrome *c*	Cyt-c
Dibenzothiophene	DBT
Differential scanning calorimetry	DSC
Diffusion-ordered spectroscopy	DOSY
Dimethylated β-cyclodextrin	β-DM
Dimethyldinonylammonium bromide	DMDNAB
Dimethylsulfoxide	DMSO
Dioctylsulfosuccinate	docSS
Diode array detector	DAD
Double-stranded DNA	dsDNA
Dual spin probe	DSP
Electrochemiluminescence	ECL

Electron impact	EI
Electroosmotic flow	EOF
Electrospray ionization	ESI
Empirical potential structure refinement	EPSR
Ethanol	EtOH
Ethyl *tert*-butyl ether	ETBE
Extended x-ray absorption fine structure	EXAFS
Fast atom bombardment	FAB
Flory–Benson–Treszczanowicz model	FBT
Fourier transform infared	FTIR
Fourier transform MS	FTMS
Gas chromatography	GC
Gas–liquid chromatography	GLC
Group contribution method of predicting activity coefficients	UNIFAC
Heteronuclear multiple-quantum correlation	HMQC
High-pressure liquid chromatography	HPLC
High-resolution magic angle spinning NMR	HR-MAS NMR
Indium tin oxide	ITO
Inductively coupled plasma	ICP
Ionic liquid	IL
Ionic liquid matrices	ILM
Laser desorption/ionization	LDI
Linear solvation free energy relationship	LSFER
Liquid chromatography	LC
Liquid phase microextraction	LPME
Liquid–liquid equilibrium	LLE
Mass spectrometry	MS
Matrix-assisted laser desorption/ionization	MALDI
Mercury film electrode	MFE
Methanol	MeOH
Micellar electrokinetic capillary chromatography	MEKC
Multiple linear regression analysis	MLRA
Near infrared	NIR
Nicotinamide adenine dinucleotide	NADH
N-methyl-2-pyrrolidinone	NMP
Nonaqueous capillary electrophoresis	NACE
Nuclear magnetic resonance	NMR
Nuclear Overhauser effect	NOE
Nuclear Overhauser effect spectroscopy	NOESY
Peak asymmetry factor	PAF
Permethylated β-cyclodextrin	β-PM
Phosphorous oxychloride	$POCl_3$
Phosphorous trichloride	PCl_3
Polydimethylsiloxane	PDMS

Poly(ethylene oxide)	PEO
Polyethylene glycol	PEG
Polyoxyethylene-100-stearylether	Brij 700
Polyoxyethylene-23-laurylether	Brij 35
Polytetrafluoroethylene	PTFE
Quality assessment and quality control	QA and QC
Radial distribution functions	RDFs
Reversed phase LC	RPLC
Rotating frame Overhauser effect spectroscopy	ROESY
Secondary ion mass spectrometry	SIMS
Self-assembled monolayer	SAM
Sinapinic acid	SA
Sodium dodecylsulfate	SDS
Solid phase microextraction	SPME
Solid–liquid phase equilibria	SLE
Static structure factor	S(Q)
Surface-confined ionic liquids	SCIL
Surface-enhanced Raman scattering	SERS
Task-specific ionic liquids	TSILs
Tetradecyltrimethylammonium bromide	TTAB
Tetrahydrofuran	THF
Thermogravimietric analysis	TGA
Time of flight	ToF
Total correlation spectroscopy	TOCSY
Ultraviolet–visible	UV–Vis
Upper critical solution temperature	UCST
Vapor–liquid equilibrium	VLE
Vogel–Tammann–Fulcher equation	VTF
Wall-coated open tubular	WCOT
X-ray photoelectron spectroscopy	XPS



Scheme 1 Numbering scheme on the 1-hexyl-3-methylimidazolium cation, $[C_6C_1Im]^+$, showing the three ring protons H2, H4, and H5.

Introduction

> In sale et sole existunt omnia
> (Life depends on salts and sunshine)

The development of analytical chemistry continues at a steady rate and every new discovery in chemistry, physics, molecular biology, and materials science finds a place in analytical chemistry as well. The place can either be a new tool for existing measurement challenges or a new challenge to develop stable and reliable methods. Two examples are the advent of nanostructure materials and alternative solvents, both of which saw their main development in the past decade. Nanostructural materials pose a new scale of measurement challenge in size and number. New solvents with their environmentally benign properties offer a possibility for wasteless operation.

What happens when salt is melting and can this melt be used in chemical processes? This question has a long history, and usually organic chemists are not interested in finding solutions because of high temperatures related to melts. It was true up to the end of the twentieth century when room temperature molten salts became available. Their difference from common liquids is emphasized by calling them *ionic liquids* (ILs). The term is used loosely to describe organic salts with their melting point close to or below room temperature. ILs define a *class* of fluids rather than a small group of individual examples. And this was a successful choice of the name. They form liquids composed in the majority of ions. This gives these materials the potential to behave very differently in contrast to conventional molecular liquids when used as solvents. ILs promise entirely new ways to do solution chemistry, which could improve both measurement and the impact of the amount of waste into the environment.

Historically, the following four main steps must be mentioned: the preparation of ethylammonium nitrate $[C_2H_5NH_3][NO_3]$ by Paul Walden in 1914 is recognized by many as the first IL. This compound has a melting point of 12°C but owing to its high reactivity has not really found a use [1]. This was the outcome of his studies of conductivity and electrical properties of salt solutions, especially nonaqueous solutions of organic salts. He conducted very systematic studies with different solvents and salts, and his special interest was in ammonium salts. But Walden himself pointed on the work of C. Schall on alkyl-quinoline triiodide's as low-melting organic salts [2], which are nowadays under the study as tailor-made ILs [3].

At that time, Paul Walden (1863–1957) (because of his Latvian origin, he is known in Latvia as Pauls Valdens) was working in Riga Polytechnicum. Later, Riga Polytechnicum was restructured and became an official university of Russian Empire—Riga Polytechnic Institute. In 1910, Walden became a member of the Russian Academy of Science. Between 1911 and 1915 in St Petersburg, Walden was head of the Laboratory of Chemistry at the Academy of Science. Later, he joined Riga Polytechnic Institute again, but during World War I, the Institute was evacuated to Moscow where Walden worked until his return to Riga in 1918. Although Latvia had gained independence, at that time free and international contacts were not supported, and Walden left for Germany and served as Head of the Chemistry Department of the University of Rostock from 1919 to 1934. Paul Walden made a series of specific discoveries in chemistry (e.g., *Walden Inversion*) and can be regarded as the founder of two new scientific fields—dynamic stereochemistry and the electrochemistry of nonaqueous solutions.

