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Solubility of Bioactive, Inorganic and Polymeric Solids in Ionic Liquids — Experimental and Prediction Perspectives

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Additional information is available at the end of the chapter

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1. Introduction

Ionic Liquids (ILs) are a well-established class of organic compounds characterized as liquid salts until 100ºC as well as higher thermal and chemical stability, negligible volatility, high conductivities and large electrochemical window. Usually the adequate cation and anion combinations from ILs can modulate their thermal, physical and chemical properties. Many experimental and theoretical studies, highlight a regular pattern of variation of the properties of ILs by the introduction of elements, functional groups or specific ions, however due to the complexity associated to such compounds, in many cases, it is not possible to establish a straightforward relation between the variation of a specific property and the introduction of a particular component. Despite very low vapor pressure of ILs, several publications reported significant toxicity behavior associated to several classes of ILs. In this line, the development of biocompatible ILs and derived systems is actually being subject of intense research by the scientific community in order to open new perspectives for the application of this class of compounds. Since the advent of ILs in extractions and chemical reactions, the range of applications, in many areas of knowledge, never stopped to grow. One of the major reasons for such expansion is due to the inherent complexity of this class of compounds, associated with the virtually infinite possibilities of combination between cations and anions. In this context, the search for an ionic liquid with the desirable physical, chemical and biological properties by trial and error is not feasible without aid of background knowledge and predictive tools. Solubility is an essential property, being present in all stages of ILs research activities. The intrinsic complexity of this class of compounds associated to the many different types of possible interactions allows the dissolution of a wide range of different solutes. The

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most common interactions observed in ILs classes can be coulombic, hydrogen bonding, permanent dipole - permanent dipole, permanent dipole - inducted dipole, inducted dipole – Inducted dipole, π-π and n- π interactions. According the solubility properties of the system, should be possible to modify, stabilize, capture, control, enhance or mitigate such properties of specific solute molecules.

In this chapter, we are interested to overview the solubility of different classes of solids such as inorganic salts including metals; bioactive compounds including active pharmaceutical drugs; biopolymers and polymers in ionic liquids in particular comparing experimental and predicted research studies. Moreover a rationalization of the inherent structural characteristics behind the observed values of solubility in relevant cases will be also explored.

2. Solubility of inorganic compounds in ionic liquids

This section includes solubility of inorganic salts, elements, metal oxides and organometallic compounds in reference and task-specific ionic liquids. The later class includes ionic liquids with coordinating and common ions which can improve their solubility capacity. Whenever its possible experimental and modeled solubility will be compared and discussed accordingly, otherwise only experimental values will be presented and discussed. In order to contextualize this section a series of applications of such systems will be also described, and the experimental and types of models used in the referenced studies will be presented and discussed.

2.1. Inorganic salts (Halides)

Yang et al [1] reported the solubility of alkali chlorides in [EMIM][EtSO$_4$] at temperatures from 293.15 to 343.15 K. In this study the experimental solubility was determined by slow addition of metal halide to the ionic liquid until precipitate remain after 8h, afterwards the chloride content was determined by the Mohr method and consequently, the solubility of the metal halide was calculated. The experimental values were fitted with an exponential equation as expressed in the legend of Table 1 with a good agreement between experimental and fitted values. Such systems can be useful in synthesis as well as extraction processes.

| MBr (mol.Kg^{-1} of solvent) / T (K)	293	298	303	308	313	318	323	328	333	338	343
NaBr(fit)	0.2643	0.2689	0.2735	0.2779	0.2823	0.2866	0.2909	0.2950	0.2991	0.3032	0.3071
KBr(fit)	0.2484	0.2522	0.2559	0.2595	0.2631	0.2666	0.2700	0.2734	0.2767	0.2799	0.2831
NaBr(exp)	0.2654	0.2692	0.2733	0.2774	0.2817	0.2859	0.2901	0.2948	0.299	0.3037	0.3083
KBr(exp)	0.25	0.2527	0.2557	0.2589	0.262	0.2654	0.2696	0.2726	0.2765	0.2807	0.2849

Table 1. Fitted vs Experimental solubility (molality) of MCl salts in 1-ethyl-3-methylimidazolium ethylsulfate. *Fitting equation (m/m^o) = exp(A1 + A2(T^o/T) + A3(T/T^o)).*

In the same year, Wang et al. [2] reported the solubility of alkali bromides in the same ionic liquid. Similarly with Yang and co-workers study a broad range of temperatures was tested with the solubility increasing with the increase of the temperature, in good agreement between experimental and fitted values as presented in Table 2. The experimental method to obtain solubility of these salts is identical when compared with Yang´s work.

MCl (mol.Kg^{-1} of solvent) / T (K)	293	298	303	308	313	318	323	328	333	338	343
LiCl(fit)	0.3679	0.3861	0.4053	0.4256	0.4471	0.4699	0.4939	0.5193	0.5461	0.5745	0.6045
KCl(fit)	0.2283	0.2299	0.2317	0.2338	0.2361	0.2385	0.2412	0.2441	0.247	0.2506	0.2541
NaCl(fit)	0.2325	0.2347	0.2369	0.2392	0.2415	0.2438	0.2461	0.248	0.2508	0.2532	0.2556
LiCl(exp)	0.3687	0.3861	0.404	0.4271	0.4453	0.4685	0.4951	0.522	0.5459	0.5722	0.6056
KCl(exp)	0.2282	0.2304	0.2322	0.2334	0.2358	0.2388	0.2416	0.2444	0.2479	0.2507	0.2535
NaCl(exp)	0.2351	0.2375	0.2399	0.2421	0.2445	0.2469	0.2491	0.2515	0.2539	0.2567	0.2594

Table 2. Fitted vs Experimental solubility (molality) of MCl salts in 1-ethyl-3 methylimidazolium ethylsulfate. *Fitting equation $(m/m^\varrho) = exp(A1 + A2(T^\varrho/T))$.*

In these two studies, the solubility measurements were performed in a thermostated cell in a glove box under dry atmosphere. In a study of preparation and characterization of alcohol and ether functionalized ionic liquids [3] (Figure 1) was measured the solubility of LiCl, HgCl$_2$, LaCl$_3$. The obtained values were expressed in the form of massic solubility constant. The quantification of Hg and La was performed using plasma spectroscopy (ICP), differently the amount of Li was attained by flame photometry. The tested salts are more soluble in these series of alcohol and ether based RTILs than in conventional alkyl based ionic liquids as can be observed in Table 3. These salts represent examples of alkaline, transition metal, lanthanide based halides and the high solubility presented in some cases constitutes potential model systems with application in green chemistry and clean synthesis.
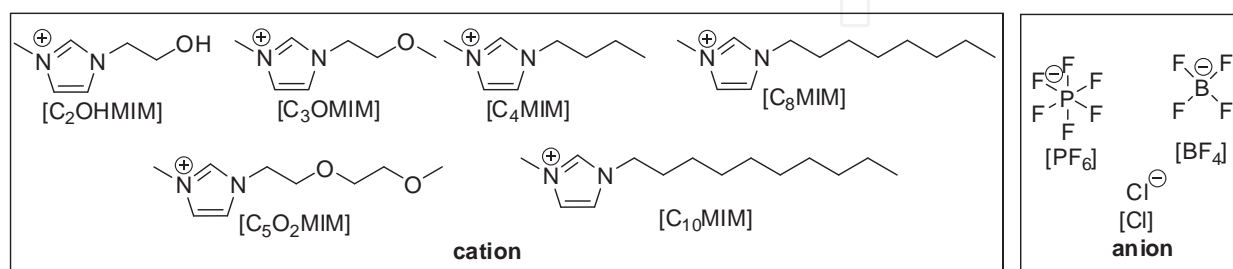
Figure 1. Structures of cations and anions used in solubility studies of Table 3.

IL / K_s x10^6 g of salt · g^{-1} of RTIL	K_s (LiCl)	K_s (HgCl$_2$)	K_s(LaCl$_3$)
[C$_2$OHMIM][PF$_6$]	144.47	44.64	32.47
[C$_2$OHMIM][BF$_4$]	18.46	84.73	54.01
[C$_3$OMIM][PF$_6$]	12.44	50.13	37.61
[C$_3$OMIM][BF$_4$]	14.43	220.86	180.27
[C$_5$O$_2$MIM][Cl]	9.98	295.34	379.23
[C$_5$O$_2$MIM][PF$_6$]	35.52	147.48	97.22
[C$_5$O$_2$MIM][BF$_4$]	21.36	174.17	292.46
[BMIM][PF$_6$]	12.08	4.06	6.58
[BMIM][BF$_4$]	15.54	41.41	10.92
[OMIM][PF$_6$]	35.32	32.98	8.49
[OMIM][BF$_4$]	56.02	35.92	53.25
[C$_{10}$MIM]BF$_4$	12.64	2.12	47.12

Table 3. Solubility constants K_s of specific salts in selected ILs at room temperature.

Metal Chloride	[Metal Chloride]/[BMIM.Cl][AlCl$_4$] molar
AlCl$_3$	1
NbCl$_5$	0.1
TaCl$_5$	0.2
TiCl$_4$	Immiscible
ZrCl$_4$	0.8
HfCl$_4$	1

Table 4. Solubility of metal chlorides in [BMIM.Cl][AlCl$_4$] at 298K.

Dotterl et al. [4] reported the solubility of different metal chlorides in [BMIM.Cl][AlCl$_4$] (Table 4), these mixtures can be used as catalysts in cationic oligomerization, electrochemical oxidation and metal deposition reactions. In this study, it is evident that Al, Zr and Hf based chlorides are highly soluble in this ionic liquid. The values of solubility were obtained by progressive solvent addition to the salt until the complete formation of a saturated solution (all the manipulations were performed under Argon atmosphere).

2.2. Inorganic salts (Miscellaneous)

Rosol et al. [5] reported the solubility of lithium based salts, commonly used as lithium batteries, in alkyl methylimidazolium based RTILs (Table 5). The values of solubility were attained by FTIR-ATR spectroscopic method, with thiocyanate based ionic liquid permitting

much higher values of solubility than other RTILs used in this study. In order to explain such behavior was used COSMO-RS and the higher polarizability of thiocyanate anion is responsible for such optimal observed solubility values.

IL/ solubility mol.dm^{-3}	$LiNTf_2$	$LiClO_4$	$LiPF_6$
[BMIM][Acetate]	0.18	0.10	0.34
[BMIM][SCN]	1.3	4.1	0.60
[BMIM][PF$_6$]	0.06	0.09	0.08
[EMIM][NTf$_2$]	0.4	0.3	0.1

Table 5. Solubility (M - mol.dm^{-3}) of specific salts in selected ILs at 298 K.

Atakilt et al. [6] reported the solubility of $NiCl_2$ and $Cu(NO_3)_2$ in [C$_4$BiPyr] and [C$_4$C$_4$BiPyr] based ionic liquids and other reference RTILs based on imidazolium and phenanthrolinium. Generally, the solubility are low, except for [C$_4$BiPyr][NTf$_2$] where the non-substituted nitrogen can coordinate the metal ions that compose the studied salts, increasing dramatically the solubility. The hypothesis of coordination ability of [C$_4$BiPyr] is confirmed by the poor solubility values in the case of [C$_4$C$_4$BiPyr][NTf$_2$]. The solubility was attained by the addition of the salt to the ionic liquid under nitrogen atmosphere and dissolution under vacuum.

Ionic Liquid/Solubility (mol %)	$NiCl_2$	$Cu(NO_3)_2$
[BMIM][BF$_4$]	< 0.05	< 0.05
[BMIM][PF$_6$]	< 0.05	< 0.05
[BMIM][NTf$_2$]	< 0.05	< 0.05
[C$_4$Phen][NTf$_2$]	< 0.05	< 0.05
[C$_4$Bipyr][NTf$_2$]	> 20	> 20
[C$_4$C$_4$Bipyr][NTf$_2$]	< 0.05	< 0.05

Table 6. Solubility of specific inorganic salts in selected ionic liquids at 343 K.

Pereiro et al. [7] reported the solubility of diverse salts in a wide range of ionic liquids at 298.15 K (Table 7), the authors described that dissolving salts in a ionic liquid is a way to boost ionicity but at same time having the possibility of working in a liquid media, these systems can be potentially applied in batteries. The solubility study was obtained by the visual method, with the more promising systems measured by spectroscopic ATR-FTIR method, such compounds were also fitted by a linear equation with a good correlation between experimental and fitted values.

IL/ mass fraction of inorganic salt	[Na][SCN] Na[OAc]	[NH$_4$][SCN] Na[SCN]	Ca Cl$_2$ [NH$_4$][SCN]	[NH$_4$]Cl Na [Lactate]	Na Cl	Na$_2$ [SO$_4$]	Na [OCN]	Na [NTf$_2$]	Cs [NTf$_2$]	Li [NTf$_2$]
[EMIM][OAc]	0.053	0.187 / 0.234[a] / 0.232[b]	0.136	0.152 / 0.161[a] / 0.159[b]	0.046	0.0097	0.034	-	-	-
	0.081	-	-	-						
[EMIM][SCN]	0.132 /0.145[a] /0.135[b]	0.089	0.042	0.021	0.037	0	0	-	-	-
	-	0.125	0.081	0						
[EMIM][C$_2$SO$_3$]	0.053	0.187/ 0.200[a]/ 0.196[b]	0	0.079 / 0.081[a] 0.076[b]	0.037	0	0.0097	-	-	-
	-	-	-	-						
[EMIM][C$_2$SO$_4$]	0.095/ 0.104[a]	0.352 / 0.379[a] / 0.372[b]	0.005	0.032	0	0.034	0	-	-	-
	-	-	-	-						
[EMIM][NTf$_2$]	0.021		0.0019	0	0	0	0	0.16	0.303 / 0.314[a] /0.311[b]	0.315 / 0.363[a] / 0.359[b]
	-	-	-	-						
[EMIM][OTf]	0.037	-	0	0	0	0	0	-	-	-
	-	-	-	--						
[EMIM][B(CN)$_4$]	0	-	0	0	0	0	-	-	-	-
	-	-	-	-						
[EMIM][PF$_3$(C$_2$F$_5$)$_3$]	0	-	0	0	0	0	-	-	-	-
	-	-	-	-						
[P$_{6,6,6,14}$][NTf$_2$]	0	-	0.002	0	0	0	-	-	-	-
	-	-	-	-						
[P$_{6,6,6,14}$][L-Lactate]	0	-	0.021	0	0	0	-	-	-	-
	-	-	-	-						
[P$_{6,6,6,14}$][OTf]	0	-	0	0	0	0	-	-	-	-
	-	-	-	-						
[P$_{4,4,4,1}$][C$_1$SO$_4$]	0	-	0	0	0	0.01	-	-	-	-

IL/ mass fraction of inorganic salt	[Na] [SCN] Na[OAc]	[NH₄] [SCN] Na[SCN]	Ca Cl₂ [NH₄][SCN]	[NH₄] Cl Na[Lactate]	Na Cl	Na₂ [SO₄]	Na [OCN]	Na [NTf₂]	Cs [NTf₂]	Li [NTf₂]
	-	-	-	-						
[Choline][L-Lactate]	0.132	-	0.016	0.01	0.021	0.02	-	-	-	-
[EtCholine][NTf₂]	0.042	-	0.002	0	0	0	-	0.176	0.322 / 0.339[a] / 0.330[b]	0.433 / 0.484[a]/ 0.479[b]
	-	-	-	-						
[P₆,₆,₆,₁₄][Cl]	-	-	0.044	0	0	-	-	-	-	-
	-	-	-	-						

[a] Obtained by ATR-FTIR spectroscopic method at 298.15 K, [b] Fitted by linear equation y = mx + b.

Table 7. Mass fraction of specific inorganic salts in selected ionic liquids.

2.3. Lanthanides

Lanthanide based systems are very useful in the fields of advanced catalysis and as lumines‐
cent materials, one of the major problems that restricts their use is the poor solubility observed
for this class of compounds. In order to circumvent this obstacle Li et al [8] developed
carboxylate functionalized TSILs (Figure 2) for the dissolution of Europium (III) and Terbium
(III) oxides (Table 8). The dissolution of the Lanthanides has been attained by addition to
specific ionic liquids which they were mixed with an alcohol, and then the suspension was
filtered and the alcohol evaporated under vacuum.

[C₂Carb-CₙIm][Br]
n = 8
n = 12
n = 16
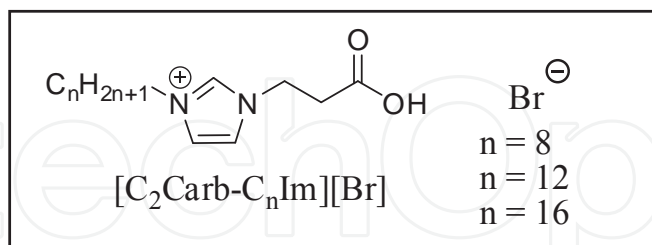
Figure 2. Structures of ILs used in Table 5.

IL/ solubility g.g⁻¹ of solvent	Eu₂O₃ (363 K)	Tb₄O₇ (393 K)
[C₂Carb-C₈Im][Br]	soluble but less than 0.176	at least 0.189
[C₂Carb-C₁₂Im][Br]	soluble but less than 0.151	at least 0.162
[C₂Carb-C₁₆Im][Br]	not solubilized	at least 0.141

Table 8. Solubility values of lanthanide oxides in TSILs (g salt/ g IL).

2.4. Organometallics

The importance of the solubility studies of organometallic complexes is addressed to their applications in catalysis and photo/electrochemical studies as well as material chemistry field. Testing a phenantrolinium based TSIL, Villar-Garcia et al. [9] studied the solubility of Nickel(II), Iron(II) and Cobalt(II) complexes containing phenantroline ligands and optimal solubility with [C_1Phen][NTf$_2$] ionic liquid when compared with reference imidazolium ionic liquids was obtained. Flame Atomic absorption Spectroscopy (AAS) analyses were performed after digesting a known amount of each sample in a 1:1 (v/v) HNO$_3$:HClO$_4$ mixture in order to obtain solubility values.