The main consensus seems to be that the first major studies of room temperature molten salts were made in the 1940s by a group led by Frank Hurley and Tom Weir at Rice University. When they mixed and gently warmed powdered pyridinium halides with aluminum chloride, the powders reacted, giving a clear, colorless liquid [4–7]. These mixtures were meant to be used in electrochemistry, particularly in electroplating with aluminum.

The third step was the introduction of alkylimidazolium salts in the early 1980s [8]. It was the discovery of 1-ethyl-3-methylimidazolium-based chloroaluminate ILs in 1982 that accelerated activities in the area of room temperature ILs (RTILs). The named salt is one of the most widely studied room temperature melt systems, which is liquid at room temperature for compositions between 33 and 67 mol% $AlCl_3$. The exciting property of halogenoaluminate ILs is their ability for acid–base chemistry, which can be varied by controlling the molar ratio of the two components. This kind of tuning makes these ILs attractive as nonaqueous reaction media. Aluminum chloride, however, reacts readily with water, which has limited the use of these types of ILs to the electrodeposition of metals and some synthetic reactions requiring very strong Lewis acid catalysts.

Almost that time, in the 1980s, the term *ionic liquid* became more popular to describe organic salts that melt below ~100°C and have an appreciable liquid range.

The fourth step is related to the search for air- and water-stable ILs, which followed 10 years later, and this gave a real push for further developments in this area. Air- and water-stable molten salts can be obtained using the weakly complexing anion in the imidazolium compound [9].

With these studies, the alkylimidazolium-based salts became almost synonyms of ILs. Possibly, the most widely studied one is 1-butyl-3-methylimidazolium hexafluorophosphate, which is liquid at room temperature and melts at −8°C. This particular IL has been studied for a wide range of applications.

An excellent short history of ILs, which covers the crucial moments of this area up to 1994, is presented by eyewitness to and participant in crucial developments, Professor John S. Wilkes [10].

ILs have proved to be as media not only for potentially *green* synthesis, but also for novel applications in the analysis, where the unique properties of these liquid materials provide new options based on different chemical and physical properties. ILs can be applied not only in the existing methods where it is always needed to improve sensitivity and selectivity of the analysis, but their different behavior and properties can offer original solutions in chemical analysis; and the search for new applications of ILs is growing in every area of chemistry including analytical chemistry.

However, introduction of the dimension of green chemistry into the assessment of analytical methods should be a natural trend of development in chemistry and it should coincide with its general policy. Some of the principles of green chemistry, such as prevention of waste generation, safer solvents and auxiliaries, design for energy efficiency, safer chemistry to minimize the potential of chemical accidents, and the development of instrumental methods are directly related to analytical chemistry. Analytical methods are developing fast, whereas concern about the safety of environment, water, and food is a strong driving force. Also, the public needs confirmation that chemical products and processes are safe.

Several reviews have been published about ILs and analytical chemistry, fortunately now we have main players in this field in one place who kindly agreed to provide their contributions. This book is an attempt to collect experience and knowledge about the use of ILs in different areas of analytical chemistry such as separation science, spectroscopy, and mass spectrometry that could lead others to new ideas and discoveries. In addition, there are chapters providing information of studies on determination of physicochemical properties, thermophysical properties and activity coefficients, phase equilibrium with other liquids, and discussion about modeling, which are essential to know beforehand, also for wider applications in analytical chemistry.

There are very promising examples of the use of these unique materials in the primary literature. ILs have good solvating properties together with broad spectral transparency, making them suitable solvents for spectroscopic measurements. It was tried to cover interest in different extraction techniques also, starting with separation of gases and ending with metals. It has been demonstrated that task-specific ILs (TSILs) have advantages compared to common solvents used as separation media in the liquid–liquid extraction process achieving both high efficiency and selectivity of separation. The main advantage of ILs for other applications in analytical chemistry lies in their low volatility, which makes ILs useful as solvents for working in both high temperature (GC stationary phases) and high vacuum (MALDI matrixes) environments. The reader will find changes in style and emphasis in different chapters that have been prepared by different authors; hopefully this variety is the strength of this book.

Using an IL as a solvent or an electrolyte medium, it is possible to achieve a broader range of operational temperatures and conditions, relative to other conventional electrolytic media, and make them promising materials in various electrochemical devices for analytical purposes, such as sensors and electrochromic windows also. However, this book is not intended to give a detailed coverage of analytical electrochemistry with ILs. To justify this, we use the words of Prof. Keith Johnson, University of Regina, Canada: "There is a vast literature on electrochemistry of ILs, both the recent organic and semiorganic salts and the inorganic 'molten' salts. This consists of papers in which the liquids are characterized by their electrochemistry or the properties of solutes in them are studied electrochemically. That does indeed give a pool of information on electrochemistry in these systems just as is available for aqueous or organic solutions (see Ohno's book [11] or Baizer's book [12] for the latter). However, if one has a problem of determining X in Y, treating the sample with an ionic system may be a means to making a solution of X, but electroanalysis of said solution to measure X may not be straightforward. It appears not to have been tried and would likely be prohibitively expensive through IL consumption. The picture may change in a few years but at present there is little to say—certainly not enough for a book chapter."

The approach in this book will be that of a tutorial providing an aid to the novice to enter the area that will include both new and senior scientists. Therefore, it is not expected to give a complete coverage of the literature in the area. Also time sets the limit and we had to stop on the middle of 2007. We do not expect that ILs will solve every problem in chemistry (in our case analytical chemistry), but our hope is to help find a proper area where the use of these materials could be the most advantageous. Thus, for ILs the future is bright and the future has to be green.

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chapter one

General review of ionic liquids and their properties

Urszula Domańska

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1.1 Introduction

Ionic liquids (ILs) can be composed from a large number of cations and anions, with an estimated number of possible ILs on order 10^{18}, which makes this class of compounds as one of the largest known in chemistry. Knowledge of the physical properties of ILs and the phase behavior with gases, liquids, and solids (including inorganic salts) is important for evaluating and selecting ILs for each application as well as process design. ILs have recently become very popular as potential solvents for industrial applications in many different disciplines of science and environment. Enormous progress was made during the recent 10 years to synthesize new low-melting ILs that can be handled under ambient conditions, and nowadays more than 350 ILs are already commercially available. Although the main interest is still focused on the synthesis in room temperature, IL as solvent/catalyst, on electrochemistry, physical chemistry in ILs, various aspects of thermodynamics, and ILs in analytical chemistry are discussed in this chapter. The focus is placed on air- and water-stable ILs as they will presumably dominate various fields of chemistry in the future. Indeed, because each IL has its own unique properties, it should be possible to design a compound, a solvent, an additive, nanostructure particles, sensors, gels, or mixtures to suite particular applications.

Relevant literature available up to February 2007 has been covered. The presentation is restricted to systems which seem to have the best prospects for successful use in different fields of chemistry and chemical engineering.

International organizations, for example, IUPAC Thermodynamics, started to collect the physical–chemical and thermodynamic properties of ILs about 10 years ago. Now, for the first time we can find massive data in two data banks: Dortmund Data Bank, Germany [1] and NIST Boulder Colorado, USA [2].

It is generally known that the examined properties and phase behavior of ILs vary on cation and anion structures changing. Some typical trends will be presented in this chapter on the basis of the structural effect on the interactions between counterpart ions (see, for example Ref. 3, the spoon-shaped structure of the unit cell of the 1-dodecyl-3-methylimidazolium hexafluorophosphate, $[C_{12}C_1Im][PF_6]$), and between the IL and the solvent, or the coexisting compound. The structure of IL and its interaction with the environment is extremely important in applications in analytical chemistry [4].

This chapter reviews developments in physical–chemical properties, thermophysical properties, phase equilibria, activity coefficients, modeling, and electrochemistry.

1.2 *Effect of the structure on physical–chemical properties*

The physical–chemical properties of ILs depend on the nature and size of both their cation and anion constituents. Their application in science and industries is merited because ILs have some unique properties, such as a negligible vapor pressure, good thermal stability, tunable viscosity and miscibility with water, inorganic and organic substances, a wide electrochemical window, high conductivity, high heat capacity and solvents available to control reactions. Despite their wide range of polarity and hydrogen-bonding ability, these new solvents are liquid from 180 K (glass transition) to 600 K. Possible choices of cation and anion that will result in the formation of ILs are numerous. The most popular five different well-known classes of ILs are as follows: imidazolium, pyridinium, pyrrolidinium quaternary ammonium, and tetra alkylphosphonium ILs. Of these, the most popular in experimental laboratory work worldwide are undoubtedly 1,3-dialkylimidazolium salts, primarily due to the attractive and easy-tailored physical properties. To do this, however, it is necessary to assume that ILs are the substances of which the local structural (i.e., electronic and steric) features may be correlated with their physical–chemical properties. The effect of the cation and anion structures has been studied in detail. The influence on physical–chemical properties and phase behavior is the subject of discussion in this chapter.

From early research it is known that ILs are hydrogen-bonded substances with strong interionic interactions. For example, the isomorphous crystals of 1-ethyl-3-methylimidazole iodide and bromide structures consist of layers of anions and cations interconnected by an extended network of hydrogen bonds. Each cation is hydrogen-bonded to three anions and each anion is hydrogen-bonded to three cations [5]. On the other hand, 1-ethyl-3-methylimidazolium chloride has a more complicated crystallographic structure—chloride anion is hydrogen-bonded to the three cations, but to different ring protons than iodide and bromide salts. Focusing on the other anions, there is a clear anion effect seen in the properties with special place for *bis*(trifluoromethylsulfony)imide, $[Tf_2N]^-$ ion, which appears not to fit in the simple trend, as this anion becomes more basic, the hydrogen bond donor ability of the IL decreases. Usually, there is an important Coulombic contribution to the hydrogen bonds formed between the IL and the other solvents especially for $[Tf_2N]^-$ and $[NO_3]^-$ anions [6]. Interactions between two molecular solvents are usually described by their polarity, as expressed through their dielectric constants. Since this scale is unable to provide adequate correlations with many experimental data with ILs, the hydrogen-bond acidity, hydrogen-bond basicity and dipolarity and polarizability effects have mainly been used. Changing the cation or anion, their solvent properties can differ considerably from one another as well as from traditional molecular solvents. Two different ILs that have essentially identical *polarity* ratings or descriptors can produce very different results when used as solvents for organic reactions, gas–liquid chromatography (GLC), or extraction. ILs with additional functional groups are capable of having additional interactions with other solvents or dissolved molecules. By demonstrating their structure and diversity of functionality, they are capable of most types of interactions as dispersive, π–π, n–π, hydrogen bonding, dipolar, and ionic/charge–charge interactions already mentioned. In every solution, there can be a number of different (in terms of type and strength) and often simultaneous solute–solvent interactions. Several approaches have been proposed that allow one to examine and categorize different IL–molecular solvent interactions. The Rohrschneider–McReynolds constants were originally developed to characterize liquid stationary phases for gas chromatography on the basis of several different interaction parameters [7]. The solvation parameter model developed by Abraham has been used to characterize either liquid- or gas-phase interactions between solute molecules and liquid phases [8–10]. The classification of the 17 ILs based on dipolarity and hydrogen-bond basicity characteristics has been presented to provide a model that can be used to pick ILs for specific organic reactions, liquid extractions, or GLC stationary phases [11].

The structural factors of the cation are focused on symmetry, polarity (charge density), number of carbon atoms in the alkane substituent and its flexibility, the rotational symmetry of the head ring, the cyclic and branched structures, and the functional tail group. Similar structural factors have an influence on the properties of anions, including charge delocalization either by a large volume of the central atom, or by the presence of the perfluoroalkyl chain. It was recently very punctiliously discussed by Hu and Xu [12], and also the discussion on many other ILs, including pyrazinium, piperazinium, and chiral ILs, has been presented.