Ionic liquid/ solubility salt mol%	[Ni(Phen)$_2$(OH$_2$)$_2$]Cl$_2$	[Fe(Phen)$_2$(OH$_2$)$_2$]Cl$_2$	[Co(Phen)$_2$(OH$_2$)$_2$]Cl$_2$
[C_1Phen][NTf$_2$]	> 10 mol %	> 10 mol %	> 10 mol %
[BMIM][NTf$_2$]	< 0.05 mol%	< 0.05 mol%	< 0.05 mol%
[BMIM][BF$_4$]	< 0.05 mol%	< 0.05 mol%	< 0.05 mol%
[BMIM][PF$_6$]	< 0.05 mol%	< 0.05 mol%	< 0.05 mol%

Table 9. Solubility of metal complexes in selected ionic liquids at 348 K.

In a different study, Yang et al. [10] compared the solubility of ferrocene, ferrocenium, and cobaltcenium based salts in [BMIM][BF$_4$] (Table 10). In this study the solubility of Ferrocenium Tetrafluoroborate was determined by the UV-Visible spectroscopy. This study was complemented by an *ab initio* quantum mechanical study in order to unveil the main interactions between solute-solvent and in the case of ferrocenium based salt, it can only be solvated by solvent anions in the first solvation shell.

Compound	Solubility in [BMIM][BF$_4$]
Ferrocene	27.5 mM
Ferrocenium Tetrafluoroborate	134 mM
Cobaltocenium Hexafluorophosphate	327.1 mM

Table 10. Solubility of ferrocene derivatives based compounds in [BMIM][BF$_4$] measured at room temperature

2.5. Elements

Finally, regarding solubility of elements, such studies are important in order to optimize systems in synthesis, electrochemistry and catalysis, among other applications. Boros et al. [11] reported the solubility of sulfur (Table 11) and phosphorous (Table 12) in a diverse range of ionic liquids. The solubility values were obtained by portion-wise addition of sulfur to the ionic liquid and measuring the temperature which the mixture becomes homogeneous

T (K)	[OMIM][NTf$_2$]	[P(Bu)$_3$CH$_3$][OTs]	[BMIM][OTs]
383	< 1	1	2
398	< 1	1	2
413	2	3	4
428	3	5	6

Table 11. Solubility values of Sulfur in different ionic liquids (wt%).

Ionic Liquid	Weight %	Ionic Liquid	Weigth %
[C$_{10}$MIM][CyOCS$_2$]	8	[P$_{6,6,6,14}$][N(CN)$_2$]	1
[BMIM][CyOCS$_2$]	5	[P$_{6,6,6,14}$][NTf$_2$]	trace
[BMIM][C$_6$H$_{13}$OCS$_2$]	4	-	-
[BMIM][C$_4$H$_9$OCS$_2$]	3	-	-
[BMIM][C$_2$H$_5$OCS$_2$]	2	-	-
[P$_{6,6,6,14}$][C$_9$H$_{19}$CO$_2$]	2	-	-

[CyOCS$_2$]: O-cyclohexyldithiocarbonate

Table 12. Solubility of Phosphorus in selected ionic liquids at 373 K.

Finally, the solubility of sulfur was checked in [EMIM][NTf$_2$] at 393 K by Chen et al [12] that observed a solubility of 80 mM using two independent techniques such as electrochemical and by microwave study of sulfur vapor measurements. The possibility to use ionic liquids as alternative and efficient media to solubilize inorganic compounds could open new horizons to develop novel materials, many of them not be possible using conventional solvents. The complexity associated to ionic liquids and the possibility to establish different interactions with solute molecules are mainly reasons behind optimal dissolution performances. In this context, the introduction of task specific ionic liquids with specific groups/moieties can be able to establish a preferential interaction with the solutes. Different experimental techniques have been used based on visual and spectroscopic techniques. Additionally, in this field the introduction of predictive tools is still in his infancy with a limited number of studies establishing a comparison between experimental and predictive measures. It can be expected that by the increment of the number of experimental measures extended to a wider range of inorganics and ionic liquids as well, more robust models with predictive capability could be defined in a near future. The introduction of non-linear machine learning methods such as neural-networks, support vector machines or random forests could propel this subject of study.

3. Solubility of bioactive compounds in ionic liquids

Bioactive compounds have been subject of great attention regarding their interaction with several ILs. Indeed, various synthetic pharmaceutical ingredients and their precursors, as well

as, proteins and natural bioactive compounds, have been processed using ILs, mainly foreseeing applications in the pharmaceutical, cosmetic and agro-food sectors. Driven by a more demanding and strict regulation on the use of hazardous substances, particularly the pharmaceutical sector, for which 80% of waste generated in APIs synthesis, is related to solvent use, is being forced to look to greener alternatives. [13,14] In an attempt to meet this necessity, several scientific papers reporting successful new strategies for the synthesis of different kinds of APIs using ILs, have been reported. [15,16] Another challenge faced by the pharmaceutical industry, relies on the development of efficient drug carrier systems, which are fundamental to overcome barriers to drug bioavailability. In this context, mixtures of ILs have been used as delivery systems, to increase solubility of poorly water-soluble drugs. Briefly, an hydrophobic IL is used as the drug reservoir, completely dissolving the bioactive substance, while another IL, this time a hydrophilic one, is used as co-solvent, with the purpose of increasing the water solubility of the system.[17,18] Also with interest for the pharmaceutical industry, the utilization of ILs for proteins stabilization and biopreservation, have also been subject of great attention.[19]

A further relevant field on the context of bioactive compounds processing with ILs, is the treatment of wastes contaminated with significant quantities of substances possessing biological activity. For example, in respect to wastewater effluents, numerous studies have alerted for the presence of a wide variety of bioactive substances, which are not eliminated by conventional treatment plants. Under this perspective, many authors have reported successful results on using ILs for the extraction of bioactives from it aqueous solutions. An interesting approach are the well-known Aqueous Biphasic Systems (ABS) that have been the focus of a significant amount of research, extensively reviewed in 2012 by Freire M.G. et al. [20]

More recently, the extraction of natural bioactive ingredients from food industry wastes and other biomass resources has emerged. In this case, the IL is used to recover these high-added value substances from cheap and available raw materials and meant for human consumption. [21] The market for natural ingredients is one of the most attractive markets of the moment and in which the use of clean technologies for extraction, fractionation and purification, is of crucial importance. It is interesting to note that ILs applications involving products for human consumption were triggered with the effort of the scientific community on the development of nontoxic (or less toxic) ILs, by selecting more biocompatible organic cations and inorganic anions.[22] Finally, also in the field of analytical chemistry, the processing of bioactive compounds using ILs, has considerably grown.[23]

Process design and success of all above referred applications, strongly relies on the interactions between bioactive compounds and ILs, which in turn, depends on several distinct and complex factors, such as chemical structure, polarity, hydrophilicity and other physico-chemical properties of both solute and solvent. Therefore, phase equilibrium data of the binary systems (IL+ bioactive compound) is of crucial importance to understand, predict and take control of existing, as well as, to figure new applications. Bogel-Lukasik E. and co-workers are the most active research group working on the experimental determination of solubilities of bioactive compounds in ILs. The authors have focused their attention in classical ILs essentially formed by cations of 1-alkyl-3-methylimidazolium (RMIM, where R= butyl, hexyl and octyl chain) and

counter-ions such as, tetrafluoroborate, $[BF_4]$; hexafluorophosphate, $[PF_6]$; trifluoromethane-sulfonate, [OTf] and bis(trifluoromethylsulfonyl)amide $[NTf_2]$. Furthermore, they were the first to address the solubility of natural phenolic compounds, namely, tannic acid, gallic acid and quercetin with the purpose of evaluating the potential of ionic liquids as solvent for their extraction from natural resources, such as biomass.[24] Solubilities were measured using a dynamic method from 273K to 413 K. For the case of tannic acid, the solubility decreased on the following order $[BMIM][BF_4] > [BMIM][PF_6] > [BMIM][OTf] > [BMIM][NTf_2]$. The authors found out a correlation between the observed differences in solubilities and the E^N_T values for the ionic liquids investigated. This parameter is considered a good scale of polarity for ILs. In addition, ILs hydrophilicity was also an important factor, $[BMIM][BF_4]$ contrary to $[BMIM][PF_6]$ is hydrophilic favoring the formation of hydrogen bonds with weak acids, such as tannic acid. However, for both ILs and for mole fractions higher than 0.2 and temperatures above 323.15 K, a strong acid odour was detected, corresponding the undesired formation of HF. This reveals instability of $[BF_4]$ and $[PF_6]$ at higher temperatures. On the other hand, the solubility of tannic acid in $[BMIM][NTf_2]$ is very low (below 0.001 mole fraction even at high tempera-tures). The authors highlighted the fact that $[BMIM][NTf_2]$ is a much worse hydrogen bond acceptor than [BMIM][OTf]. This is due to a higher basic character of the [OTf] anion. Com-paring the solubilities of tannic acid, gallic acid and quercetin in [BMIM][OTf], at around 380 K, the solubility of phenols particularly gallic acid and quercetin are close to or higher than 0.4 mol fraction of phenolic compound. However, the experimental liquid curve trend is difficult to explain, specially for gallic acid that at lower temperatures is the most soluble phenol, but for higher temperatures stands as the less soluble. In fact, after around 330 K and above 0.2 mol fraction, the solubility of gallic acid increases much more slowly with temperature in comparison with the solubility of tannic acid and quercetin. Curiously, the temperature at which this reversed behavior occurs is around the same temperature at which the thermogh-raph of gallic acid presents a solid-solid phase transition (β_1 crystalline form undergoes to a α_1 plastic form at 351 K). The same phenomena but much less pronounced is observed for tannic acid. This kind of phenomena can be exploited to achieve separation of different compounds by varying temperature conditions. In another work addressing the interaction between natural bioactive compounds and ILs, that was recently published by Alevizou and Voutas [25], the authors measured the solubilities of p-coumaric acid and caffeic acid in six 1-alkyl-3-methyl imidazolium based ionic liquids composed of the same anions, BF_4^-, PF_6^-, OTf^-, NTf_2^-. Caffeic acid was found to be less soluble in all ILs due to higher melting temperature and heat of fusion comparing to p-coumaric acid. Furthermore hydrophilic ILs based on BF_4^- and OTf^- were better solvents that hydrophobic ones based on PF_6^- and NTf_2^-. This is due to the fact that hydrophilic ILs interact more stongly with both compounds through hydrogen bonds. Comparing ILs with same imidazolium cation, solubility decreased in the following order $BF_4^- > OTf^- > PF_6^- > NTf_2^-$. The authors highlighted that results obtained are in agreement with relative polarity, hydrophilicity and hydrogen bond basicity of studied ILs. For the case of BF_4^- and OTf^- they were even better solvents than pentanol and ethyl acetate. Comparing ILs with the same anion, as the alkyl chain increases, the solubility of both compounds decreases in the case of hydrophilic BF_4^-, and increases in the case of PF_6^-. For biomass-derived compounds, Carneiro et al. [26] proposed the utilization of ionic liquids as future solvents for

biorefining. In this context, the authors investigated the potential of three ionic liquids for the processing of the sugar alcohols sorbitol and xylitol, obtained respectively from glucose/frutose and xilose. The authors [26] measured the solubility of sorbitol and xylitol within the temperature range of 288 K to 328 K in three ionic liquids, specifically, 1-ethyl-3-methylimidazolium ethylsulfate, [EMIM][EtSO₄], [Aliquat]Cl (a mixture of methyltrioctylammonium chloride and methyltridecylammonium chloride), and [Aliquat][NO₃] (the same cation mixture with nitrate as anion). The solubility of both compounds decreased in the following order [EMIM][EtSO₄] > [Aliquat][Cl] > [Aliquat][NO₃]. Since sorbitol and xylitol are very polar and hydrophylic, the hydrophobicity of [Aliquat] cation causes weaker interactions between the ILs and the solutes. As a result lower solubilities were obtained when using the two ammonium based ILs, compared to those obtained using the hydrophilic ionic liquid, [EMIM][EtSO₄]. Furthermore, the study explained the differences on solubility observed between the two Aliquat's, as a result of two factors. The first factor pointed out, was the water content of [Aliquat][Cl], allowing greater quantities of solute to dissolve. The second factor, was the higher Lewis basicity of chloride over nitrate anions, supplying a better capability to establish hydrogen bonds with xylitol and sorbitol hydroxyl groups. For the three ILs, sorbitol was always more soluble than xylitol. For the case of [EMIM][EtSO₄], an additional hydroxyl group in sorbitol resulted in a significant solubility difference due to stronger solute–solvent interactions. In relation to hydrophobic [Aliquat][Cl] and [Aliquat][NO₃], the additional OH group does not play such an important role. The authors also noted that the solubility of the two sugar alcohols could be connected with their melting properties, as lower attraction between solutes and Aliquat based ILs occurs. In this way, because melting enthalpy is lower for sorbitol, its solubility is expected to be higher

Bioactive compound	Ionic liquid	Solubility	T/K	Modelling	Ref.
Caffeic acid	[BMIM][PF₆]	0.0012-0.0024(x_mol)	303.1-317.4	NRTL, UNIQUAQ	[26]
	[OMIM][PF₆]	0.0014-0.0024(x_mol)	303.1-317.4		
	[BMIM][BF₄]	0.1536-0.1827(x_mol)	303.1-317.4		
	[OMIM][BF₄]	0.0451-0.0626(x_mol)	303.1-317.4		
	[BMIM][NTf₂]	0.0003-0.0011(x_mol)	303.1-317.4		
	[BMIM][OTf]	0.0242-0.0541(x_mol)	303.1-317.4		
Caffeine	[BMIM][BF₄]	84(mmol/L)	298.15	NA	[18]
	[OMIM][BF₄]	83(mmol/L)	298.15		
	[BMIM][PF₆]	100(mmol/L)	298.15		
	[OMIM][PF₆]	34(mmol/L)	298.15		
p-Coumaric acid	[BMIM][PF₆]	0.0062-0.0102(x_mol)	303.1-317.4	NRTL, UNIQUAQ	[25]
	[OMIM][PF₆]	0.0063-0.0119(x_mol)	303.1-317.4		
	[BMIM][BF₄]	0.1951-0.2513(x_mol)	303.1-317.4		

Bioactive compound	Ionic liquid	Solubility	T/K	Modelling	Ref.
	[OMIM][BF$_4$]	0.0803-0.1100(x_{mol})	303.1-317.4		
	[BMIM][NTf$_2$]	0.0028-0.0051(x_{mol})	303.1-317.4		
	[BMIM][OTf]	0.1054-0.1481(x_{mol})	303.1-317.4		
Gallic acid	[BMIM][OTf]	0.0580-0.3596(x_{mol})	273.78-398.42	NA	[24]
	[BMIM][NTf$_2$]	0.0052(x_{mol})	400.15		
Quercetin	[BMIM][OTf]	0.0109-0.3954(x_{mol})	294.40-363.97	NA	[24]
	[BMIM][NTf$_2$]	0.0022(x_{mol})	411.21		
D-(-)- Sorbitol	[EMIM][EtSO$_4$]	0.113-0.310(w_{mass})	289.2-328.3	UNIQUAQ, NRTL, eNRTL	[26]
	[Aliquat]Cl	0.123-0.250(w_{mass})	308.2-343.0		
	[Aliquat][NO$_3$]	0.036-0.115(w_{mass})	308.0-344.9		
Tannic acid	[BMIM] [BF$_4$]	0.1437-0.2509(x_{mol})	275.91-325.15	NA	[24]
	[BMIM] [PF$_6$]	0.0717-0.2544(x_{mol})	289.54-340.04		
	[BMIM] [OTf]	0.0052-0.2601(x_{mol})	276.71-351.13		
	[BMIM] [NTf$_2$]	0.008(x_{mol})	410.59		
Xylitol	[EMIM][EtSO$_4$]	0.200-0.3377(w_{mass})	298.1-328.3	UNIQUAQ, NRTL, eNRTL	[26]
	[Aliquat]Cl	0.186-0.248(w_{mass})	318.0-343.0	UNIQUAQ, NRTL, eNRTL	
	[Aliquat][NO$_3$]	0.056-0.103(w_{mass})	317.8-344.4	UNIQUAQ, NRTL, eNRTL	