Chemical structures, names, and abbreviations of modern typical ILs, most of which will be discussed in this chapter, are listed in Table 1 of the Introduction.

The structure of the extremely popular anion $[Tf_2N]^-$ is specified—the charge from the central nitrogen is delocalized onto the neighboring sulfur atoms, but not to any great extent onto the four sulfonyl oxygen atoms. Thus, the delocalized charge is confined to the molecule and shielded by the oxygens and terminal $-CF_3$ groups from Coulombic interactions with neighboring cations [13]. The cations or anions containing oxygen, such as alkoxy groups, for example $[C_6H_{13}OCH_2–C_1Im]^+$ or $[MDEGSO_4]^-$, tend to have specific interactions due to hydrogen bonding, or the dipole–dipole interactions. The acidic C(2)-H group of the imidazolium ring is bonded to a carbon located between two electronegative nitrogen atoms and contrary to ammonium, phosphonium, and sulfonium, ILs could engage in H-bonding. C(2)-H has greater ability to hydrogen bonding than the D(4), or C(5)-H groups, proved by the phase equilibria measurements and the interaction with alcohols [14], spectroscopic nuclear magnetic resonance (NMR) measurements, and *ab initio* calculations [15–17]. The H-bonding ability of the anion strongly depends, on its effective charge density and its symmetry.

1.3 Densities, viscosities, and transport properties

The effect of the cation/anion structure on density was perfectly discussed for more than 300 ILs in a recent publication [12]. ILs are mostly denser than water with values ranging from 1 for typical ILs to 2.3 g cm^{-3} for fluorinated ILs. For example, the densities of three salts are: $[C_8C_1Im][BF_4]$ 1.08 g cm^{-3} or $[C_{10}C_1Im][BF_4]$ 1.04 g cm^{-3}, whilst trifluoromethylethylpyridazinium *bis*(trifluoromethylsulfonyl)imide, 2.13 g cm^{-3} at $T = 298.15$ K [18,19]. Density depends strongly on the size of the ring in the cation, on the length of the alkyl chain in the cation, on the symmetry of ions and on the interaction forces between the cation and the anion. The ILs with aromatic head ring, in general, present greater densities than pyridinium head ring ILs and than do imidazolium ring ILs. Density increases with increasing symmetry of their cations. The increases of an alkyl chain diminish the densities in a systematic manner (sometimes only slightly, as was shown above) [12,20]. ILs with functional groups reveal higher densities than those of alkyl chains. The densities of ILs based on 1,3-dialkylimidazolium cations increase for typical anions in the order: $[Cl]^- < [BF_4]^- < [C_2SO_4]^- < [PF_6]^- < [Tf_2N]^-$. Very popular in many recent studies, especially in the liquid–liquid extraction research, $[C_6C_1Im][Tf_2N]$ displayed density equal to 1.372 g cm^{-3} at $T = 298.15$ K [12]. For ammonium salts, an increase in an alkyl chain at cation increases densities. The influence of popular anions and cations of imidazolium salts is presented in Figure 1.1.

It is clearly shown that salts with $[Tf_2N]^-$ anion have higher density than salts with $[PF_6]^-$ anion. The influence of the alkyl chain on the density of specific alkoxy- and acetoxy-ammonium salts is shown in Figure 1.2.

Densities are higher for the alkoxymethyl(2-hydroxyethyl)-dimethylammonium salts than for (2-acetoxyethyl)alkoxymethyl-dimethylammonium salts [21]. The increases of the alkyl chain at the cation from ethyl- to dodecyl- decrease the density from 1.45 to 1.21 g cm^{-3}. The densities of imidazolium salts with popular cation $[C_2C_1Im]^+$ are presented in Table 1.1.

It is easy to notice that the lowest value of density is with dicyanamide anion, $[dca]^-$, and the highest with the *bis*(trifluoromethylsulfonyl)imide anion, $[Tf_2N]^-$.

There is little data available covering on density as a function of pressure and temperature. Typical imidazolium salts, $[C_4C_1Im][PF_6]$, $[C_4C_1Im][BF_4]$, $[C_4C_1Im][Tf_2N]$, $[C_6C_1Im][Tf_2N]$, and $[C_8C_1Im][BF_4]$, as well as $[C_8C_1Im][PF_6]$, were measured from 298 to 333/343 K and up to 60, or 200 MPa [28–30]. Recently, the densities of phosphonium salts (trihexyltetradecylphosphonium

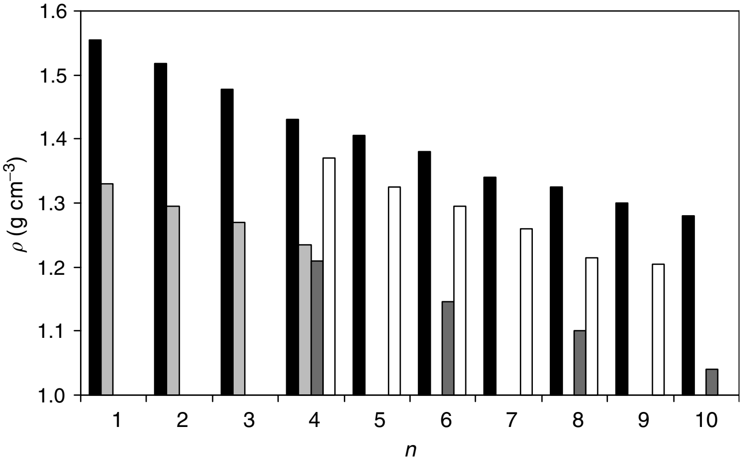

Figure 1.1 The influence of cation and anion on the density of imidazolium $[C_nC_1Im][X]$ ionic liquids at $T = 298.15$ K, where $n = 1$–10 and anions $[X]^-$ are $[Tf_2N]^-$ (black), $[AlCl_4]^-$ (light grey), $[BF_4]^-$ (dark grey), and $[PF_6]^-$ (white).