Table 13. Solubility of natural and natural-derived bioactive compounds in ILs

The first work regarding solubility of pharmaceutical compounds in ILs was published in 2008 by the group of Florence and co-workers.[18] In this study, different drugs were used as models for water-insoluble drugs (albendazole and danazol) and water-soluble drugs (acetaminophen and caffeine). Their solubility in different ionic liquids were measured. ILs formed by the cation 1-alkyl-3-methylimidazolium with butyl, hexyl or octyl as alkyl chains and by the anions, [PF$_6$] and [BF$_4$] were studied. The authors [18] underlined that drug structures indicate that solute–solvent interactions are likely to involve hydrogen bonds, van der Waal's forces as well as π–π interactions between aromatic ring. For the case of hydrophobic drugs, albendazole presented precisely the expected results, in other words, a higher solubility for ILs with the [PF$_6$] anion and an increase in the solubility with an increase in the alkyl chain, was observed. For the case of danazole, an increase in the alkyl chain has also resulted in an increase in the solubility, but curiously, danazole presented a higher solubility in ILs with [BF$_4$] anions. As the [PF$_6$] salts are more hydrophobic than the [BF$_4$] salts it might have been expected that the former would dissolve more a hydrophobic drug molecule as danazole (as indeed was observed for albendazole). For the hydrophilic compound acetaminophen, solubility results were, as expected, higher for ILs with [BF$_4$] anions and decreased with the alkyl chain increase of the imidazolium ring. Again, for the case of caffeine, however, none of these expected results

were verified and it was the only case for which solubilities obtained were always lower than it solubility in water. This highlights the difficulty in predicting solubility and the need for systematic studies on drug solubility in a wider range of ILs. After that, Smith K.B. et al.[27] have published solubilities of ibuprofen and acetaminophen on ILs at temperatures of 298.15 K, 308.15 K, 318.15 K, 328.15 K, and 338.15 K. Selected ILs were 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF$_6$] and 1-hexyl-3-methylimidazoliumhexafluoro phosphate [HMIM][PF$_6$]. The authors observed that, both ILs were good solvents for ibuprofen and paracetamol, which suggests that drug-solvent interactions are taking place for dissolution to occur. Furthermore and contrary to what was expected, solubilities of both solutes were greater in [HMIM][PF$_6$] than [BMIM][PF$_6$] over the conditions studied. Since acetaminophen is water –soluble and ibuprofen is poorly water-soluble, one would expect opposite behaviours. Acetaminophen as observed before, decreased solubility with an increase in the alkyl chain, but not ibuprofen. Ibuprofen is a water poorly soluble drug and it solubility should increase for more hydrophobic ILs. The author referred that [HMIM][PF$_6$] may have a larger population of cavities within which the drug dissolved leading to the observed higher solubility. Again, these results highlight the difficulty predicting solute solubility in ILs. Furthermore, Bogel-Lukasik E. and co-workers have focus their attention on the solubility of two anti-tuberculosis drugs, namely, isoniazid and pyrazine-2-carboxamide in a series of 1-alkyl-3-methylimidazo-lium bis(trifluoromethylsulfonyl)amide [RMIM][NTf$_2$] and 1-hexyl-3-methylimidazolium trifluoromrthenesulfonate [HMIM][OTf] ionic liquids. [28,29] Regarding the [NTf$_2$] ionic liquids and for both drugs studied, the solubility decreases with an increase of the alkyl chain (R). This is a direct result of the decrease of the acidity of the proton in the position 2 of the imidazolium ring for longer alkyl chains. For comparison between [HMIM][NTf$_2$] and [HMIM][OTf], the solubility of both drugs in [HMIM][OTf] was significantly higher, in agreement with general recognition that [OTf] ILs are better solvents for compounds capable of forming hydrogen bonds. However, isoniazid was slightly less soluble than pyracarboxamide which is very likely due to basic character of hydrazine. The solubility of these anti-tuberculosis drugs were further tested in ammonium-based ILs. [30] Ammonium ionic liquids, namely, didecyl-dimethylammonium nitrate [DDA][NO$_3$], (benzyl)dimethylalkylammonium nitrate (where alkyl= C12H25 (w=0.4) and C14H29 (w=0.6)) [BDMA][NO$_3$], ethyl(2-hydroxyethyl)dimethy-lammonium bis(trifluoromethylsulfonyl)amide [N$_{2,2OH,1,1}$][NTf$_2$], were studied. Both drugs presented similar solubility trends, with the highest solubility observed for [DDA][NO$_3$], followed by [N$_{2,2OH,1,1}$][NTf$_2$] and [BDMA][NO$_3$]. For ammonium ILs, contrary to what was found for imidazolium ILs, isoniazid was slightly more soluble than pyrazicarboxide. Results obtained allowed to conclude that ammonium ILs are better solvents than imidazolium, even imidazolium triflate. Finally Bogel-Lukasik E. and co-workers [31] extended their investigation to other pharmaceutical compounds, namely, N-acetyl-cysteine, coumarin and 4-hydroxy-coumarin. In this case ionic liquids investigated were again imidazolium ILs containing the [NTf$_2$] and [OTf] anions. For hydrophilic compounds (e.g. N-acetyl-cysteine and 4-hydroxy-coumarin) and as expected, solubility was higher in the [OTf] ILs than in [NTf$_2$] ILs, further-more it decreased with increasing alkyl chain. A longer alkyl chain decreases the acidity of the proton in position 2 of the imidazolium ring, therefore reducing capability of forming hydrogen bonds.

Bioactive compound	Ionic liquid	Solubility	T/K	Modelling Equation/Deviations	Ref.
Acetaminophen	[BMIM][BF$_4$]	"/>132(mmol/L)	298.15	NA	[18,27]
	[OMIM][BF$_4$]	126(mmol/L)	298.15		
	[BMIM][PF$_6$]	52(mmol/L)	298.15		
	[OMIM][PF$_6$]	10(mmol/L)	298.15		
N-acetyl-L-cysteine	[EMIM][OTf]	0.0889-0.9295(x$_{mol}$)	283.34-378.61	Wilson, UNIQUAQ, UNIQUAQ ASM, NRTL, NRTL1, NRTL2	[31]
	[BMIM][OTf]	0.0644-0.9054(x$_{mol}$)	293.11-379.13		
	[BMIM][NTf$_2$]	0.0866-0.8775(x$_{mol}$)	306.47-377.79		
	[HMIM][NTf$_2$]	0.0635-0.8843(x$_{mol}$)	298.36-378.10		
	[DMIM][NTf$_2$]	0.0102-0.8984(x$_{mol}$)	305.35-381.04		
Albendazole	[BMIM][BF$_4$]	1.49(mmol/L)	298.15	NA	[18]
	[HMIM][BF$_4$]	2.97(mmol/L)	298.15		
	[OMIM][BF$_4$]	7.2(mmol/L)	298.15		
	[BMIM][PF$_6$]	29(mmol/L)	298.15		
	[HMIM][PF$_6$]	53(mmol/L)	298.15		
	[OMIM][PF$_6$]	>75(mmol/L)	298.15		
Coumarin	[EMIM][OTf]	0.0714-0.8995(x$_{mol}$)	275.51-338.77	Wilson, UNIQUAQ, UNIQUAQ, ASM, NRTL, NRTL1, NRTL2	[31]
	[BMIM][OTf]	0.1463-0.9060(x$_{mol}$)	278.38-337.47		
	[EMIM][NTf$_2$]	0.1387-0.8865(x$_{mol}$)	263.58-334.28		
	[BMIM][NTf$_2$]	0.2879-0.8844(x$_{mol}$)	274.32-332.38		
	[HMIM][NTf$_2$]	0.2651-0.8788(x$_{mol}$)	267.71-330.92		
	[DMIM][NTf$_2$]	0.4034-0.8906(x$_{mol}$)	276.24-332.36		
Danazole	[BMIM][BF$_4$]	18.9(mmol/L)	298.15	NA	[18]
	[OMIM][BF$_4$]	>59(mmol/L)	298.15		
	[BMIM][PF$_6$]	11.9(mmol/L)	298.15		
	[OMIM][PF$_6$]	35(mmol/L)	298.15		
Erythromycin	[BMIM][NTf$_2$]	0.030-0.047(x$_{mol}$)	285.1-348.2	Grant equation	[32]
	[DMIM][NTf$_2$]	0.070-0.074(x$_{mol}$)	288.2-356.2		
	[P$_{6,6,6,14}$][Cl]	0.085-0.097(x$_{mol}$)	298.0-357.2		
	[N$_{4,1,1,1}$][NTf$_2$]	0.053- 0.056(x$_{mol}$)	296.8-354.5		
	[N$_{1,8,8,8}$][NTf$_2$]	0.097-0.106(x$_{mol}$)	310.2-358.0		
	[Pyrr$_{4,1}$][NTf$_2$]	0.016-0.020(x$_{mol}$)	284.4-354.2		

Bioactive compound	Ionic liquid	Solubility	T/K	Modelling Equation/Deviations	Ref.
4-Hydroxycoumarin	[EMIM][OTf]	$0.0711\text{-}0.4887(x_{mol})$	283.02-408.56	Wilson, UNIQUAQ, UNIQUAQ, ASM, NRTL, NRTL1, NRTL2	[31]
	[BMIM][OTf]	$0.0566\text{-}0.4625(x_{mol})$	293.46-415.20		
	[BMIM][NTf$_2$]	$0.0203\text{-}0.2667(x_{mol})$	321.38-411.60		
Isoniazid	[EMIM][NTf$_2$]	$0.008\text{-}0.187(x_{mol})$	331.06-409.47	Wilson, UNIQUAQ, UNIQUAQ, ASM, NRTL, NRTL1, NRTL2	[28]
	[BMIM][NTf$_2$]	$0.004\text{-}0.213(x_{mol})$	323.60-415.89		
	[HMIM][NTf$_2$]	$0.003\text{-}0.169(x_{mol})$	324.61-413.00		
	[OMIM][NTf$_2$]	$0.003\text{-}0.140(x_{mol})$	325.64-409.46		
	[DMIM][NTf$_2$]	$0.003\text{-}0.139(x_{mol})$	326.69-410.82		
	[DMIM][OTf]	$0.006\text{-}0.350(x_{mol})$	314.17-406.42		
	[DDA] [NO$_3$]	$0.0452\text{-}0.4927(x_{mol})$	308.36-418.48	Wilson, UNIQUAQ, UNIQUAQ, ASM, NRTL, NRTL1, NRTL2	[30]
	[BDMA][NO$_3$]	$0.0429\text{-}0.3817(x_{mol})$	321.38-415.71		
	[N$_{2,2OH,1,1}$][NTf$_2$]	$0.0167\text{-}0.3236(x_{mol})$	292.15-402.51		
Pyrazine-2-carboxamide	[EMIM][NTf$_2$]	$0.0048\text{-}0.2122(x_{mol})$	294.40-409.43	Wilson, UNIQUAQ, UNIQUAQ, ASM, NRTL, NRTL1, NRTL2	[29]
	[BMIM][NTf$_2$]	$0.0036\text{-}0.2823(x_{mol})$	279.27-423.73		
	[HMIM][NTf$_2$]	$0.0020\text{-}0.2318(x_{mol})$	275.27-415.25		
	[OMIM][NTf$_2$]	$0.0030\text{-}0.1940(x_{mol})$	275.37-416.66		
	[DMIM][NTf$_2$]	$0.0027\text{-}0.1726(x_{mol})$	275.32-413.79		
	[DMIM][OTf]	$0.0076\text{-}0.4867(x_{mol})$	290.40-417.42		
	[DDA] [NO$_3$]	$0.0343\text{-}0.3912(x_{mol})$	320.30-403.83	Wilson, UNIQUAQ, UNIQUAQ, ASM, NRTL, NRTL1, NRTL2	[30]
	[BDMA][NO$_3$]	$0.0168\text{-}0.2414(x_{mol})$	319.63-401.32		
	[N$_{2,2OH,1,1}$][NTf$_2$]	$0.0068\text{-}0.3375(x_{mol})$	293.19-409.67		

Table 14. Solubility of pharmaceutical compounds in ILs

Manic and Najdanovic-Visak [32] reported on the solubility of erythromycin in imidazolium, ammonium and phosphonium ILs, namely, 1-butyl-3-methylimidazolium bis(trifluorome-thylsulfonyl)imide ([BMIM][NTf$_2$]), 1-decyl-3-methylimidazolium bis(trifluoromethylsulfon-yl)imide ([HMIM][NTf$_2$]), trihexiltertadecilphosphonium chloride ([P$_{6,6,6,14}$][Cl]), butyltrimethylammonium bis(trifluoromethylsulfonyl)imide ([N$_{4,1,1,1}$][NTf$_2$]), methyltriocty-lammonium bis(trifluoromethylsulfonyl)imide ([N$_{1,8,8,8}$][NTf$_2$]), and 1-butyl-1-methylpyrroli-dinium bis(trifluoromethylsulfonyl)imide ([Pyrr$_{4,1}$][NTf$_2$]). Results obtained indicate that solubility decreased in the following order, [N$_{1,8,8,8}$][NTf$_2$]> [P$_{6,6,6,14}$][Cl] > [C$_{10}$mim][NTf$_2$]> [N$_{4,1,1,1}$][NTf$_2$] > [BMIM][NTf$_2$] > [Pyrr$_{4,1}$][NTf$_2$]. Furthermore, longer alkyl chains for both imidazolium and ammonium based ILs led to higher solubility of the studied compound. Azevedo et al. [33] have studied the solubility of a new cardioactive prototype drug, 2-

thienylidene-3,4-methylenedioxybenzoylhydrazine (LASSBio-294) in seven different imidazolium based ILs at room temperature. Selected ILs were the following, 1-ethyl-3-methylimidazolium methyl phosphonate [EMIM][CH$_3$O(H)PO$_2$], 1-ethyl-3-methylimidazolium ethyl phosphonate [EMIM][C$_2$H$_5$O(H)PO$_2$], 1-ethyl-3-methylimidazolium acetate [EMIM][CH$_3$COO], 1,3-dimethylimidazolium methyl phosphonate [DMIM][CH$_3$O(H)PO$_2$], 1-butyl-3-methylimidazolium acetate [BMIM][CH$_3$COO], 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF$_4$], 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [BMIM][NTf$_2$]. This time, classical [BMIM][BF$_4$] and [BMIM][NTf$_2$] were not able to solubilize LASSBio-294. On the other hand, one of the higher solubility was observed for [BMIM][CH$_3$COO], probably due to the good capacity of the anion to form hydrogen bond and delocalize charges between the oxygen atoms. Furthermore, the solubility decreased with a decrease in the cation alkyl chain for [EMIM][CH$_3$COO] due to drug hydrophobicity. At the same level of [BMIM][CH$_3$COO] is the IL, [EMIM][C$_2$H$_5$O(H)PO$_2$] but decreasing the alkyl chain of the anion for [EMIM][CH$_3$O(H)PO$_2$] decreases the drug solubility (also due to a decrease of hydrophobicity). Curiously by comparing LASSBio-294 solubility in [EMIM][CH$_3$O(H)PO$_2$] and [DMIM][CH$_3$O(H)PO$_2$], the solubility was higher in [DMIM][CH$_3$O(H)PO$_2$]. Since in this case an increase in the hydrophobicity was not observed, the authors concluded that the solubility depends not only of each ion separately but also on a combined cation-anion effect. The future of processing bioactive compounds, either synthetic or natural, with ILs, is certainly very promising, which was evidenced by the number of articles published, reporting successful results on several applications. However, with respect to experimental data regarding fundamental studies, to determine interactions between bioactives and ILs (e.g. solubility), until now, very few compounds were explored. Also very few ILs have been tested. Actually most of the authors, have addressed classic imidazolium cations combined with [BF$_4$], [PF$_6$], [OTf] and [NTf$_2$] anions, which are the most studied in terms of thermophysical properties. In this way, some of the authors have actually correlated their results, mainly using local composition models like UNIQUAQ and NRTL, with acceptable deviations and good representations of the experimental data. Nevertheless fundamental data is scarce and it is necessary to further understand and design new successful processes.

4. Solubility of biopolymers in ionic liquids

Biomass is regarded as a permanent source of renewable feedstock on the planet for both material and energy [34]. Various lignocellulosic materials, such as agricultural residues, forestry wastes, waste paper, and energy crops, have been recognized as potential sustainable fonts of sugars for transformation into fuel or value-added products currently derived from petroleum [35]. Biomass primarily consists of polymeric carbohydrates: cellulose and hemicellulose, and the aromatic polymer lignin. These components are firmly cross-linked by numerous inter- and intramolecular hydrogen bonds making processing of biomass an extremely challenging task. In order to access the carbohydrates in the biomass an additional deconstruction step (so called pretreatment) is required. The goal is to disrupt the lignin-

carbohydrate complex, decrease cellulose crystallinity and partially remove lignin and hemicelluloses. Traditional methods currently used either for pretreatment or carbohydrates dissolution typically demand harsh conditions (elevated temperature, and often also elevated pressure, usage of strong acids or bases), and sometimes cause serious environmental, energy, or safety problems [36]. Less energy consuming, more environmentally friendly, and highly efficient approaches are in great need. New solvents systems are crucial for not only deconstruction and separation of biomass components, but also for successful regeneration or derivatisation of sugar polymers under homogeneous conditions.

The capability of ILs to act as media for biomass processing has already been reported [37-42]. After Rogers et al. [43] first reported in 2002 that cellulose could be dissolved in IL, 1-butyl-3-methylimidazolium chloride ([BMIM][C1]), the research on application of ILs to carbohydrate chemistry started to attract a great deal of attention. This subchapter is meant to provide an update on recent advances in the field of solubility of carbohydrates in ILs which has already been reviewed elsewhere [44]. This work covers the solubility data that were published since 2009 till present. Since many comprehensive and excellent reviews on modification of carbohydrates in ILs are already available [45-47], this subject is omitted in the subsequent discussion. Interest in using ILs as media for carbohydrates has so far been centered on the dissolution and processing of cellulose [48-53]. One of the major drawbacks of cellulose concerning its industrial application is the insolubility in water and most of conventional solvents due to its compact structure and chemical complexity. The capacity of certain ILs to dissolve cellulose is primarily related with strong hydrogen bonding between the ILs anion and the hydroxyl groups of cellulose [48,54-57]. This association was confirmed for cellulose or glucose/glucose oilgomer models by means of NMR [58-60], neutron scattering [60], molecular dynamic [61-65] and density functional theory computational approaches [66]. It is commonly accepted that the anion of the ILs plays a predominant role in dissolution. A high basicity of the anion is considered as a major criterion to effectively dissolve cellulose [67,68]. The stronger the hydrogen bond basicity of the anion, the stronger the ability of the IL to dissolve cellulose. However, the exact mechanism of cellulose dissolution has not been completely understood so far. In particular, some speculations exist into the role of the cation [48, 69-74]. Most of the researchers attribute the dissolution ability of ILs only to the anion, while the interactions between the cation and the carbohydrate play secondary role [58,60,61,65,75]. However, the idea that both IL ions, anion and cation, participate in the dissolution process by formation of hydrogen bonds has been considered as well [52,71,74,76,77]. Some data have even suggested that since cellulose is amphiphilic the hydrophobic interactions between the IL cation and the cellulose are responsible for the dissolution of cellulose [41,70].

To date, ILs that have been found suitable for cellulose dissolution contain imidazolium- or pyridinium-based cations combined with anions of basic character such as chloride [43,78], carboxylates (formate [79], acetate [56,78]), phosphates [80] or phosphonates [67]. On the other hand, some IL ions have been shown to be unable to dissolve cellulose. Examples include pyrrolidinium and piperidinium cations and tetrafluoroborate, hexafluorophosphate, dicyanamide, bis(trifluoromethanesulfonyl)amide or trifluoromethanesulfonate anions [40,53,56,74]. Bromide and dicyanamide ILs are known to dissolve cellulose only with low

degree of polymerization [81-83]. Dicyanamide-based ILs are not efficient for cellulose dissolution but they are capable of dissolving monosaccharides [84-86]. Table 15 presents solubility data for main lignocellulosic polymers: cellulose, hemicelluloses and lignin [56,74,82,83,87-90]. It is interesting to note, that replacing proton in the acetate anion with electron-withdrawing group, such as hydroxyl (-OH), thiol (-SH), amine ($-NH_2$) or hydroxy-methyl ($-CH_2OH$) group, results in a decreased solubility of cellulose [56]. Changes in the cation structure are also not insignificant. When the alkyl chain length in the cation is increased, the solvent power of ILs for cellulose seems to decrease [43]. Moreover, for the small alkyl chains (pentyl and shorter) of 1-alkyl-3-methylimidazolium chloride, the strong odd-even effect was observed [58]. Even-numbered alkyl side chains proved to be better suited for cellulose dissolution than odd-numbered chains. Alkyloxy and alkyloxyalkyl groups attached to the imidazolium ring may either enhance or decrease solubility of cellulose [74,91,92]. In some cases IL solvent systems can also be used. Mixtures of ILs and polar organic co-solvent (e.g, dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF) or N,N-dimethylacetamide (DMA) have been successfully applied [93,94], even at ambient temperature [90]. The great advantage of such mixtures is reduced viscosity of the cellulose solutions that leads to acceleration of the dissolution process from hours down to minutes. Addition of lithium salts (e.g., Li(OAc), LiCl, LiBr, $LiNO_3$ or $LiClO_4$) into [BMIM][OAc] significantly increases the solubility of cellulose [56]. This observation was studies by ^{13}C NMR spectra, and the results suggest that the enhanced solubility originates from the disruption of the intermolecular hydrogen bond owing to the interaction of lithium cations with the hydroxyl oxygen of cellulose.

The desired high basicity that allows an IL to dissolve cellulose unfortunately makes the IL very hydroscopic. Water is found to perturb the solvation of carbohydrates considerably [43,89,94]. It hydrogen-bonds to the ILs anion or to cellulose removing the primary driving force for the solubility of cellulose, the anion-cellulose hydrogen bonds. Amounts even as low as 0.15 wt% were reported to start precipitation of cellulose in the 1-ethyl-3-methylimidazolium chloride ([EMIM][C1]) [89]. On the other hand, this is very advantageous for the regeneration of carbohydrates already dissolved in ILs [95]. Cellulose can be easily precipitated from the cellulose-IL solution by addition of solvents, such as water, alcohol, acetone or acetonitrile [38,43,56,68,78]. The regenerated cellulose exhibits typically lower degrees of crystallinity compared to the native cellulose. Various novel cellulose materials can be prepared from cellulose-IL solutions, such as composites [96,97], membranes [98], films [78,99], fibers [100,101] or nanofibrillar cellulose aerogels [102]. The conventional pulping techniques are primarily focused on maximizing the cellulose yield neglecting the potential of lignin and hemicellulose. The first is typically degraded during the delignification step or used as a fuel in subsequent processing, often at really low efficiency [103]. The second can be isolated from cellulose, after the delignification, but this typically involves its partial degradation. The clean fractionation of these polymers is very important for the successful utilization of biomass [39]. Although it is difficult to achieve this goal, the possibility of separation of lignocelluloses components with ILs has already been explored [42]. There exist some reports on selective extraction of hemicellulose [104-107] or lignin [88,108]. Dissolution of wood in ILs has also been studied [38,42,109-111]. However, the data on the solubility of the particular polymers is still scarce [82,88,112-114].

Carbohydrate	Ionic liquid	Solubility	T [K]	Ref.
microcrystalline cellulose	[AMIM][Cl]	~ 2-11 %wt	358.15-383.15	[87]
	[BMIM][Cl]	14 g/100g IL	363.15	[88]
commercial cellulose	[BMIM][Cl]	18.4 mg/g IL	353.15-363.15	[82]
	[BMIM][Cl]	6.2 g/100g IL	363.15	[89]
wood cellulose sulfate (DP=495)	[BMIM][Cl]	5 %wt	363.15	[83]
	[BMIM][Cl]	10 %wt	373.15	[83]
	[BMIM][Br]	4 %wt	373.15	[83]
	[BMIM][SCN]	3.5 %wt	373.15	[83]
	[BMIM][OAc]	10 %wt	363.15	[83]
microcrystalline cellulose (DP=229)	[BMIM][OAc]	11.5-19 wt%	313.15-353.15	[56]
	[BMIM][OAc]/Li[OAc]	12-20 wt%	313.15-353.16	[56]
	[BMIM][OAc]/LiCl	12-20 wt%	313.15-353.17	[56]
	[BMIM][OAc]/LiBr	11.5-19.5 wt%	313.15-353.18	[56]
	[BMIM][OAc]/LiClO$_4$	12-21 wt%	313.15-353.19	[56]
	[BMIM][OAc]/LiNO$_3$	12-21 wt%	313.15-353.20	[56]
	[BMIM][OAc]	23-58 g/mol IL	313.15-393.15	[74]
	[BMIM][OAc]/DMSO	15%	298.15	[90]
	[BMIM][OAc]/DMF	12.5%	298.15	[90]
	[BMIM][OAc]/DMA	5.5%	298.15	[90]
	[BMIM][(C$_6$H$_5$)COO]/DMSO	9%	298.15	[90]
	[BMIM][(C$_6$H$_5$)COO]	< 1-12 wt%	313.15-343.15	[56]
	[BMIM][CH$_3$CHOHCOO]	8-9.5 wt%	333.15-343.15	[56]
	[BMIM][HCOO]	7.5-12.5 wt%	313.15-343.15	[56]
	[BMIM][HOCH$_2$COO]	7.5-10.5 wt%	323.15-343.15	[56]
	[BMIM][HSCH$_2$COO]	< 1-13.5 wt%	313.15-343.15	[56]
	[BMIM][H$_2$NCH$_2$COO]	< 1-12 wt%	313.15-343.15	[56]
microcrystalline cellulose	[DMIM][Cl]	~ 4-23 %wt	343.15-383.15	[87]
	[EMIM][OAc]	22 g/100g IL	363.15	[88]
commercial cellulose	[(CN)EMIM][Br]	33.8 mg/g IL	353.15-363.15	[82]
	[PrMIM][Br]	16.6 mg/g IL	353.15-363.15	[82]
microcrystalline cellulose (DP=229)	[BDMIM][OAc]	5-37 g/mol IL	323.15-393.15	[76]
	[C$_2$OHMIM][OAc]	1-34 g/mol IL	323.15-393.15	[76]
	[C$_3$OMIM][OAc]	8-56 g/mol IL	313.15-393.15	[76]

Carbohydrate	Ionic liquid	Solubility	T [K]	Ref.
	[BzMIM][OAc]	1-34 g/mol IL	323.15-393.15	[76]
	[BEBIM][OAc]	< 1 g/mol IL	393.15	[76]
	[EEBIM][OAc]	< 1 g/mol IL	393.15	[76]
	[AMMOR][OAc]	1-28 g/mol IL	323.15-393.15	[76]
	[EMMOR][OAc]	1-31 g/mol IL	333.15-393.15	[76]
	[AMPIP][OAc]	10-19 g/mol IL	363.15-393.16	[76]
	[BMPIP][OAc]	1-7 g/mol IL	353.15-393.17	[76]
	[BEBT][OAc]	< 1 g/mol IL	393.15	[76]
	[BMPL][OAc]	1-3 g/mol IL	373.15-393.15	[76]
commercial lignin	[(CN)EMIM][Br]	95.3 mg/g IL	353.15-363.15	[82]
	[PRMIM][Br]	62.4 mg/g IL	353.15-363.15	[82]
	[BMIM][Cl]	87.8 mg/g IL	353.15-363.15	[82]
Kraft lignin Indulin AT	[EMIM][OAc]	2 g/100g IL	363.15	[88]
	[BMIM][Cl]	< 0.1 g/100g IL	363.15	[88]
	[MeMe(EtOH)NH][HCOO]	2 g/100g IL	363.15	[88]
xylan from birch wood	[EMIM][CH$_3$COO]	2 g/100g IL	363.15	[88]
	[BMIM][Cl]	< 0.1 g/100g IL	363.15	[88]
	[MeMe(EtOH)NH][HCOO]	2 g/100g IL	363.15	[88]

DP-degree of polymerisation

Table 15. Solubility of main lignocellulosic polysaccharides in ILs

Chitin is structurally similar to cellulose with one hydroxyl group on each monomer replaced by an acetylamine group, while chitosan is N-deacetylated product of chitin. In contrast to cellulose, only a few examples of the dissolution of chitin or chitosan in ILs have been reported [87,115,116]. Recently, a series of ILs containing alkylimidazolium chloride, alkylimidazolium dimethylphosphate, and 1-allyl-3methylimidazolium acetate ([AMIM][OAc]) to dissolve chitin were used. It was noticed that the degree of acetylation, the crystallinity, the molecular weights of chitin, as well as the nature of the anion of the IL all affect the dissolution behavior of chitin in ILs [117]. The acetate anion was strong enough to cleave the hydrogen bond network of chitin, while the chloride anion and dimethylphosphate anion were less efficient. The same was observed for chitosan [118,119]. The dissolving power of acetate ILs for chitosan seems stronger than that of chloride ILs. At a given temperature, the dissolution performance of the ILs for chitosan decreases in the order: [BMIM][OAc] > [BMIM][CH$_3$CH$_2$COO] > [BMIM][CH$_3$CH$_2$CH$_2$OO] > [BMIM][C$_6$H$_5$COO] > [BMIM][HOCH$_2$COO] > [BMIM][HCOO] > [BMIM][CH$_3$CHOHCOO] > [BMIM][N(CN)$_2$]. The influence of the cation on the solubility of chitosan in chloride-

based ILs was also determined and the solubility decreases as follow: 1,3-dimethylimidazolium chloride ([DMIM][Cl]) > [AMIM][Cl] > [BMIM][Cl] [87]. In the same study, the mixtures of ILs have been tested for the dissolution of chitosan and good results were obtained. Both chitin and chitosan due to their favorable properties such as good biocompatibility, biodegradability, absorptivity and nontoxicity find many applications in the field of tissue engineering, drug delivery, food preservation, waste water purification, packaging or cosmetics [120-123]. Very recently it was reported that chitosan together with agarose [124], or agarose on its own [125,126], were used to prepare ionogels which are shown to be smart polymeric conducting materials [127]. Agarose is an algal polysaccharide comprising alternating D-galactose and 3,6-anhydro-L-galactose repeating units, essentially uncharged. Over the years it was often use for its gelling properties. Similarly to cellulose, due to the large number of hydroxyl groups in its structure, agarose is insoluble in many common organic solvents and cold water. ILs that were found to dissolve agarose are of basic character and are able to disrupt the hydrogen-bonding network of the polymer leading to dissolution [125,126]. Unlike cellulose, where the alkyl chain length of the cation has very limited effect on solubility [58,60,61,65,75], a remarkable decrease of solubility of agarose with increase in alkyl chain length of the cation was observed (compare [bmim][Cl] with 1-octyl-3methylimidazolium chloride ([OMIM][Cl]) in Table 16 [125]. When compared to neat ILs, an increase in the solubility of agarose is observed in general in the mixed IL-IL system (e.g., compare [MeNH$_3$][HCOO] with [MeNH$_3$][HCOO]/[BMPy][Cl] or [MeNH$_3$][HCOO]/[BMIM][Cl] in Table 16 [126].

Carbohydrate	Ionic liquid	Solubility	T [K]	Ref
Chitin (DA=91.6%)	[AMIM][OAc]	5 %wt	383.15	[117]
	[AMIM][Cl]	0.5 %wt	< 318.15	[117]
	[BMIM][Cl]	ns	453.15	[117]
	[EMIM][(CH$_3$O)$_2$PO$_2$]	1.5 %wt	< 333.15	[117]
	[DMIM][CH$_3$O)$_2$PO$_2$]	1.5 %wt	< 333.15	[117]
	[C$_2$OHMIM][Cl]	ns	453.15	[117]
Chitosan (DC=75-85%)	[BMIM][HCOO]	0.6-8.4 %	343.15-423.15	[119]
	[BMIM][OAc]	0.8-14.4 %	343.15-423.15	[119]
	[BMIM][CH$_3$CH$_2$COO]	0.2-12.4 %	343.15-423.15	[119]
	[BMIM][CH$_3$(CH$_2$)$_2$COO]	0.2-10.4 %	343.15-423.15	[119]
	[BMIM][HOCH$_2$COO]	0.6-9.6 %	343.15-423.15	[119]
	[BMIM][CH$_3$CHOHCOO]	0.4-6.2 %	343.15-423.15	[119]
	[BMIM][(C$_6$H$_5$)COO]	1.4-7.6 %	343.15-423.15	[119]
Chitosan (DC > 90%)	[AMIM][Cl]/[MIM][Cl]	~1-12 %wt	353.15-383.15	[87]
	[DMIM][Cl]/[MIM][Cl]	~ 3-16 %wt	343.15-383.15	[87]

Carbohydrate	Ionic liquid	Solubility	T [K]	Ref
corn starch	[AMIM][Cl]	11.75%	363.15	[128]
wheat starch	[AMIM][Cl]	11.25%	363.15	[128]
rice starch	[AMIM][Cl]	11%	363.15	[128]
mung bean	[AMIM][Cl]	10.50%	363.15	[128]
potato starch	[AMIM][Cl]	9%	363.15	[128]
maiz starch	[BMIM][Cl]	10 wt%	373.15	[131]
Agarose	[BMIM][Cl]	16 %wt	343.15	[125]
	[BMIM][CH$_3$OSO$_3$]	5 %wt	343.15	[125]
	[OMIM][Cl]	4.5 %wt	343.15	[125]
	[BMPy][Cl]	13 %wt	343.15	[125]
	[HOEtNH$_3$][HCOO]	5 %wt	343.15	[126]
	[MeNH$_3$][HCOO]	14 %wt	343.15	[126]
	[EtNH$_3$][HCOO]	20 %wt	343.15	[126]
	[HOEtNH$_3$][HCOO]/[BMIM][Cl]	8 %wt	343.15	[126]
	[MeNH$_3$][HCOO]/[BMIM][Cl]	18 %wt	343.15	[126]
	[EtNH$_3$][HCOO]]/[BMIM][Cl]	7 %wt	343.15	[126]
	[HOEtNH$_3$][HCOO]/[BMPy][Cl]	7 %wt	343.15	[126]
	[MeNH$_3$][HCOO]/[BMPy][Cl]	21 %wt	343.15	[126]
	[EtNH$_3$][HCOO]/[BMPy][Cl]	25 %wt	343.15	[126]
	[HOEtNH$_3$][HCOO]/[BMIM][CH$_3$OSO$_3$]	14 %wt	343.15	[126]
	[MeNH$_3$][HCOO]/[BMIM][CH$_3$OSO$_3$]	23 %wt	343.15	[126]
	[EtNH$_3$][HCOO]/[BMIM][CH$_3$OSO$_3$]	26 %wt	343.15	[126]

DA-degree of acetylation; DC-degree of deacetylation

Table 16. Solubility of polysaccharides in ILs

Starch is another example of one the most abundant natural polymers. Its utilization in its native form is often limited though. This is due to some undesirable characteristics such as poor solubility, low mechanical properties, and instability at high temperature and pH during processing. The derivatisation of starch is typically required in order to overcome these shortcomings and improve its functionality for industrial applications [129]. During the last few years an increasing interest in manufacturing value-added products based on starch utilizing ILs has been observed, whilst much less attention has been paid to the subject of solubility of starch in ILs [130-132]. Very recently, reports comparing the dissolution of starch in IL, [EMIM][OAc], with gelatinization process in water ware published [133,134]. Consid-

ering the mechanism of dissolution, it was stated that in case of pure IL, the solvent penetrates starch granule making outer layer slightly swollen and transparent. With time, less and less granules can be seen, up to complete visual disappearance. In water, starch granules first swell with temperature increase and then burst. For mixed [EMIM][OAc]-water systems, the behavior of the solvent depends on the [EMIM][OAc]-water ratio. For 25–75% and 50–50% [EMIM][OAc]–water systems the gelatinisation takes place. The dissolution similar to the one in pure ILs occurs for 75% [EMIM][OAc]–25%water system and the presence of water strongly accelerates it. It seems that water swells the outer layer first facilitating penetration of the IL, and thus starch dissolution. Additionally, the viscosity of the 75% [EMIM][OAc]–25%water system is much lower than that of a pure [EMIM][OAc].

Carbohydrate	Ionic liquid	Solubility	T [K]	Ref.
β-cyclodextrin	[AMIM][Cl]	79.4-112.3 g/100g IL	333.15-353.15	[141]
	[BMIM][Cl]	69.7-106.7 g/100g IL	343.15-363.15	[141]
	[C$_2$OHMIM][Cl]	78.4-110.4 g/100g IL	338.15-358.15	[141]
	[AMIM][N(CN)$_2$]	102.3-132.2 g/100g IL	333.15-353.15	[141]
	[BMIM][N(CN)$_2$]	73-105.1 g/100g IL	333.15-353.15	[141]
	[C$_2$OHMIM][N(CN)$_2$]	90.5-121.5 g/100g IL	333.15-353.15	[141]

Table 17. Solubility of oligosaccharides in ILs

Hydrolysis of starch produces a group of low-molecular-weight carbohydrates named dextrins [135]. Dextrins are mixtures of linear and branched (1,4)-linked α-glucose polymers, while cyclodextrins are a series of cyclic oligosaccharides composed of 6, 7, or 8 D-(+)-glucose units named α-, β-, and γ-cyclodextrin, respectively. The structures of cyclodextrins are identical as each of them contains a molecular cavity. The hydroxyl groups of the oligomer are on the outside of the cavity, while the inner cavity is hydrophobic. Cyclodextrins are able to form inclusion complexes with a number of organic and inorganic guest molecules that are encapsulated in their molecular cavities. Most of the investigations concerning ILs and cyclodextrins are focused on understaning the nature of interactions [136-143].The solubility data are very limited [44]. Fan and co-workers investigated the solubility of β-cyclodextrin in six kinds of hydrophilic ILs [141]. It is shown that the solubilities were remarkable and followed the order [AMIM][N(CN)$_2$] > [C$_2$OHMIM][N(CN)$_2$] > [AMIM]Cl > [BMIM][N(CN)$_2$] > [C$_2$OHMIM]Cl > [BMIM]Cl. Monosaccharides (especially glucose and fructose) and disaccharides (mainly sucrose), after cellulose, are the most studied carbohydrates in ILs.

Table 18 and 19 summarizes the solubility data for disaccharides [85,133,144-146] and monosaccharides [85,86,144-148], respectively. Solubility of sugar in a given IL decreases in the following order: D-(-)-fructose > D-(+)-glucose > sucrose. It can be justified by the chemical structure of sugars and their basic thermal properties (i.e., temperature and enthalpy of fusion), independent of the IL [85,86,147]. The melting temperature and melting enthalpy of carbohydrates are related with their solubility and the larger the properties, the lower the solubility.