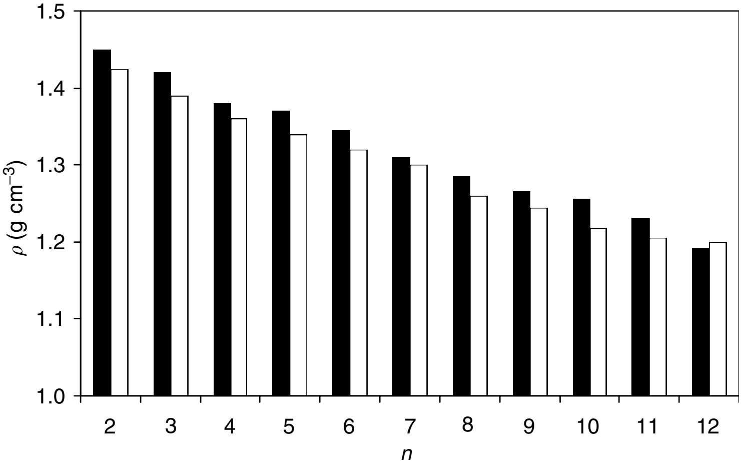

Figure 1.2 The influence of anion on the density of ammonium ionic liquids with alkoxy and acetoxy cations and $[Tf_2N]^-$ anion at $T = 298.15$ K: alkoxymethyl(2-hydroxyethyl)-dimethyl cation (black) and (2-acetoxyethyl)alkoxymethyl-dimethyl cation (white). (Adapted from Pernak, J., Chwała, P., and Syguda, A., *Polish. J. Chem.*, 78, 539, 2004.)

Table 1.1 Densities, ρ, at 298.15 K of Several Ionic Liquids with $[C_2C_1Im]^+$ Cation

Anion	ρ (g cm^{-3})	Reference
$[BF_4]^-$	1.240	22
	1.279	23
	1.280	24
$[Tf_2N]^-$	1.520[a]	25
	1.518	23
$[CF_3SO_3]^-$	1.390[a]	25
$[CF_3CO_2]^-$	1.390	26
	1.285[a]	25
$[C_2SO_4]^-$	1.236	Our value
$[dca]^-$	1.060	27

[a] At $T = 295.15$ K.

chloride, or acetate, or *bis*(trifluoromethylsulfonyl)imide) at 298–333 K and up to 65 MPa were published [31]. The densities of these ILs are significantly lower than that of commonly used imidazolium-based ILs. With an increasing pressure the density increases.

Transport properties play an important role in chemical reactions, electrochemistry, and liquid–liquid extraction. This concerns mainly the viscosity of ILs and their solutions with molecular solvents. Viscosity of ILs, typically at the level of 10–500 cP at room temperature, is much higher than that characteristic of water ($\eta(H_2O) = 0.89$ cP at 298.15 K) and aqueous solutions. The high dynamic viscosity (viscosity coefficient) of ILs causes difficulties

Table 1.2 Viscosity, η, at 298.15 K of Several Ionic Liquids with $[C_4C_1Im]^+$ Cation

Anion	η (cP)	Reference
$[I]^-$	963	37
$[NO_3]^-$	266	38
$[BF_4]^-$	233[a]	32
$[PF_6]^-$	312[a]	32
$[NbF_6]^{-b}$	95	39
$[CF_3SO_3]^-$	90[c]	32
$[CF_3CO_2]^-$	73[c]	32
$[Tf_2N]^-$	52[c]	32

[a] At T = 303.15 K.

[b] Hexafluoroniobate anion.

[c] At T = 293.15 K.

in practice. It affects the diffusion of solutes and practical issues, such as stirring and pumping. Data of viscosity at different temperatures were published by many authors [12,32–36]. The influence of the anion for a few salts with the $[C_4C_1Im]^+$ cation is presented in Table 1.2.

The viscosity of ILs is determined by van der Waals forces and hydrogen-bonded structures. Electrostatic forces and the shift of charge at the anion may also play an important role. For the same $[C_4C_1Im]^+$ cation, the viscosities for typical anions decrease in the order: $[I]^- > [PF_6]^- > [BF_4]^- > [TfO]^- > [CF_3CO_2]^- > [Tf_2N]^-$. For a series of 1-alkyl-3-methylimidazolium cations, increasing the alkyl chain length from butyl to octyl increases the hydrophobicity and the viscosity of the IL (for $[PF_6]^-$ and $[BF_4]^-$anions), whereas densities and surface tension values decrease. This is due to stronger van der Waals forces between cations, leading to an increase in the energy required for molecular motion [40]. It is expected that the replacement of the alkyl chain by a hydroxyl functional group would increase the viscosity by increasing the H-bonding. Pernak et al. [21] found that for alkyl chain lengths from 2 to 12 on alkoxymethyl(2-hydroxymethyl)dimethylammonium, (A), or (2-acetoxyethyl)-alkoxymethyldimethyl-ammonium, (B), salts with $[Tf_2N]^-$ anion, the viscosity monotonously increases (75–225 cP for A and 160–290 cP for B). The same effect was observed for the 1-[(1*R*,2*S*,5*R*)-(-)-menthoxymethyl]-3-alkylimidazolium *bis*(trifluoromethylsulfonyl)imides [41]; and new, chiral ammonium-based ILs containing the same (1*R*,2*S*,5*R*)-(-)-menthyl group and $[Tf_2N]^-$ anion [42]. Unfortunately, the values of viscosity of chiral ammonium-based ILs, 710–880 cP (303.15 K), as well as chiral pyridinium-based ILs, 550–1003 cP (323.15 K), were very high [42,43].

Viscosity temperature dependence in ILs is more complicated than in most molecular solvents, because most of them do not follow the typical Arrhenius behavior. Most temperature studies fit the viscosity values into the Vogel–Tammann–Fulcher (VTF) equation, which adds an additional adjustable parameter (glass transition temperature) to the exponential term.

In general, all ILs show a significant decrease in viscosity as the temperature increases. A systematic study of a possible description covering ILs by the Arrhenius or VTF equations was made by Okoturo and Van der Noot [44].

The viscosity decreases and the transport properties will improve after adding one or two organic solvents or water [45]. Pure ILs with $[dca]^-$ have much lower viscosities [27]; for $[C_2C_1Im][dca]$ the viscosity value is 21 cP at 298.15 K. Small contamination of $[Cl]^-$ or $[Br]^-$ anions in ILs from the synthesis increases the viscosity.