Regarding the influence of the cation and anion structure of the ILs on the solubility of carbohydrates, some general conclusions can be drawn from the collected data. Similarly as in the case of cellulose, the role of the cation is not insignificant. It was found that imidazolium-based ILs are capable of dissolving monosaccharides, whereas pyridinium and phosphonium ILs are rather poor solvents for these sugars [145]. Novel ILs containing dimethylguanidinium cation and anions such as saccharine, acesulfame and thiocyanate has also been investigated and some remarkable results were obtained. It was demonstrated that introduction of functionality in the alkyl chain of the dimethylguanidinium-based ILs can improve the dissolution of carbohydrates [146]. Sugars are more soluble in ILs with shorter alkyl chains in their chemical structure. The same as for polycarbohydrates, increasing length of the chain results in a more hydrophobic nature of the cation and IL as a whole, and thus weakens the capacity of dissolving polar solutes like sugars [85,86]. As an example, the lower solubilities of monosaccharides such as D-(+)-glucose, D-(−)-fructose, D-(+)-xylose and D-(+)-galactose in [Aliquat][Cl], in comparison to [EMIM][EtSO$_4$], can be given. [Aliquat][C]l is a mixture of methyltrioctylammonium chloride and methyltridecylammonium chloride. The hydrophobicity and larger non-polar alkyl chains on the [Aliquat][Cl] which have not much affinity with the hydroxyl groups of the sugars explains its poor solubility power [147]. Among hydrophobic ILs, the more bulky (more hydrophobic) [P$_{6,6,6,14}$][N(CN)$_2$] was less capable to dissolve less sugars, when compared with [Aliquat][N(CN)$_2$] [86]. Regarding the effect of the anion on the solubility of sugars it was observed that all from the investigated carbohydrates (glucose, fructose and sucrose) were more soluble in [BMIM][OTf] compared to [BMIM][N(CN)$_2$] [85,86]. Glucose and xylose showed the highest solubilities, among the seven various ILs investigated, in either [BMIM][HSO$_4$] or [BMIM][SCN] [145]. The authors of the study explained that it can be a result of a large affinity of anions towards monosaccharides. In particular, it can be caused by a highly acidic effect of [HSO$_4$] which acts as strong hydrogen bond donor, and [SCN] responsibility for the strong hydrogen bond accepting interactions due to a high polarizability of the anion and the specific structure stabilised by the resonance. Also, the study of cyano-based ILs revealed that, in general, the monocyano anion is a stronger hydrogen bond acceptor than a more complex multicyano anion. Thus, the solubility of carbohydrates can be higher in [SCN] than in [N(CN)$_2$] or even in [C(CN)$_3$]-based ILs.

Carbohydrate	Ionic liquid	Solubility	T [K]	Modeling	Ref.
sucrose	[BMIM][Cl]	5-40 wt%	343.95-380.3	NRTL, UNIQUAC	[144]
	[BMIM][SCN]	2-35.3 wt%	315.2-411.67	-	[145]
	[BMIM][N(CN)$_2$]	18.8-75.3 mol %	325.9-369	PC-SAFT	[85]
	[BMIM][C(CN)$_3$]	2-35.3 wt%	381.2-406.64	-	[145]
	[BMIM][OTf]	19.2-86.8 mol %	316.2-365.2	PC-SAFT	[85]
	[BMIM][HSO$_4$]	235 wt%	358.74-388.5	-	[145]
	[EMIM][(MeO)(EtO)EtOSO$_3$]	2.1-25.3 wt%	343.6-410.63	-	[145]

Carbohydrate	Ionic liquid	Solubility	T [K]	Modeling	Ref.
	[EMIM][SCN]	2.5-30 wt%	284.25-383.15	NRTL, UNIQUAC	[144]
	[DMIM][CH$_3$PO$_3$]	5-50 wt%	286.15-376.45	NRTL, UNIQUAC	[144]
	[C$_2$OHMIM][Cl]	5-40 wt%	356.15-384.15	NRTL, UNIQUAC	[144]
	[C$_5$O$_2$MIM][Cl]	17.11 wt%	308.15	-	[146]
	[C$_5$O$_2$MIM][N(CN)$_2$]	11.06 wt%	308.15	-	[146]
	[P$_{4,4,4,1}$][CH$_3$C$_6$H$_4$SO$_2$]	3.1-10.1 wt%	378.97-402.13	-	[145]
lactose	[BMIM][Cl]	2.5-28 wt%	344.15-381.55	NRTL, UNIQUAC	[133]
	[EMIM][SCN]	2.5-18 wt%	288.05-382.55	NRTL, UNIQUAC	[133]
	[DMIM][CH$_3$PO$_3$]	5-39.3 wt%	290.55-356.25	NRTL, UNIQUAC	[133]
	[C$_2$OHMIM][Cl]	2.5-25 wt%	355.75-384.15	NRTL, UNIQUAC	[133]
	[C$_5$O$_2$MIM][Cl]	10.69 wt%	308.15	-	[146]
	[C$_5$O$_2$MIM][N(CN)$_2$]	16.55 wt%	308.15	-	[146]

Table 18. Solubility of disaccharides in ILs

As it was mentioned before, cellulose can be easily precipitated from the cellulose-IL solution by means of selective precipitation [38,43,56,68,78]. However, separation of smaller carbohydrates such as glucose from ILs remains a challenging task. Glucose and ILs have extremely low vapor pressure. Therefore, conventional vacuum distillation methods do not serve for their separation. Also, no suitable organic solvent capable of extracting sugar from ILs have been found. In 2011, it was reported for the first time that antisolvent method can be applied to the separation of glucose and IL [149]. An antisolvent method is based on discrepancies in the interactive forces between solute, solvent and antisolvent. An addition of an antisolvent to a binary solution (solute+solvent) causes a reduction in the original solubility of the solute in the binary solution, leading to its crystallization and precipitation. Very recently, the method was adopted for separation of other systems, differing in carbohydrates and ILs [150,144,148].

Carbohydrate	Ionic liquid	Solubility	Temperature [K]	Modeling	Ref.
	[BMIM][Cl]	5-50 wt%	343.15-359.25	NRTL, UNIQUAC	[144]
	[BMIM][N(CN)$_2$]	11-74.9 mol %	297.2-367.6	PC-SAFT	[85]
D-(-)-fructose	[BMIM][N(CN)$_2$]	28.1-41 wt%	288.15-328.45	NRTL, UNIQUAC	[86]
	[BMIM][OTf]	20.5-88.2 mol %	313.8-365.4	PC-SAFT	[85]
	[EMIM][SCN]	5-45 wt%	281.15-358.15	NRTL, UNIQUAC	[144]
	[EMIM][N(CN)$_2$]	33.3-49.5 wt%	288.25-328.25	NRTL, UNIQUAC	[86]

Carbohydrate	Ionic liquid	Solubility	Temperature [K]	Modeling	Ref.
	[EMIM][OTf]	35.5-41.5 wt%	288.05-308.3	NRTL, UNIQUAC	[86]
	[EMIM][EtSO$_4$]	25.7-43.5 wt%	288.2-329.3	NRTL, UNIQUAC	[147]
	[DMIM][CH$_3$PO$_3$]	5-60 wt%	284.95-344.15	NRTL, UNIQUAC	[144]
	[C$_2$OHMIM][Cl]	10-60 wt%	355.05-369.15	NRTL, UNIQUAC	[144]
	[Aliquat][NO$_3$]	13.1-21.8 wt%	307.75-339.75	NRTL, UNIQUAC	[86]
	[Aliquat][N(CN)$_2$]	3.2-13 wt%	299.95-339.74	NRTL, UNIQUAC	[86]
	[Aliquat][Cl]	15.4-25.2 wt%	298.2-328.2	NRTL, UNIQUAC	[147]
	[P$_{6,6,6,14}$][N(CN)$_2$]	0.276-5.52 wt%	298.37-328.21	NRTL, UNIQUAC	[86]
	[C$_5$O$_2$MIM][Cl]	14.10 wt%	308.15	-	[146]
	[C$_5$O$_2$MIM][N(CN)$_2$]	48.99 wt%	308.15	-	[146]
D-(+)-galactose	[EMIM][EtSO$_4$]	4-14 wt%	288.8-328.2	NRTL, UNIQUAC	[147]
	[Aliquat][Cl]	4.2-8.6 wt%	298.3-329.2	NRTL, UNIQUAC	[147]
	[BMIM][Cl]	5.9-50 wt%	343.15-360.45	-	[148]
	[BMIM][SCN]	2-50 wt%	300.77-406.17	-	[145]
	[BMIM][N(CN)$_2$]	18.6-76.6 mol %	304.4-366.5	PC-SAFT	[85]
	[BMIM][N(CN)$_2$]	13.3-23.6 wt%	288.15-328.45	NRTL, UNIQUAC	[86]
	[BMIM][N(CN)$_2$]	18.56 wt%	308.15	-	[146]
	[BMIM][NTf$_2$]	0.59 wt%	308.15	-	[146]
	[BMIM][C(CN)$_3$]	2-15 wt%	362.18-404.6	-	[145]
	[BMIM][OAc]	39.41 wt%	308.15	-	[146]
D-(+)-glucose	[BMIM][OTf]	16.1-88.9 mol %	298.5-365.3	PC-SAFT	[85]
D-(+)-glucose	[BMIM][HSO$_4$]	2-50.2 wt%	350.9-384.8	-	[145]
	[BMIM][C$_4$F$_9$SO$_3$]	2-5 wt%	401.13-422.17	-	[145]
	[EMIM][SCN]	6-40 wt%	283.15-345.95	-	[148]
	[EMIM][N(CN)$_2$]	17.1-28.1 wt%	288.25-328.25	NRTL, UNIQUAC	[86]
	[EMIM][OAc]	43.89 wt%	308.15	-	[146]
	[EMIM][OTf]	26.1-34.9 wt%	288.47-329.07	NRTL, UNIQUAC	[86]
	[EMIM][EtSO$_4$]	10.4-23.7 wt%	288.2-328.3	NRTL, UNIQUAC	[147]
	[EMIM][(MeO)(EtO)EtOSO$_3$]	2.4-33.9 wt%	328.33-393.37	-	[145]
	[DMIM][BF$_4$]	0.44 wt%	308.15	-	[146]
	[DMIM][CH$_3$PO$_3$]	5-60 wt%	285.15-360.25	-	[148]

Carbohydrate	Ionic liquid	Solubility	Temperature [K]	Modeling	Ref.
	[C2OHMIM][Cl]	12-58 wt%	355.15-370.35	-	[148]
	[C5O2MIM][Cl]	29.28 wt%	308.15	-	[146]
	[C5O2MIM][N(CN)$_2$]	19.01 wt%	308.15	-	[146]
	[C5O2MIM][SCN]	18.38 wt%	308.15	-	[146]
	[C5O2MIM][SAC]	18.97 wt%	308.15	-	[146]
	[C5O2MIM][ACES]	14.39 wt%	308.15	-	[146]
	[Aliquat][Cl]	2.26 wt%	308.15	-	[146]
	[Aliquat][NO$_3$]	3.93-8.65 wt%	307.75-339.75	NRTL, UNIQUAC	[86]
	[Aliquat][N(CN)$_2$]	0.78-3.23 wt%	299.95-339.74	NRTL, UNIQUAC	[86]
	[Aliquat][N(CN)$_2$]	1.25 wt%	308.15	-	[146]
	[Aliquat][OAc]	4.05 wt%	308.15	-	[146]
	[Aliquat][Cl]	9-12.5 wt%	297.9-327.9	NRTL, UNIQUAC	[147]
	[P$_{6,6,6,14}$][Cl]	4.69 wt%	308.15	-	[146]
	[P$_{6,6,6,14}$][N(CN)$_2$]	0.18-0.48 wt%	298.37-329.21	NRTL, UNIQUAC	[86]
	[P$_{6,6,6,14}$][N(CN)$_2$]	0.5 wt%	308.15	-	[146]
	[P$_{6,6,6,14}$][OAc]	4.9 wt%	308.15	-	[146]
	[P$_{4,4,4,1}$][CH$_3$C$_6$H$_4$SO$_2$]	2-15.4 wt%	365.29-392.89	-	[145]
	[(C$_3$O)$_4$DMG][Cl]	38.58 wt%	308.15	-	[146]
	[(C$_3$O)$_4$DMG][SCN]	11.34 wt%	308.15	-	[146]
	[(C$_3$O)$_4$DMG][N(CN)$_2$]	6.19 wt%	308.15	-	[146]
	[(C$_3$O)$_4$DMG][OAc]	31.73 wt%	308.15	-	[146]
	[(C$_3$O)$_4$DMG][SAC]	20.59 wt%	308.15	-	[146]
	[(C$_3$O)$_4$DMG][ACES]	8.44 wt%	308.15	-	[146]
	[(di-h)$_2$DMG][Cl]	6.61 wt%	308.15	-	[146]
	[(di-h)$_2$DMG][SCN]	1.95 wt%	308.15	-	[146]
	[(di-h)$_2$DMG][N(CN)$_2$]	2.88 wt%	308.15	-	[146]
	[(di-h)$_2$DMG][OAc]	14.4 wt%	308.15	-	[146]
	[(di-h)$_2$DMG][SAC]	3.66 wt%	308.15	-	[146]
	[(di-h)$_2$DMG][ACES]	2.27 wt%	308.15	-	[146]
D-(+)-xylose	[BMIM][SCN]	2-45.1 wt%	288.93-388.08	-	[145]
	[BMIM][C(CN)$_3$]	3.1-20 wt%	351.57-390.04	-	[145]
	[BMIM][C$_4$F$_9$SO$_3$]	2-10.5 wt%	382.84-408.5	-	[145]

Carbohydrate	Ionic liquid	Solubility	Temperature [K]	Modeling	Ref.
	[BMIM][HSO$_4$]	2-50 wt%	349.58-380.18	-	[145]
	[EMIM][EtSO$_4$]	15-27.41 wt%	288.1-328.5	NRTL, UNIQUAC	[147]
	[EMIM][(MeO)(EtO)EtOSO$_3$]	2.1-29.9 wt%	325-387.26	-	[145]
	[Aliquat][Cl]	12.6-16.7 wt%	298.5-330	NRTL, UNIQUAC	[147]
	[P$_{4,4,4,1}$][CH$_3$C$_6$H$_4$SO$_2$]	1.8-20 wt%	350.16-395.46	-	[145]

Table 19. Solubility of monosaccharides in ILs

The ability to predict whether a given IL dissolves a particular carbohydrate or not is of outmost interest. There are several empirical and semi-empirical measuring techniques and polarity scales that can predict and explain the solubility of carbohydtares in a solution, e.g. COSMO-RS, Hansen solubility parameters and Kamlet-Taft solvent parameters [41]. The empirical Kamlet–Taft model [67,79] and the quantum mechanical COSMO-RS model [151-153] have been used most frequently to predict or explain the solubility of carbohydrates in ILs, while few literature data exist for Hansen solubility parameters of ionic liquids [154]. The Kamlet-Taft parameters (α, hydrogen bond acidity; β, hydrogen bond basicity; and π^*, polarity) are determined by measuring the UV-VIS spectra of dyes when dissolved in a solvent of interest. It was suggested that solubility of carbohydrates increases with an increase of ILs basicity (ILs that are capable of dissolving carbohydrates are generally characterized by high hydrogen-bond basicity parameter; $\beta > 0.8$), and polarity [41,56,74,119,126,144,148]. The potential of COSMO-RS-based screening of ILs with respect to their dissolving power for cellulose was evaluated in the pioneer research of Kahlen et al. [151]. Cellulose solubility was modeled for more than 2000 ILs using activity coefficients as reference property and the results were in good agreement with the data available in the literature. Later on, the work was extended to the computational COSMO-RS analysis of the affinity of both cellulose and lignin for 320 different ILs [153]. A new reference property, namely the excess enthalpy of the IL + lignin/cellulose mixtures, was used to predict solubilites of lignin and cellulose in ILs. The conclusions achieved were validated in the laboratory for a selected set of ILs. The ability of more than 20 hydrophilic ILs to dissolve Miscanthus was also interpreted using Abraham solvation parameters obtained from COSMO-RS [151]. In case of smaller carbohydrates, Carneiro et al. were the first group to correlate the solubility data of monosaccharides in ILs using the NRTL and UNIQUAC thermodynamic models [147]. They investigated solubility of D-(+)-glucose, D-(−)-fructose, D-(+)-xylose and D-(+)-galactose in two ILs: [Aliquat][Cl] and [EMIM][EtSO$_4$]. Following their success, other works on application of NRTL and UNIQUAC thermodynamic models for correlation of solubilities of glucose [86,148,144], fructose [86,144], sucrose and lactose [144] have been reported. Very recently, perturbed-chain statistical associating fluid theory (PC-SAFT) was applied to model experimental data on solubility of glucose, fructose and sucrose [85,154,155].This approach occurred to be more promising since it showed better predictive capacity and quite reasonable accuracy. As an equation-of-state model, it enables

the capture of properties of both pure fluids and mixtures. Although some data concerning solubility of carbohydrates in ILs is already available in the literature, it is not sufficient to have a good knowledge of phase equilibra. These investigations cover essentially only the most well-known sugars, glucose, fructose, and sucrose, as well as polysaccharides such as cellulose. In most cases, data are measured by using different experimental procedures and contain single data points at fixed temperature. It makes application of existent or the development of new thermodynamic models a very difficult task. Moreover, solubility of carbohydrates in ILs is sensitive to the presence of impurities, especially water, and even though authors do not report on the water content. ILs have provided a new processing platform for the dissolution, regeneration and functionalization of carbohydrates, thus increasing their chances of exploitation. However, for the purpose of successful process design and optimization, more reliable data on solubility of various carbohydrates in ILs is fundamental.

5. Solubility of specific polymers and macromolecules in ionic liquids

Concerning other classes of polymers and macromolecules, the use of Ionic Liquids represents real challenges in order to solubilize those allowing future modifications and depolymerization in the constitutive monomers.

Wang et al reported the possibility to dissolve and regenerate polybenzimidazole in 1-butyl-3-methylimidazolium chloride, [BMIM][Cl] and other hydrophilic ionic liquids [156]. The authors describe ionic liquids as alternative solvents for dissolution of different organic polymers. Polybenzimidazole (PBI), also known as poly-2,20-(mphenylene)-5,50-bibenzimidazole), is a polymer composed by linear aromatic polymer chains as well as both donor and acceptor hydrogen-bonding sites. This class of polymers exhibits high thermal stabilities, chemical resistance, and mechanical strength [157]. According with their relevant properties, PBI has been developed as membranes [158], textile fibers [159], and high-temperature matrix resins [160]. One of the problems associated with PBI and similar polymers is their poor solubility and infusibility in common organic solvents. PBI is only soluble after heating highly polar aprotic solvents such as dimethylformamide, dimethylacetamide or dimethyl sulfoxide. The authors described that PBI was insoluble for all tested solvents at room temperature but it was completely soluble in [BMIM][Cl] and [BMIM][OH] yielding brown viscous solutions at 80 to 140ºC. It is important to note that PBI was four times more soluble in [BMIM][Cl] or [BMIM][OH] at 140ºC than in DMAc (+ 4.5 wt% LiCl) as solvent. The possibility to use a microwave process showed a significant improvement in the dissolution rates as well as an efficient heating of ILs [161,162]. However, ILs having 'non-coordinating' anion like BF_4 was non-effective solvent even with microwave heating. The dissolving mechanism of PBI in ILs is not clear but some publications suggested the use of [BMIM][Cl] due an effective hydrogen-bonding breaking, allowing faster dissolution times as well as higher ability to dissolve PBI. For comparison, [BMIM][Cl] presents almost 3 times higher chloride concentration (around 20 mol%) than in the case of conventional DMAc (+ 10 wt% LiCl; free chloride concentration is around 6.7 mol%) solvent. For complete elucidation of dissolution mechanism of different polymers in ionic liquids is important to perform other dissolution studies and complementary

techniques which can validate the previous proposals. Wang and co-workers reported a similar dissolution mechanism in the case of [BMIM][OH] as well as the use of this IL in order to prepare PBI-based anion-exchange gel electrolyte membranes for alkaline fuel cells. Another attractive point is related with the possibility to precipitate or regenerate PBI from the IL solution by addition of water or other precipitating solutions. The regenerated PBI fibers show no change in chemical structure and thermal stability comparing with fibers formed by conventional systems.

Watanabe and co-workers reported the solubility of poly(methyl methacrylate) (PMMA) in 1-alkyl-3-methylimidazolium ionic liquids (ILs) with different anionic structures [163]. For evaluation of PMMA solubility in ILs were tested monodisperse PMMA-grafted silica nanoparticles (PMMA-g-NPs) as a measurement probe. The solubility was mainly affected by the anionic structures of the ILs rather than by the alkyl chain length of the cationic structure. It is empirically known that PMMA is soluble in hydrophobic ILs such as [BMIM][PF$_6$] and [BMIM][NTf$_2$].[164,165] Previously, Watanabe group reported different hydrodynamic radii exhibited by PMMA-grafted silica nanoparticles (PMMA-g-NPs) in these ILs. Additionally, the grafted PMMA chain was more swollen in [BMIM][NTf$_2$] than in [BMIM][PF$_6$] [166] suggesting that [BMIM][NTf$_2$] is a better solvent for PMMA. In conclusion, PMMA solubility in relation to the solvent parameters of the ILs, it is focused in two important factors in order to predict PMMA solubility in ILs. The predominant one is the nonpolar properties of the anion. However, the non-polarity cation IL effect can also contribute for overall PMMA solubility. In general, the PMMA solubility is dependent of two relevant contributions: one from anionic unit (primary) and other from cationic unit (secondary) nonpolarity. The authors considered that the solubility behavior could not be justified by ILs solvent because of complexity in ILs. All published results can contribute for future predictions of PMMA derivatives solubility's such as polyacrylates or polymethacrylates. Wang and Liang groups [167] described a detailed study of the solubility and chain conformation of different types of homopolymers in low viscosity ionic liquids (ILs) in particular 1-allyl-3-methylimidazolium chloride ([AMIM][Cl]) at 50ºC and 1-butyl-3-methylimidazolium formate ([BMIM][COOH]) at 25ºC using laser light scattering technique (LLS). This technique allows the polymer solubility determination in ILs at low concentrations. The study of polymer and IL systems by LLs is restricted to higher IL viscosities as well as the slow diffusion of polymer chains in IL and water content or other impurities from ILs. Normally, selected ILs are hygroscopic and the water content changes with time. The aggregation effect was observed for all neutral tested polymers (e.g. polyvinyl alcohol and polysulfonamide), except in the case of polyvinyl alcohol in [BMIM][COOH]. Single chain conformations have been observed in the case of DNA and polystyrene sulfonate as negative polyelectrolytes. The authors suggested the condensation of the polymer chains in ILs according with their smaller hydrodynamic polymer radius. In general, the solubility of homopolymers could be qualitatively explained by treating polymer/IL as a ternary system: polymer, cation, and anion. The authors suggested that mutual interactions determined the polymer conformation and solubility in ILs. However, preliminary results indicated us those strong interactions between polymers and bulky cations in ILs are relevant for higher dissolution performance. Several publications proof an effective dissolution of different synthetic polymers in ILs (for example poly(ethylene oxide) (PEO) [168],

poly(methyl methacrylate) [169], polyacrylonitrile [170], poly(m-phenylene isophthal amide) [171], and polyarylsulfone [172]) while many others (e.g. polyethylene, polyester, polyurethane, and nylon) were not soluble in the tested ILs.

In different perspective, efficient polymerization processes as well as preparation of specific polymeric materials using ILs have been also described. In this context, Zhang and co-workers [173] reported the polymerization of acrylonitrile in the presence of [BMIM][Cl] and then for the first time polyacrylonitrile fibers were directly produced from spinning process of the previous polymer solution. According to remarkable acrylic fibers properties (in particular soft and wool-like aesthetics and resistance ultraviolet fading) different fields of application (e.g. home furnishings, outdoor articles, aviation and space fields). From 1980s the wet and dry spinning technologies have been used as most effective processes for PAN fibers production. [174] For wet and dry spinning processes, the use of large amounts of unfriendly solvents to the environment have been required.

It seems that [BMIM][Cl] is a suitable solvent for the polymerization, spinning and dissolution of the acrylic fibers. In this context, different acrylic polymers with tunable properties (higher concentration of acrylonitrile, large molecular weight, and low polydispersitive index PDI). The solutions of PAN and [BMIM][Cl] allowed the development of PAN fibers containing good mechanical properties and round profile after efficient spun using dry–jet wet spinning technology.

In 2009, Rodriguez et al [175] reported that 1-alkyl-3-methylimidazolium chloride ionic liquids (ILs) can form immiscible liquid mixtures with some polyethylene glycols (PEGs). PEGs have been largely used in industry because of their reduced toxicity and cost as well as higher biodegradability. [176] Additionally low volatility and melting points of PEGs facilitate their use as alternative solvents or additives in several aqueous biphasic systems. [177] Many publications indicate the possibility to tune PEG properties as relevant characteristic (for example PEGs with shorter chain lengths are liquid at room temperature and water miscible while PEGs with longer chain lengths melt at higher temperatures and with variable water solubility.
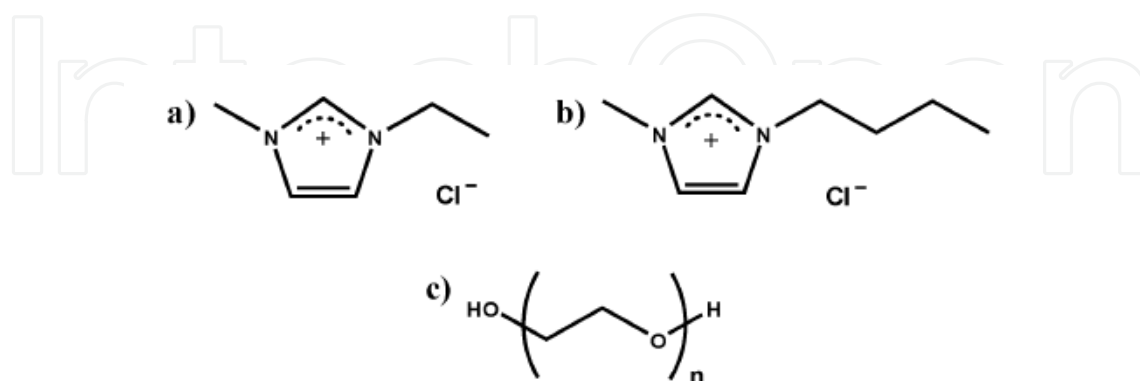
Figure 3. Selected chemical structures: a) [EMIM][Cl]; b) [BMIM][Cl]; c) PEG (PEG-1500)

Recently, PEGs and ILs have been combined for application as polymer electrolytes in batteries, [178] or, homogeneous mixed solvents with distinctive properties. [179] Binary

mixtures between [EMIM][Cl] and PEGs (PEG-1500, 2000, or 3400), or [BMIM][Cl] and PEGs (PEG-2000 or 3400) giving stable biphasic systems over a significant temperature range (from 333.15 K to 413.15 K). [EMIM][Cl]/ PEG-1000 and [BMIM][Cl]/PEG-1000 or PEG-1500 are miscible. Negative values for the change of enthalpy and entropy of IL/PEG mixtures have been observed by thermodynamic analysis of the liquid–liquid equilibrium data. The possible tunability according with adequate IL/PEG combinations could be applied for separation of complex solutes by solvent extraction processes at high temperature. The authors tried applied these biphasic, entirely liquid systems, with low volatility and good solvation properties, for the dissolution and separation of cellulose and lignin at elevated temperature, although only modest results have been achieved to date. Samitsu et al [180] reported the dissolution behavior of polyrotaxanes, consisting of alfa-cyclodextrin and poly(ethylene glycol), with different molecular weights (2000 and 35.000).

Harada et al. and other authors reported some polyrotaxanes, containing alfa-cyclodextrins (α-CD) as the cyclic molecules and poly(ethylene glycol) (PEG) as a linear polymer. [181, 182] Polyrotaxanes have been largely applied in different fields, in particular drug delivery systems for biological applications [183], insulated molecular wires [184] and photo-induced energy transfer systems for electrical applications. [185] Interlocked polymer networks built from polyrotaxanes have been also tested as gels and rubbery materials for industrial applications.

Several studies reported polyrotaxane solubilities in several ionic liquids mainly based on 1-butyl-3- methylimidazolium cation [BMIM] combined with different anions (e.g. [Cl], [Br], [BF$_4$], [PF$_6$], [NTf$_2$], and [MDEGSO$_4$]). Transparent homogeneous solutions were obtained in the case of addition of polyrotaxanes to ILs [BMIM][Cl] and [BMIM][Br]. The solubility results indicate that the polyrotaxanes are readily soluble in [BMIM][Cl] and [BMIM][Br] but not in the other tested ionic liquids. Recently, the dissolution performance were studied using ILs containing chloride anions and a variety of organic cations including [EMIM], [BMIM], [HMIM], [OMIM], [C$_{10}$MIM]. Transparent homogeneous solutions were obtained for the dissolution of polyrotaxanes in all tested ILs.

IL + PEG System	W$_{IL}$, PEG-rich phase	W$_{IL}$, IL-rich phase
[EMIM][Cl] + PEG-1500	0.17-0.27	0.88-0.97
[EMIM][Cl] + PEG-2000	0.08-0.14	0.94-0.99
[EMIM][Cl] + PEG-3400	0.02-0.06	0.95-0.98
[BMIM][Cl] + PEG-2000	0.32-0.38	0.86-0.93
[BMIM][Cl] + PEG-3400	0.09-0.16	0.83-0.99

Table 20. Variation of mass fraction of IL (W$_{IL}$) in the equilibrium phases for the LLE of the binary systems IL +PEG over the temperature range 60- 140 ºC.

The solubilities of two polyrotaxanes in ILs as well as the α-CD and PEG solubilities for comparison are summarize in Table 21

Ionic Liquids	PR-A	PR-B	α-CD	PEG 35.000
[BMIM][Cl]	+	+	+	+
[BMIM][Br]	+	+	+	+
[BMIM][BF$_4$]	-	-	-	-
[BMIM][PF$_6$]	-	-	-	-
[BMIM][NTf$_2$]	-	-	-	+
[BMIM][MDEGSO$_4$]	-	-	+	-
[EMIM][Cl]	+	+	+	+
[HMIM][Cl]	+	+	+	+
[OMIM][Cl]	+	+	+	+
[C$_{10}$MIM][Cl]	+	+	+	+

Table 21. Solubility of Polyrotaxanes (PR-A and PR-B), α-CD and PEG

As shown in Table 21, ILs are good solvents for both α-CD and PEG, in particular for the cases of ILs with chloride and bromide anions. The same halogenated ILs showed an effective solubilization of polyrotaxanes at room temperature. Both PR-A and PR-B (1 wt %) could be dissolved in ILs [HMIM][Cl], [OMIM][Cl], and [C$_{10}$MIM][Cl] at room temperature after 2 days of stirring. In general, ILs can dissolve polyrotaxanes at room temperature, but this dissolution process is slower because higher IL viscosity values (the viscosity of DMSO is 1.98 mPa.s at 25ºC, while the viscosities of [HMIM][Cl] and [OMIM][Cl] are 10.222 and 33.060 mPa.s at 25ºC). Polyrotaxanes dissolved in ILs can be recovered by precipitation after simple addition of organic solvents or water to solution. The authors reported the use of ILs as new solvents for polyrotaxanes in order to develop ionic liquid-containing slide-ring gels (SR gels), that is supramolecular networks of polyrotaxane swollen with ILs, using an integrative non-drying technique followed by optimized solvent exchange method.

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References

[1] Yang J-Z., Wang B., Zhang Q-G., Tong J. Study on solid-liquid phase equilibria in ionic liquid 1. The solubility of alkali chloride (MCl) in ionic liquid EMISE. Fluid Phase Equilibria 2007;251 68-70.

[2] Wang B., Zhang Q-G., Yang J-Z. Study on solid-liquid phase equilibria in ionic liquid 2. The solubility of alkali bromide in ionic liquid 1-ethyl-3-methylimidazolium ethyl sulfate. Fluid Phase Equilibria 2007; 254 163-166.

[3] Branco L. C., Rosa J. N., Moura Ramos J. J., Afonso C. A. M. Preparation and Characterization of New Room Temperature Ionic Liquids. Chemistry European Journal 2002;8 3671-3677.

[4] Dotterl M., Haas I., Alt H. G. Solubility Behaviour of TiCl4, ZrCl4 and HfCl4 in chloroaluminate ionic liquids. Zeitschrift für anorganische und allgemeine Chemie 2011;637 1502-1506.

[5] Rosol Z. P., German N. J., Gross S. M. Solubility, ionic conductivity and viscosity of lithium salts in room temperature ionic liquids. Green Chemistry 2009;11 1453-1457.

[6] Atakilt A., Admassie S., Villar-Garcia I. J., Chebude Y. 4,4-Bipyridinium ionic liquids exhibiting excellent solubility for metal salts: Potential solvents for electrodeposition. Inorganic Chemistry Communications. 2013;29 210-212.

[7] Pereiro A. B., Araújo, J. M. M., Oliveira F. S., Esperança J. M. S. S., Canongia Lopes J. N., Marrucho I. M. Solubility of inorganic salts in pure ionic liquids. Journal of Chemical Thermodynamics 2012;55 29-36.

[8] Li H., Li D., Wang Y., Ru Q. A series of carboxylic-functionalized ionic liquids and their solubility for lanthanide oxides. Chemistry Asian Journal. 2011;6 1443-1449.

[9] Villar-Garcia I. J., Abebe A., Chebude T. 1,10-Phenantrolinium ionic liquids exhibiting excellent solubility for metal complexes: Potential solvents for biphasic and supported ionic liquid phase. Inorganic Chemistry Communications. 2012;19 1-3.

[10] Yang Y., Yu L. Theoretical investigations of ferrocene/ferrocenium solvation in imidazolium-based room-temperature ionic liquids. Physical Chemistry Chemical Physics. 2013;15 2669-2683.

[11] Boros E., Earle M. J., Gilea, M. A., Metlen A., Mudring A-V., Rieger F., Robertson A. J., Seddon K. R., Tomaszowsksa, A. A. Trusov L., Vyle J. S. On the dissolution of non-metallic solid elements (sulfur, selenium, tellurium and phosphorous) in ionic liquids. Chemical Communications. 2010;46 716-718.

[12] Chen Y., Tarascon J-M., Guery C., Exploring sulfur solubility in ionic liquids for the electrodeposition of sulfide films with their electrochemical reactivity toward lithium. Electrochimica Acta. 2013;99 46-53.

[13] Marrucho, I. M.; Branco, L. C.; Rebelo, L. P. N. Ionic liquids in pharmaceutical applications. Annual review of chemical and biomolecular engineering 2014, 5, 527-546.

[14] Tucker, J. L. Green chemistry, a pharmaceutical perspective. Organic Process Research & Development 2006, 10, 315-319.

[15] Siodmiak, T.; Marszall, M. P.; Proszowska, A. Ionic Liquids: A New Strategy in Pharmaceutical Synthesis. Mini-Reviews in Organic Chemistry 2012, 9, 203-208.

[16] Earle, M. J.; McCormac, P. B.; Seddon, K. R., The first high yield green route to a pharmaceutical in a room temperature ionic liquid. Green Chemistry 2000, 2, 261-262.

[17] Jaitely, V.; Karatas, A.; Florence, A. T. Water-immiscible room temperature ionic liquids (RTILs) as drug reservoirs for controlled release. International Journal of Pharmaceutics 2008, 354, 168-173.

[18] Mizuuchi, H.; Jaitely, V.; Murdan, S.; Florence, A. T. Room temperature ionic liquids and their mixtures: Potential pharmaceutical solvents. European Journal of Pharmaceutical Sciences 2008, 33, 326-331.

[19] Patel, R.; Kumari, M.; Khan, A. B., Recent Advances in the Applications of Ionic Liquids in Protein Stability and Activity: A Review. Applied Biochemistry and Biotechnology 2014, 172, 3701-3720.