New lithium salts used in electrochemistry (e.g., $LiPF_6$, $LiCF_3SO_3$, $LiAsF_6$, and so on) have much lower melting points and ion transport properties than conventional lithium salts, and they could be considered as ILs. The viscosity values for lithium salts, LiTFA-*n*, depending on the number of oxyethylene groups in the oligo-ether substituents, are from 370 to 790 cP (303.15 K) [46].

Because the properties (melting point, density, viscosity) and behavior of the ILs can be adjusted to suit an individual synthesis type, extraction, heat transfer, or electrochemistry problems, they can truly be described as designer solvents.

1.3.1 Molar volume

Values of molar volumes can be calculated from densities measured for the liquid salt, or can be calculated as for hypothetical subcooled liquid at 298.15 K using the group contribution method [47]. As expected, the molar volumes of 1,3-dialkylimidazolium salts and quaternary ammonium salts increase progressively as the length of alkyl chain of the substituent increases. Some molar volumes values at 298.15 K are listed in Table 1.3.

The molar volumes at higher temperatures and the influence of the increasing temperature can be shown for *N*-butylpyridinium tetrafluoroborate,

Table 1.3 Molar Volume, V_m, at 298.15 K of Several Ionic Liquids

Ionic Liquid	$V_m(cm^3\ mol^{-1})$	Reference
$[C_6C_1Im][BF_4]$	221.3	48
$[C_6C_1Im][PF_6]$	244.3	48
$[C_6C_1Im][Tf_2N]$	325.9	49
$[C_1C_1Im][C_1SO_4]$	156.7	50
$[C_4C_1Im][C_1SO_4]$	206.5	50
$[C_4C_1Im][C_8SO_4]$	326.2	50
$[C_4C_1Im]Cl$	186.7	51
$[C_{12}C_1Im]Cl$	325.8	51
$[(C_1)_2C_2HOC_2N]Br$	179.8	52
$[(C_8H_{17}OCH_2)_2Im][Tf_2N]$	542.9	53
$[(C_4)_4P][C_1SO_3]$	387.3	54

[C_4py][BF_4]. Three molar volume values at three temperatures are 185.4 cm^3 mol^{-1} (313.15 K), 186.3 cm^3 mol^{-1} (323.15 K), and 187.4 cm^3 mol^{-1} (333.15 K) [55]. A detailed discussion of the influence of the nature of cations and anions on the molar volume has to follow from densities.

1.3.2 Excess molar volume

To design any process involving ILs for use on an industrial scale, it is necessary to know the range of densities in binary mixtures and the intermolecular IL—solvent interactions. From the first literature data [56] for {[C_4C_1Im][BF_4] + H_2O} at temperatures 315.15 and 353.15 K, positive values of the excess molar volumes were observed. For the similar system [57] of {[C_2C_1Im][BF_4] + H_2O} at 286.15 K and the equimolar composition, $V^E_{m(max)}$, was 0.21 cm^3 mol^{-1}. For [C_1C_1Im][C_1SO_4] with water, the V^E_m values were observed as a sinusoidal curve with $V^E_{m(min)} = -0.18$ cm^3 mol^{-1} at $x_{IL} = 0.42$ [50]. With longer the alkyl chain on the cation from methyl to butyl, V^E_m decreased; for [C_4C_1Im][C_1SO_4] with water, $V^E_{m(min)} = -0.26$ cm^3 mol^{-1} at equimolar composition [50]. For the same cation and $[PF_6]^-$ anion measured with acetonitrile and methanol (298.15–318.15 K) [58] and with acetone, 2-butanone, 3-pentanone, cyclopentanone, and ethyl acetate at 298.15 K [59], negative values of V^E_m were found. Recently, new data were presented for [C_4C_1Im][PF_6], [C_6C_1Im][PF_6], [C_8C_1Im][PF_6], and [C_1C_1Im][C_1SO_4] with 2-butanone, ethyl acetate, and 2-propanol (293.15–303.15 K) [60], and negative excess molar volumes were also observed ($V^E_{m(min)} = -2.18$ cm^3 mol^{-1} at $x_{2\text{-but}} = 0.3$ at 303.15 K). The excess molar volumes, V^E_m, have been determined for [C_1C_1Im][C_1SO_4] with an alcohol (methanol, or ethanol, or 1-butanol), and for [C_4C_1Im][C_1SO_4] with an alcohol (methanol, or ethanol, or 1-butanol, or 1-hexanol, or 1-octanol, or 1-decanol) and for [C_4C_1Im][C_8SO_4] with an alcohol (methanol, or 1-butanol, or 1-hexanol, or 1-octanol, or 1-decanol) at 298.15 K and atmospheric pressure [50]. These systems exhibit very negative or positive molar excess volumes, V^E_m, and negative, or positive excess molar enthalpies, H^E_m, predicted by the Flory–Benson–Treszczanowicz (FBT) model [61]. Negative molar excess volumes, V^E_m, are attributed to hydrogen bonding between the short chain alcohols and the ILs, and to efficient packing effects. The FBT model overestimates the self-association of an alcohol in the solutions and shifts the calculated curves to the higher alcohol mole fraction [50].

V^E_m was negative for all mixtures of {[C_4C_1Im][C_1SO_4] (1) + an alcohol (methanol, or ethanol, or 1-butanol), or water (2)} and positive for mixtures of {[C_4C_1Im][C_1SO_4] (1) + an alcohol (1-hexanol, or 1-octanol, or 1-decanol) (2)} over the entire composition range (see Figure 1.3 for [C_4C_1Im][C_1SO_4] + 1-hexanol) [50].

Less negative values of the excess molar volumes were obtained for the IL with the longer alkyl chain in the cation for the same alcohol. The structure of [C_4C_1Im][C_1SO_4] is less *H*-bonded than [C_1C_1Im][C_1SO_4] in the pure state.