[20] Freire, M. G.; Claudio, A. F. M.; Araujo, J. M. M.; Coutinho, J. A. P.; Marrucho, I. M.; Canongia Lopes, J. N.; Rebelo, L. P. N., Aqueous biphasic systems: a boost brought about by using ionic liquids. Chemical Society Reviews 2012, 41, 4966-4995

[21] Tang, B.; Bi, W.; Tian, M.; Row, K. H., Application of ionic liquid for extraction and separation of bioactive compounds from plants. Journal of Chromatography B-Analytical Technologies in the Biomedical and Life Sciences2012, 904, 1-21

[22] Ventura, S. P. M.; Goncalves, A. M. M.; Sintra, T.; Pereira, J. L.; Goncalves, F.; Coutinho, J. A. P. Designing ionic liquids: the chemical structure role in the toxicity. Ecotoxicology 2013, 22, 1-12

[23] Sun, P.; Armstrong, D. W. Ionic liquids in analytical chemistry. Analytica Chimica Acta 2010, 661, 1-16.

[24] Bogel-Lukasik, R.; Nobre Goncalves, L. M.; Bogel-Lukasik, E., Phase equilibrium phenomena in solutions involving tannins, flavonoids and ionic liquids. Green Chemistry 2010, 12, 1947-1953.

[25] Alevizou, E. I.; Voutsas, E. C., Solubilities of p-coumaric and caffeic acid in ionic liquids and organic solvents.Journal of Chemical Thermodynamics 2013, 62, 69-78.

[26] Carneiro, A. P.; Rodriguez, O.; Macedo, E. A., Solubility of xylitol and sorbitol in ionic liquids - Experimental data and modeling. Journal of Chemical Thermodynamics 2012, 55, 184-192

[27] Smith, K. B.; Bridson, R. H.; Leeke, G. A., Solubilities of Pharmaceutical Compounds in Ionic Liquids. Journal of Chemical and Engineering Data 2011, 56, 2039-2043.

[28] Forte, A.; Melo, C. I.; Bogel-Lukasik, R.; Bogel-Lukasik, E., A favourable solubility of isoniazid, an antitubercular antibiotic drug, in alternative solvents. Fluid Phase Equilibria 2012, 318, 89-95.

[29] Lourenco, C.; Melo, C. I.; Bogel-Lukasik, R.; Bogel-Lukasik, E., Solubility Advantage of Pyrazine-2-carboxamide: Application of Alternative Solvents on the Way to the Future Pharmaceutical Development. Journal of Chemical and Engineering Data 2012, 57, 1525-1533.

[30] Melo, C. I.; Bogel-Lukasik, R.; da Ponte, M. N.; Bogel-Lukasik, E., Ammonium ionic liquids as green solvents for drugs. Fluid Phase Equilibria 2013, 338, 209-216.

[31] dos Santos, A. D.; Morais, A. R. C.; Melo, C.; Bogel-Lukasik, R.; Bogel-Lukasik, E., Solubility of pharmaceutical compounds in ionic liquids. Fluid Phase Equilibria 2013, 356, 18-29.

[32] Manic, M. S.; Najdanovic-Visak, V., Solubility of erythromycin in ionic liquids. Journal of Chemical Thermodynamics2012, 44, 102-106.

[33] de Azevedo, J. R.; Letourneau, J.-J.; Espitalier, F.; Re, M. I., Solubility of a New Cardioactive Prototype Drug in Ionic Liquids. Journal of Chemical and Engineering Data 2014, 59, 1766-1773.

[34] Clark J. H. Green chemistry for the second generation biorefinery - sustainable chemical manufacturing based on biomass. Journal of Chemical Technology and Biotechnology 2007; 82(7) 603–609.

[35] Corma A., Iborra S., Velty A. Chemical Routes for the Transformation of Biomass into Chemicals. Chemical Reviews 2007; 107(6) 2411–2502.

[36] [36] Kumar P., Barrett D. M., Delwiche M. J., Stroeve P. Methods for Pretreatment of Lignocellulosic Biomass for Efficient Hydrolysis and Biofuel Production. Industrial and Engineering Chemistry Research 2009; 48(8) 3713–3729

[37] Tadesse H., Luque R. Advances on biomass pretreatment using ionic liquids: An overview. Energy and Environmental Science 2011; 4(10) 3913-3929

[38] Mäki-Arvela P., Anugwom I., Virtanen P., Sjöholm R., Mikkola J.P. Dissolution of lignocellulosic materials and its constituents using ionic liquids—A review Industrial Crops and Products 2010; 32(3) 175–201

[39] Sun N., Rodríguez H., Rahman M., Rogers R. D. Where are ionic liquid strategies most suited in the pursuit of chemicals and energy from lignocellulosic biomass? Chemical Communications 2011; 47(5) 1405–1421

[40] Vancov T, Alston A S, Brown T, McIntosh S Use of ionic liquids in converting lignocellulosic material to biofuels Renewable Energy 2012; 45 1 - 6

[41] Brandt A., Gräsvik J., Halletta J. P., Welton T. Deconstruction of lignocellulosic biomass with ionic liquids. Green Chemistry 2013; 15(3) 550-583.

[42] da Costa Lopes A. M., João K. G., Morais A.R.C., Bogel-Łukasik E., Bogel-Łukasik R Ionic liquids as a tool for lignocellulosic biomass fractionation. Sustainable Chemical Processes 2013; 1(3) 1-31.

[43] Swatloski R.P., Spear S.K.H., Rogers R.D. Dissolution of Cellose with Ionic Liquids. Journal of the American Chemical Society 2002; 124(18) 4974–4975.

[44] Zakrzewska M. E., Bogel-Łukasik E., Bogel-Łukasik R. Solubility of Carbohydrates in Ionic Liquids. Energy and Fuels 2010; 24(2) 737–745.

[45] Murugesan S., Linhardt R. J. Ionic liquids in carbohydrate chemistry – current trends and future directions. Current Organic Synthesis 2005; 2(4) 437-451.

[46] El Seoud O. A., Koschella A., Fidale L. C., Dorn S., Heinze T. Applications of Ionic Liquids in Carbohydrate Chemistry: A Window of Opportunities. Biomacromolecules 2007; 8(9) 2629–2647

[47] Zakrzewska M. E., Bogel-Łukasik E., Bogel-Łukasik R. Ionic Liquid-Mediated Formation of 5-Hydroxymethylfurfurals – Promising Biomass-Derived Building Block. Chemical Reviews 2011; 111(2) 397–417

[48] Wang H., Gurau G., Rogers R.D. Ionic liquid processing of cellulose. Chemical Society Reviews 2012; 41(4) 1519-1537

[49] Ohno H., Fukaya Y. Task specific ionic liquids for cellulose technology. Chemistry Letters 2009; 38(1) 1-7

[50] Liebert T., Heinze T. Interaction of ionic liquids with polysaccharides 5. Solvents and reaction media for the modification of cellulose. BioResources 2008; 3(2) 576–601.

[51] Cao Y., Wu J., Zhang J., Li H. Q., Zhang Y., He J. S. Room temperature ionic liquids (RTILs): A new and versatile platform for cellulose processing and derivatization. Chemical Engineering Journal 2009; 147(1), 13–21.

[52] Feng L., Chen Z. Research progress on dissolution and functional modification of cellulose in ionic liquids. Journal of Molecular Liquids 2008; 142(1-3) 1–5.

[53] Pinkert A., Marsh K. N., Pang S., Staiger M. P. Ionic Liquids and Their Interaction with Cellulose. Chemical Reviews 2009; 109(12) 6712–6728.

[54] Pinkert A., Marsh K.N., Pang S. Reflections on the Solubility of Cellulose. Industrial and Engineering Chemistry Research 2010; 49(22) 11121–11130.

[55] Sellin M., Ondruschka B., Stark A. Hydrogen Bond Acceptor Properties of Ionic Liquids and Their Effect on Cellulose Solubility. ACS Symposium Series 2010; 1033(6) 121–135.

[56] Xu A., Wang J., Wang H. Effects of anionic structure and lithium salts addition on the dissolution of cellulose in 1-butyl-3-methylimidazolium-based ionic liquid solvent systems. Green Chemistry 2010; 12(2) 268–275.

[57] Brandt A., Hallett J. P., Leak D. J., Murphy R. J. Welton T. The effect of the ionic liquid anion in the pretreatment of pine wood chips. Green Chemistry 2010;12(4) 672-679.

[58] Remsing R. C., Swatloski R. P., Rogers R. D., Moyna G. Mechanism of cellulose dissolution in the ionic liquid 1-n-butyl-3-methylimidazolium chloride: a 13C and 35/37Cl NMR relaxation study on model systems. Chemical Communications 2006; 28(12) 1271–1273.

[59] Moulthrop J. S., Swatloski R. P., Moyna G., Rogers R. D. High-resolution 13C NMR studies of cellulose and cellulose oligomers in ionic liquid solutions. Chemical Communications 2005; 28(12) 1557–1559.

[60] Remsing R. C., Hernandez G., Swatloski R. P., Massefski W. W., Rogers R. D., Moyna, G. Solvation of Carbohydrates in N,N′-Dialkylimidazolium Ionic Liquids: A Multinuclear NMR Spectroscopy Study. Journal of Physical Chemistry B 2008; 112(35) 11071-11078.

[61] Liu H., Sale K.L., Holmes B.M., Simmons B.A., Singh S. Understanding the Interactions of Cellulose with Ionic Liquids: A Molecular Dynamics Study. Journal of Physical Chemistry B 2010; 114(12) 4293–4301

[62] Gross A.S., Bell A.T., Chu J.-W. Thermodynamics of Cellulose Solvation in Water and the Ionic Liquid 1-Butyl-3-Methylimidazolim Chloride. Journal of Physical Chemistry B 2011; 115(46) 13433–13440.

[63] Youngs T. G. A., Holbrey J. D., Deetlefs M., Nieuwenhuyzen M., Costa Gomes M. F., Hardacre C. A Molecular Dynamics Study of Glucose Solvation in the Ionic Liquid 1,3-Dimethylimidazolium Chloride. ChemPhysChem 2006; 7(11), 2279–2281

[64] Youngs T.G.A., Holbrey J.D., Mullan C.L., Norman S.E., Lagunas M.C., D'Agostino C., Mantle M.D., Gladden L.F., Bowron D.T., Hardacre C. Neutron diffraction, NMR and molecular dynamics study of glucose dissolved in the ionic liquid 1-ethyl-3-methylimidazolium acetate. Chemical Science 2011; 2(8) 1594-1605.

[65] Youngs T. G. A., Hardacre C., Holbrey J. D. Glucose Solvation by the Ionic Liquid 1,3-Dimethylimidazolium Chloride: A Simulation Study Journal of Physical Chemistry B 2007; 111(49) 13765-13774.

[66] Guo J., Zhang D., Duan C., Liu C. Probing anion-cellulose interactions in imidazolium-based room temperature ionic liquids: a density functional study. Carbohydrate Research 2010; 345(15) 2201-2205.

[67] Fukaya Y., Hayashi K., Wada M., Ohno H. Cellulose dissolution with polar ionic liquids under mild conditions: required factors for anions. Green Chemistry 2008; 10(1) 44–46

[68] Vitz J., Erdmenger T., Haensch C., Schubert U. S. Extended dissolution studies of cellulose in imidazolium based ionic liquids. Green Chemistry 2009; 11(3) 417–424.

[69] Feng L., Chen Z., Research progress on dissolution and functional modification of cellulose in ionic liquids. Journal of Molecular Liquids 2008; 142(1-3) 1.

[70] Lindman B., Karlström G., Stigsson L. On the mechanism of dissolution of cellulose. Journal of Molecular Liquids 2010; 156(1) 76–81.

[71] Zhang J., Zhang H., Wu J., Zhang J., He J., Xiang J. NMR spectroscopic studies of cellobiose solvation in EmimAc aimed to understand the dissolution mechanism of cellulose in ionic liquids. Physical Chemistry Chemical Physics 2010; 12(8) 1941–1947,

[72] Remsing R. C., Petrik I. D., Liu Z., Moyna G. Comment on "NMR spectroscopic studies of cellobiose solvation in EmimAc aimed to understand the dissolution mechanism of cellulose in ionic liquids Physical Chemistry Chemical Physics 2010; 12(44) 14827-14828.

[73] Zhang J., Zhang H., Wu J., Zhang J., He J., Xiang J. Reply to "Comment on 'NMR spectroscopic studies of cellobiose solvation in EmimAc aimed to understand the dissolution mechanism of cellulose in ionic liquids'" Physical Chemistry Chemical Physics 2010; 12(44) 14829-14830.

[74] Lu B., Xu A., Wang J. Cation does matter: how cationic structure affects the dissolution of cellulose in ionic liquids. Green Chemistry 2014; 16(3) 1326-1335.

[75] Novoselov N. P., Sashina E. S., Petrenko V. E., Zaborsky M. Study of Dissolution of Cellulose in Ionic Liquids by Computer Modelling. Fibre Chemistry 2007; 39(2) 153–158.

[76] Heinze T., Dorn S., Schöbitz M., Liebert T., Köhler S. Meister F. Interactions of Ionic Liquids with Polysaccharides – 2: Cellulose. Macromolecular Symposia 2008; 262(1) 8–22.

[77] Ebner G., Schiehser S., Potthast A., Rosenau T. Side reaction of cellulose with common 1-alkyl-3-methylimidazolium-based ionic liquids. Tertahedron Letters 2008; 49(51) 7322-7324.

[78] Zhang H., Wu J., Zhang J., He J. 1-Allyl-3-methylimidazolium Chloride Room Temperature Ionic Liquid: A New and Powerful Nonderivatizing Solvent for Cellulose. Macromolecules 2005; 38(20) 8272–8277.

[79] Fukaya Y., Sugimoto A., Ohno H. Superior Solubility of Polysaccharides in Low Viscosity, Polar, and Halogen-Free 1,3-Dialkylimidazolium Formates. Biomacromolecules 2006; 7(12), 3295–3297.

[80] Zhao D., Li H., Zhang J., Fu L., Liu M., Fu J., Ren P. Dissolution of cellulose in phosphate-based ionic liquids. Carbohydrate Polymers 2012, 87(2) 1490– 1494.

[81] Kosan B., Schwikal K., Meister F. Solution states of cellulose in selected direct dissolution agents. Cellulose 2010; 17(3) 495.

[82] Lateef H., Grimes S., Kewcharoenwong P., Feinberg B. Separation and recovery of cellulose and lignin using ionic liquids: a process for recovery from paper-based waste. Journal of Chemical Technology and Biotechnology 2009; 84(12) 1818–1827.

[83] Sashina E. S., Novoselov N. P. Effect of Structure of Ionic Liquids on Their Dissolving Power Toward Natural Polymers Russian Journal of General Chemistry 2009; 79(6) 1057–1062.

[84] Zhao H., Baker G. A., Song Z., Olubajo O., Crittle T., Peters D. Designing enzyme-compatible ionic liquids that can dissolve carbohydrates. Green Chemistry 2008; 10(6) 696–705.

[85] Paduszyński K., Okuniewski M., Domańska U., "Sweet-in-Green" Systems Based on Sugars and Ionic Liquids: New Solubility Data and Thermodynamic Analysis" Industrial and Engineering Chemistry Research 2013; 52(51) 18482–18491.

[86] Carneiro A.P., Rodríguez O., Macedo E.A. Fructose and Glucose Dissolution in Ionic Liquids: Solubility and Thermodynamic Modeling Industrial and Engineering Chemistry Research 2013; 52(9) 3424–3435.

[87] Xiao W., Chen Q., Wu Y., Wu T., Dai L. Dissolution and blending of chitosan using 1,3-dimethylimidazolium chloride and 1-H-3-methylimidazolium chloride binary ionic liquid solvent. Carbohydrate Polymers 2011; 83(1), 233–238.

[88] Fu D., Mazza G., Tamaki Y. Lignin Extraction from Straw by Ionic Liquids and Enzymatic Hydrolysis of the Cellulosic Residues. Journal of Agricultural and Food Chemistry 2010; 58(5) 2915–2922.

[89] Mazza M., Catana D.-A., Vaca-Garcia C., Cecutti C. Influence of water on the dissolution of cellulose in selected ionic liquids. Cellulose 2009; 16(2) 207–215

[90] Xu A., Zhang Y., Zhao Y., Wang J. Cellulose dissolution at ambient temperature: Role of preferential solvation of cations of ionic liquids by a cosolvent. Carbohydrate Polymers 2013; 92(1) 540–544.

[91] Kimizuka N., Nakashima T. Spontaneous Self-Assembly of Glycolipid Bilayer Membranes in Sugar-philic Ionic Liquids and Formation of Ionogels. Langmuir 2001, 17(22) 6759–6761.

[92] Liu Q., Janssen M. H. A., van Rantwijk F., Sheldon R. A. Room-temperature ionic liquids that dissolve carbohydrates in high concentrations. Green. Chem. 2005, 7(1) 39–42.

[93]   Rinaldi R. Instantaneous dissolution of cellulose in organic electrolyte solutions. Chemical Communications., 2011, 47(1) 511–513.

[94]   Gericke M., Liebert T., El Seoud O.A., Heinze T. Tailored Media for Homogeneous Cellulose Chemistry: Ionic Liquid/Co-Solvent Mixtures. Macromolecular Materials and Engineering 2011; 296(6) 483–493.

[95]   Hauru L. K. J., Hummel M., King A. W. T., Kilpeläinen I., Sixta H. Role of Solvent Parameters in the Regeneration of Cellulose from Ionic Liquid Solutions. Biomacromolecules 2012; 13 (9) 2896–2905.

[96]   Zhao Q., Yam R. C. M., Zhang B., Yang Y., Cheng X., Li R. K. Y. Novel all-cellulose ecocomposites prepared in ionic liquids. Cellulose 2009, 16(2) 217–226.

[97]   Tsioptsias C., Stefopoulos A., Kokkinomalis I., Papadopoulou L., Panayiotou C. Development of micro- and nano-porous composite materials by processing of cellulose with ionic liquids and supercritical CO2. Green Chemistry 2008; 10(9) 965–971.

[98]   Li X.-L., Zhu L.-P., Zhu B.-K., Xu Y.-Y. High-flux and anti-fouling cellulose nanofiltration membranes prepared via phase inversion with ionic liquid as solvent. Separation and Purification Technology 2011; 83 66–73.

[99]   Turner M. B., Spear S. K., Holbrey J. D., Rogers R. D. Production of bioactive cellulose films reconstituted from ionic liquids. Biomacromolecules 2004; 5(4) 1379–1384.

[100]   Cai T., Zhang H., Guo Q., Shao H., Hu X. Structure and Properties of Cellulose Fibers from Ionic Liquids. Journal of Applied Polymer Science 2010; 115(2) 1047–1053.

[101]   Quan S. L., Kang S. G., Chin I. J. Characterization of cellulose fibers electrospun using ionic liquid. Cellulose 2010; 17(2) 223–230.

[102]   Aaltonen O. Jauhiainen O. The preparation of lignocellulosic aerogels from ionic liquid solutions. Carbohydrate Polymers 2009; 75(1) 125–129.

[103]   Lee S. Y., Hubbe M. A., Saka H. Prospects for biodiesel as a byproduct of wood pulping - A review. BioResources 2006; 1(1) 150-171.

[104]   Ren J.L., Sun R.C., Liu C.F., Cao Z.N., Luo W. Acetylation of wheat straw hemicelluloses in ionic liquid using iodine as a catalyst. Carbohydrate Polymers 2007; 70(4) 406–414.

[105]   Froschauer C., Hummel M., Laus G., Schottenberger H., Sixta H., Weber H.K., Zuckerstatter G. Dialkyl Phosphate-Related Ionic Liquids as Selective Solvents for Xylan. Biomacromolecules 2012; 13(6) 1973–1980.

[106]   Anugwom I., Mäki-Arvela P., Virtanen P., Willför S., Sjöholm R., Mikkola J.-P. Selective extraction of hemicelluloses from spruce using switchable ionic liquids. Carbohydrate Polymers 2012; 87(3) 2005– 2011.

[107]   Hummel M., Froschauer C., Laus G., Röder T., Kopacka H., Hauru L.K.J., Weber H.K., Sixta H., Schottenberger H. Dimethyl phosphorothioate and phosphorosele-

noate ionic liquids as solvent media for cellulosic materials. Green Chemsitry 2011; 13(9) 2507-2517.

[108]   Tan S. S. Y., MacFarlane D. R., Upfal J., Edye L. A., Doherty W. O. S., Patti A. F., Pringle J. M., Scott J. L. Extraction of lignin from lignocellulose at atmospheric pressure using alkylbenzenesulfonate ionic liquid. Green Chemistry 2009; 11(3) 339–345.

[109]   Abe M., Fukaya Y., Ohno H. Extraction of polysaccharides from bran with phosphonate or phosphinate-derived ionic liquids under short mixing time and low temperature. Green Chemistry 2010; 12(7) 1274–1280.

[110]   Sun N., Rahman M., Qin Y., Maxim M. L., Rodríguez H., Rogers R. D. Complete dissolution and partial delignification of wood in the ionic liquid 1-ethyl-3-methylimidazolium acetate. Green Chemistry, 2009; 11(5) 646-655.

[111]   Li W., Sun N. Stoner B., Jiang X., Lu X., Rogers R. D. Rapid dissolution of lignocellulosic biomass in ionic liquids using temperatures above the glass transition of lignin. Green Chemistry 2011; 13(8) 2038-2047.

[112]   Lee S. H., Doherty T. V., Linhardt R. J., Dordick J. S. Ionic Liquid-Mediated Selective Extraction of Lignin From Wood Leading to Enhanced Enzymatic Cellulose Hydrolysis. Biotechnology and Bioengineering 2009; 102(5) 1368–1376.

[113]   Pu Y. Q., Jiang N., Ragauskas A. J. Ionic Liquid as a Green Solvent for Lignin. Journal of Wood Chemistry and Technology 2007; 27(1) 23-33.

[114]   Bylin S., Olsson C., Westman G., Theliander H. Solvation Behavior of Cellulose and Xylan in the MIM/EMIMAc Ionic Liquid Solvent System: Parameters for Small-Scale Solvation. BioResources 2014; 9(1) 1038-1054.

[115]   Yamazaki S., Takegawa A., Kaneko Y., Kadokawa J., Yamagata M., Ishikawa M. An acidic cellulose–chitin hybrid gel as novel electrolyte for an electric double layer capacitor. Electrochemistry Communications2009; 11(1) 68–70.

[116]   Meng Z., Zheng X., Tang K., Liu J., Qin S. Dissolution of natural polymers in ionic liquids: A review. e Polymers 2012; 12(1) 1-20.

[117]   Wang W.-T., Zhu J., Wang X.-L., Huang Y., Wang Y.-Z, Dissolution Behavior of Chitin in Ionic Liquids. Journal of Macromolecular Science, Part B Physics 2010; 49(3) 528-541

[118]   Zhu Q. S., Han X. J., Cheng C. Z., Wu C. C. Study on dissolubility of chitosan in four kinds of imidazole-based ionic liquids. Acta Polymerica Sinica 2011 11, 1173-1179.

[119]   Chen Q., Xu A., Li Z., Wang J., Zhang S. Influence of anionic structure on the dissolution of chitosan in 1-butyl-3-methylimidazolium-based ionic liquids. Green Chemistry 2011; 13(12) 3446–3452.

[120] Quignard F., Di Renzo F., Guibal E. From natural polysaccharides to materials for catalysis, adsorption, and remediation. Topics in Current Chemistry 2010; 294, 165–197.

[121] Ngah W.S.W., Teong L.C., Hanafiah M.A.K.M. Adsorption of dyes and heavy metal ions by chitosan composites: A review. Carbohydrate Polymers 2011; 83(4) 1446–1456.

[122] Sanchez C., Belleville P., Popall M., Nicole L. Applications of advanced hybrid organic-inorganic nanomaterials: from laboratory to market. Chemical Society Reviews 2011; 40(2) 696–753.

[123] Muzzarelli R.A.A. Biomedical Exploitation of Chitin and Chitosan via Mechano-Chemical Disassembly, Electrospinning, Dissolution in Imidazolium Ionic Liquids, and Supercritical Drying. Marine Drugs 2011; 9(9) 1510-1533.

[124] Trivedi T.J., Rao K. S., Kumar A. Facile preparation of agarose–chitosan hybrid materials and nanocomposite ionogels using an ionic liquid via dissolution, regeneration and sol–gel transition. Green Chemistry 2014; 16(1) 320-330.

[125] Singh T., Trivedi T.J., Kumar A. Dissolution, regeneration and ion-gel formation of agarose in room-temperature ionic liquids. Green Chemistry 2010; 12(6) 1029–1035.

[126] Trivedi T.J., Srivastava D.N., Rogers R.D., Kumar A. Agarose processing in protic and mixed protic–aprotic ionic liquids: dissolution, regeneration and high conductivity, high strength ionogels. Green Chemistry 2012; 14(10) 2831-2839.

[127] Le Bideau J., Viau L., Vioux A. Ionogels, ionic liquid based hybrid materials. Chemical Society Reviews 2011; 40(2) 907-925.

[128] Luo Z., Lu X., Kong X., Fu X., Li F., Luo F. Physicochemical properties of starch dispersed in 1-allyl-3- methylimidazolium chloride. Industrial Crops and Products 2013; 46 197– 204.

[129] Huber K. C., BeMiller J. N. Modified starch: chemistry and properties. Boca Raton: CRC Press; 2010.

[130] Wilpiszewska K., Spychaj T. Ionic liquids: Media for starch dissolution, plasticization and modification. Carbohydrate Polymers 2011; 86(2) 424– 428.

[131] Lu X., Luo Z., Fu X., Xiao Z. Two-Step Method of Enzymatic Synthesis of Starch Laurate in Ionic Liquids. Journal of Agricultural and Food Chemistry 2013; 61(41) 9882–9891.

[132] Jordan T., Schmidt S., Liebert T., Heinze T. Molten imidazole – a starch solvent. Green Chemistry 2014; 16(4) 1967-1973.

[133] Liu W., Budtova T. Dissolution of unmodified waxy starch in ionic liquid and solution rheological properties. Carbohydrate Polymers 2013; 93(1) 199– 2064.

[134] Mateyawa S., D. F. Xie, Truss R.W., Halley P.J., Nicholson T.M., Shamshina J.L., Rogers R.D., Boehm M.W., McNally T. Effect of the ionic liquid 1-ethyl-3-methylimidazolium acetate on the phase transition of starch: Dissolution or gelatinization? Carbohydrate Polymers 2013; 94(1) 520– 530.

[135] Wang Y.J., Wang Y., Structures and properties of commercial maltodextrins from corn, potato, and rice starches. Starch 2000; 52(8/9) 296–304.

[136] Gao Y. A., Li Z. H., Du J. M., Han B. X., Li G. Z., Hou W. G., Shen D., Zheng L. Q., Zhang G. Y. Preparation and Characterization of Inclusion Complexes of β-Cyclodextrin with Ionic Liquid. Chemistry A European Journal 2005; 11(20) 5875-5880.

[137] Gao Y., Zhao X., Dong B., Zheng L., Li N., Zhang S. Inclusion Complexes of β-Cyclodextrin with Ionic Liquid Surfactants. The Journal of Physical Chemistry B 2006; 110(17) 8576–8581.

[138] Li N., Liu J., Zhao X. Y., Gao Y. A., Zheng L. Q., Zhang J., Yu L. Complex formation of ionic liquid surfactant and β-cyclodextrin. Colloids and Surfaces A 2007; 292(2-2) 196-201.

[139] Francois Y., Varenne A., Sirieix-Plenet J., Gareil P. J. Determination of aqueous inclusion complexation constants and stoichiometry of alkyl(methyl)-methylimidazolium-based ionic liquid cations and neutral cyclodextrins by affinity capillary electrophoresis. Journal of Separation Science 2007; 30(5) 751–760.

[140] Amajjahe S., Choi S., Munteanu M., Ritter H. Pseudopolyanions Based on Poly(NIPAAM-co-β-Cyclodextrin Methacrylate) and Ionic Liquids Angewandte Chemie International Edition 2008 47(18) 3435-3437.

[141] Zheng Y., Xuan X., Wang J., Fan M. The Enhanced Dissolution of β-Cyclodextrin in Some Hydrophilic Ionic Liquids. The Journal of Physical Chemistry A 2010; 114(11) 3926–3931.

[142] Ondo D., Tkadlecov M., Dohnal V., Rak J., Kvíčala J., Lehmann J.K., Heintz A., Ignatiev N. Interaction of Ionic Liquids Ions with Natural Cyclodextrins. The Journal of Physical Chemistry B 2011; 115(34) 10285–10297.

[143] Zhang J., Shen X. Multiple Equilibria Interaction Pattern between the Ionic Liquids CnmimPF6 and β-Cyclodextrin in Aqueous Solutions. The Journal of Physical Chemistry B 2011; 115(41) 11852–11861.

[144] Hassan E.-S.R.E., Mutelet F., Moïse J.-C. From the dissolution to the extraction of carbohydrates using ionic liquids. RSC Advances 2013; 3(43) 20219-20226.

[145] Conceic L.J.A., Bogel-Łukasik E., Bogel-Łukasik R. A new outlook on solubility of carbohydrates and sugar alcohols in ionic liquids. RSC Advances 2012, 2(5) 1846–1855.

[146]   Rosatella A. A., Branco L C., Afonso C. A. M. Studies on dissolution of carbohydrates in ionic liquids and extraction from aqueous phase. Green Chemistry 2009; 11(9) 1406–1413.

[147]   Carneiro A.P., Rodríguez O., Macedo E.A. Solubility of monosaccharides in ionic liquids – Experimental data and modeling. Fluid Phase Equilibria 2012; 314, 22– 28.

[148]   Hassan E.-S.R.E., Mutelet F., Pontvianne S., Moïse J.-C. Studies on the Dissolution of Glucose in Ionic Liquids and Extraction Using the Antisolvent Method. Environmental Science and Technology 2013; 47(6) 2809–2816.

[149]   Liu W., Hou Y., Wu W., Ren S., Jing Y., Zhang B. Solubility of Glucose in Ionic Liquid + Antisolvent Mixtures. Industrial and Engineering Chemistry Research 2011; 50(11) 6952–6956.

[150]   Carneiro A.P., Rodríguez O., Macedo E.A. Separation of carbohydrates and sugar alcohols from ionic liquids using antisolvents. Separation and Purification Technology 2014; 132 496–504

[151]   Padmanabhan S., Kim M., Blanch H. W., Prausnitz J. M. Solubility and rate of dissolution for Miscanthus in hydrophilic ionic liquids. Fluid Phase Equilibria 2011; 309(1) 89-96.

[152]   Kahlen J., Masuch K., Leonhard K. Modelling cellulose solubilities in ionic liquids using COSMO-RS. Green Chemistry 2010; 12(12) 2172–2181.

[153]   Casas A., Palomar J., Alonso M.V., Oliet M., Omar S., Rodriguez F. Comparison of lignin and cellulose solubilities in ionic liquids by COSMO-RS analysis and experimental validation. Industrial Crops and Products 2012(1); 37() 155– 163.

[154]   Mora-Pale M., Meli L., Doherty T. V., Linhardt R. J., Dordick J. S. Room temperature ionic liquids as emerging solvents for the pretreatment of lignocellulosic biomass. Biotechnology and Bioengineering 2011; 108(6) 1229-1245.

[155]   Carneiro A.P., Held C., Rodríguez O., Sadowski G., Macedo E.A., Solubility of Sugars and Sugar Alcohols in Ionic Liquids: Measurement and PC-SAFT Modeling. The Journal of Physical Chemistry B 2013; 117 (34) 9980–9995.

[156]   Wang B., Tang Y., Wen Z., Wang H. Dissolution and regeneration of polybenzimidazoles using ionic liquids. European Polymer Journal 2009, 45, 2962–2965.

[157]   Serad G.A., Polybenzimidazoles, new thermally stable polymers – Comments. J Polym Sci A Polym Chem 1996;34(7):1123–4.

[158]   Wainright J.S., Wang J.T., Weng D., Savinell R.F., Litt M. Acid-doped polybenzimidazoles – a new polymer electrolyte. J Electrochem Soc 1995;142(7):L121–3.

[159]   Holmes G.A., Rice K., Snyder C.R., Ballistic fibers: a review of the thermal, ultraviolet and hydrolytic stability of the benzoxazole ring structure. J Mater Sci 2006;41(13): 4105–16.

[160] Kim J.S., Reneker D.H. Mechanical properties of composites using ultrafine electro-spun fibers. Polym Compos 1999;20(1):124–31.

[161] Varma R.S., Solvent-free accelerated organic syntheses using microwaves. Pure Appl Chem 2001;73(1):193–8.

[162] Varma R.S., Namboodiri VV. An expeditious solvent-free route to ionic liquids using microwaves. Chem Commun 2001(7):643–4.

[163] Ueno K., Fukai T., Nagatsuka T., Yasuda T., Watanabe W. Solubility of Poly(methyl methacrylate) in Ionic Liquids in Relation to Solvent Parameters, Langmuir 2014, 30, 3228–3235.

[164] Susan, M. A.; Kaneko, T.; Noda, A.; Watanabe, M. Ion Gels Prepared by in Situ Radical Polymerization of Vinyl Monomers Ionic Liquid and Their Characterization as Polymer Electrolytes. J. Am. Chem. Soc. 2005, 127 (13), 4976–4983.

[165] Lee, S. Y.; Ogawa, A.; Kanno, M.; Nakamoto, H.; Yasuda, T.;Watanabe, M. Nonhumi-dified Intermediate Temperature Fuel Cells Using Protic Ionic Liquids. J. Am. Chem. Soc. 2010, 132 (28), 9764–9773.

[166] Ueno, K.; Inaba, A.; Kondoh, M.; Watanabe, M. Colloidal Stability of Bare and Poly-mer-Grafted Silica Nanoparticles in Ionic Liquids. Langmuir 2008, 24 (10), 5253–5259.

[167] Chen Y., Zhang Y., Ke F., Zhou J., Wang J., Liang D. Solubility of neutral and charged polymers in ionic liquids studied by laser light scattering. Polymer 2011, 52, 481-488.

[168] Triolo A.,Russina O., Keiderling U., Kohlbrecher J. J Phys ChemB 2006;110:1513-1515.

[169] Kawauchi T., Kumaki J., Okoshi K., Yashima E. Macromolecules 2005; 38:9155-9160.

[170] Liu W.W., Cheng L.Y,. Zhang H.Y., Zhang Y.M., Wang H.P., Yu M.F. Int J Mol Sci 2007;8:180-188.

[171] Zhao T.T., Wang H.P., Wang B., Tu X.P., Zhang Y.M., Jiang J.M. Polym Bull 2006;57: 369-375.

[172] Tu X.P., Zhang Y.M., Zhao T.T., Wang H.P. J Macromol Sci Phys 2006;45: 665-669.

[173] Wan S., Zhang Y., Wang H. Acrylic fibers processing with ionic liquid as solvent. Polym. Adv. Technol. 2009, 20 857–862.

[174] Frushour, B.G. Polym. Bull. 1982, 7, 1–8.

[175] Rodrıguez H., Francisco M.,Rahman M., Sun N., Rogers R.D. Biphasic liquid mix-tures of ionic liquids and polyethylene glycols. Phys. Chem. Chem. Phys., 2009, 11, 10916–10922.

[176] Herold D., Keil K., Burns D.E., Biochem. Pharmacol., 1989, 38, 73–76.

[177] Bridges N.J., Gutowski K.E., Rogers R.D., Green Chem. 2007, 9, 177–183.

[178] Shin J.H., Henderson W.A., Passerini P., Electrochem. Commun. 2003, 5, 1016–1020.

[179] Sarkar A., Trivedi S., Pandey S., J. Phys. Chem. B, 2008, 112, 9042–9049.

[180] Samitsu S., Araki J., Kataoka T., Ito K. New Solvent for Polyrotaxane. II. Dissolution Behavior of Polyrotaxane in Ionic Liquids and Preparation of Ionic Liquid-Containing Slide-Ring Gels. Journal of Polymer Science: Part B: Polymer Physics, 2006, 44, 1985–1994.

[181] Harada, A.; Li, J.; Kamachi, M. Nature 1992, 356, 325–327.

[182] Wenz,G.Angew. Chem. Int. Ed. Engl.,1994, 33,803–822.

[183] Ooya, T.; Arizono, K.; Yui, N. Polym Adv Technol 2000, 11, 642–651.

[184] Silva, C.; Friend, R. H.; Severin, N.; Samori, P.; Rabe, J. P.; O'Connell, M. J.; Taylor, P. N.; Anderson, H. L. Nat Mater 2002, 1, 160–164.

[185] Tamura, M.; Gao, D.; Ueno, A. Chem. Eur. J. 2001, 7, 1390–1397.