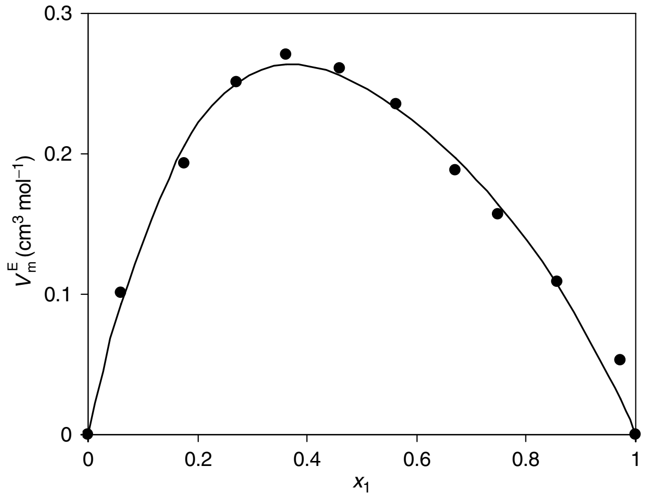

Figure 1.3 V_m^E for {[C_4C_1Im][C_1SO_4] (1) + 1-hexanol (2)} mixtures at 298.15 K. Points, experimental results from Domańska, U. et al. Solid line, Redlich–Kister correlation. (Adapted from Domańska, U., Pobudkowska, A., and Wiśniewska, A., *J. Solution Chem.*, 35, 311, 2006.)

This is probably due to the fact that the molecule of [C_4C_1Im][C_1SO_4] is more flat and that is why this salt is liquid at room temperature in contrast to [C_1C_1Im][C_1SO_4]. There is no doubt that the corresponding values for the self-association of ILs and alcohols are responsible for these results. V_m^E was positive for all mixtures of {[C_4C_1Im][C_8SO_4] (1) + an alcohol (2)} over the entire composition range with the exception of methanol. The excess molar volume data become more positive in the following order: methanol < ethanol < 1-butanol < 1-hexanol < 1-octanol < 1-decanol. Comparison between [C_4C_1Im] [C_1SO_4] and [C_4C_1Im][C_8SO_4] shows that by increasing the alkyl chain length in the anion, the interaction between unlike molecules decreases and the packing effect is the worst. V_m^E is more positive for [C_4C_1Im][C_8SO_4] in every alcohol.

The excess molar volumes for {[C_8C_1Im][BF_4] + 1-butanol, or 1-pentanol} were found very small and negative in the alcohol-rich range of the mixture composition and positive in the alcohol-poor range [62]. More positive values were observed for 1-pentanol ($V_{m(max)}^E$ = 0.92 cm^3 mol^{-1} at equimolar composition and 298.15 K).

The influence of temperature and pressure on the excess molar volume is not very well known. For ILs the V_m^E values were observed more negative at higher temperature [60,63]. Increasing the pressure from 0.1 to 20 MPa at the same temperature, less negative values of V_m^E were observed [63]. The influence of temperature on the V_m^E values at the pressure 15 MPa for {[C_1C_1Im][C_1SO_4] + methanol} is presented in Figure 1.4.

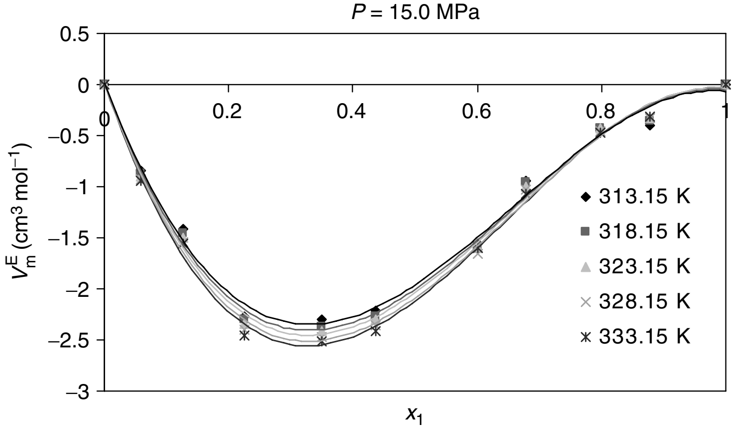

Figure 1.4 V_m^E for {[C_1C_1Im][C_1SO_4] (1) + methanol (2)} under the high pressure 15.0 MPa for five temperatures [63]. Solid lines, Redlich–Kister correlation. (Adapted from Heintz, A. et al., *J. Solution Chem.*, 34, 1135, 2005.)

Strong intermolecular interactions between the hydroxyl group and the IL lead to the negative values of excess molar volumes, V_m^E, and excess molar enthalpies H_m^E. The strongly negative H_m^E curve for {[C_1C_1Im][C_1SO_4] + water}, predicted by the FBT model, was dominated by the chemical contribution, and the curve was strongly shifted to the higher IL mole fraction range. The negative excess molar enthalpies were predicted at the equimolar composition for {[C_1C_1Im][C_1SO_4] + methanol, or ethanol, or 1-butanol}. For the negative values of H_m^E, the strongest IL-alcohol hydrogen bond exceeds that for the O—H···O between the alcohol molecules (−21.8/−21.9 kJ mol^{-1}) and between the IL molecules themselves. The values of H_m^E were found mainly positive for IL mixtures with hydrocarbons [64,65] and only for ([C_2C_1Im][Tf_2N] + benzene) value of H_m^E have appeared negative. Using the Progogine–Defay expression, an estimation of the excess molar volume and enthalpy for the system {[C_4C_1Im][BF_4] + water} was done [66] and the results at 278 K were: $V_{m(max)}^E = 0.92$ cm^3 mol^{-1} and $H_{m(max)}^E = 3000$ J mol^{-1}. The results indicate that IL interactions with water are weaker than in many studied alcoholic solutions, especially in the presence of alcohols with the short alkyl chain. The observed inverse dependence on the temperature for aqueous or alcoholic mixtures refers to the special trend of the packing effect of ILs into hydroxylic solvents and its strong dependence on the steric hindrance of aliphatic residues in the cation, or anion, or an alcohol (e.g., [C_4C_1Im][C_8SO_4]).

1.3.3 Isobaric expansivity and isothermal compressibility

Knowledge of temperature and pressure dependence of physical–chemical properties is very useful to estimate the values of derived parameters, such as the thermal expansion coefficient, α_p, and the isothermal compressibility, κ_T.

The ILs do not expand appreciably at the commonly measured temperature range from 298.15 to 343.15 K. This small expansion with the temperature is best quantified by the volume expansivity, defined as

$$\alpha_p \equiv -\left(\frac{\partial \ln \rho}{\partial T}\right)_p \equiv \left(\frac{\partial \ln V}{\partial T}\right)_p \tag{1.1}$$

Because the molar volumes and densities of ILs are usually linear functions of temperature, the isobaric expansivities are easy to obtain from linear fits of the density data. The α_p values of ILs are in the range of $4-6 \times 10^{-4}\ \mathrm{K}^{-1}$, whereas the values of α_p for most molecular organic liquids are significantly higher ($8-12 \times 10^{-4}\ \mathrm{K}^{-1}$). The isobaric expansivities of ILs are similar to those of water [28], which range from $2.57 \times 10^{-4}\ \mathrm{K}^{-1}$ (298.2 K) to $5.84 \times 10^{-4}\ \mathrm{K}^{-1}$ (343.2 K). For example the isobaric expansivities are: $\alpha_p = 8.63 \times 10^{-4}\ \mathrm{K}^{-1}$ (298.2 K) for 1-methylimidazole [28] and $\alpha_p = 8.47 \times 10^{-4}\ \mathrm{K}^{-1}$ (298.2 K) for *N*-methyl-2-pyrrolidinone [67]. Some values of the isobaric expansivities at ambient pressure for typical ILs are presented in Table 1.4.

Systematic density measurements at a wide range of temperature and pressure [28,31,63,68,69] were helpful to obtain isothermal compressibility, which is calculated using the isothermal pressure derivative of density according to Equation 1.2

$$\kappa_T \equiv \left(\frac{\partial n\rho}{\partial p}\right)_T \equiv \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T \tag{1.2}$$

The isothermal compressibility, κ_T, for some ILs at ambient pressure is presented in Table 1.5.

For the long alkyl chain phosphonium ILs, the isothermal compressibilities were found at ambient pressure about 20% higher than those for the

Table 1.4 The Isobaric Expansivities, α_p, at 298.2 K of Several Ionic Liquids

Ionic Liquid	$\alpha_p \cdot (10^4/\mathrm{K}^{-1})$	Reference
$[C_4C_1Im][PF_6]$	6.11	28
$[C_8C_1Im][BF_4]$	6.24	28
$[4C_4py][BF_4]$	5.43	28
$[C_4C_1Im][Tf_2N]$	6.36	68
$[C_1C_1Im][C_1SO_4]$	5.25	50
$[C_2C_1Im][C_2SO_4]$	5.65	Our value
$[(C_6H_{13})_3P(C_{14}H_{29})][Tf_2N]$	7.43[a]	31

[a] At 0.21 MPa.

Table 1.5 The Isothermal Compressibility, κ_T at Different Temperatures of Several Ionic Liquids

Ionic Liquid	$\kappa_T \cdot (10^4 / \mathrm{MPa}^{-1})$	T/K	Reference
$[C_4C_1Im][BF_4]$	3.96	298.2	29
$[C_4C_1Im][PF_6]$	4.17	298.2	29
$[C_4C_1Im][Tf_2N]$	5.26	298.2	68
$[C_6C_1Im][Tf_2N]$	5.61	298.2	68
$[C_1C_1Im][C_1SO_4]$	3.63	313.15	63
$[C_2C_1Im][C_2SO_4]$	3.41	298.15	Our value
$[(C_6H_{13})_3P(C_{14}H_{29})][Tf_2N]$	6.12	298.2/0.21 MPa	31

imidazolium-based ILs [31]. At higher pressures this effect was diminished. This was suggested as the typical influence of long alkyl chains on the packing effect and free-volume effect.

1.4 *Surface tension and micellization*

Without doubt, a complete picture of the surface tension of pure ILs and their solution and the parameters that govern the mechanism of adsorption connected with ILs would be incredibly useful in the study and improvement of industrially relevant catalysis and surface reaction processes. This information will be necessary for chemical engineering of larger scale reactions. Surface tension can reveal some fundamental features of a liquid, but few studies of this property have been reported [12]. A single compilation of surface tension values, including eight variously substituted imidazolium liquids, has shown [33] that the values of surface tension range from 33.8 $\mathrm{mNm^{-1}}$ for $[C_8C_1Im]Cl$ through 46.6 $\mathrm{mNm^{-1}}$ for $[C_4C_1Im][BF_4]$ and 48.8 $\mathrm{mNm^{-1}}$ for $[C_4C_1Im][PF_6]$ to 54.7 $\mathrm{mNm^{-1}}$ for $[C_4C_1Im]I$. The values of surface tension for $[C_1C_1Im][C_1SO_4]$ and $[C_4C_1Im][C_1SO_4]$ at 298.15 K are 56.5 and 41.4 $\mathrm{mNm^{-1}}$ (our results), respectively.

The surface tension of ILs are lower than that for water (72.7 $\mathrm{mNm^{-1}}$ at 293.15 K, 0.1 MPa) but higher than that for alkane (23.39 $\mathrm{mNm^{-1}}$ for decane at 298.15 K, 0.1 MPa). The aromatic substituent at the imidazolium ring in place of the alkyl chain lowers the surface tension [70], for example, $Ph(CH_2)_n$, where $n = 1$–3 in 1-alkyl(aralkyl)-3-methylimidazolium salts, $[Ph(CH_2)_nC_1Im][Tf_2N]$ salts show values 40.8–43.5 $\mathrm{mNm^{-1}}$. The only lower values were observed for the tetralakylammonium salts with perchlorate anion, $[ClO_4]^-$; from 9.6 to 9.7 $\mathrm{mNm^{-1}}$ for different alkyl substituents [71]. The surface tension is observed to increase as the number of methylene units at the imidazolium or ammonium cation is increased. The value of surface tension of $[C_4C_1Im][PF_6]$ is close to that of imidazole, whereas the surface tension of the $[C_{12}C_1Im][PF_6]$ salt approaches those of an alkane. In general, the surface tension of 1,3-dialkylimidazolium ILs decreases in the order: $[I]^- > [PF_6]^- > [BF_4]^- > [C_1SO_4]^- > [Tf_2N]^-$.