ILS AS EXTRACTORS OF CARBOHYDRATES FROM AQUEOUS SOLUTIONS

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Introduction: In 2000, Sheldon and co-workers were the first to explore the use of ionic liquids (ILs) as reaction media for carbohydrate transformations.[1] Since then several works have been published, comprising carbohydrates solubility and/or carbohydrates transformations in ILs. The complete dissolution of carbohydrates using an adequate media is an important factor in the carbohydrate chemistry, but for specific cases is also relevant the possibility to remove or recover these compounds from aqueous solutions.[2] Hydrophobic ILs have been recently reported as potential extractors of metals [3], or polar organic compounds [4] such as alcohols [5] from aqueous phase. Carbohydrate extractions from aqueous solutions have been reported using quaternary ammonium salts and lipophilic boronic acids, which can form reversible covalent complexes with diol groups from carbohydrates moieties.[2, 6] Here is described a much simpler method for the extraction of carbohydrates from aqueous phase using hydrophobic ILs.

Experimental: It were performed extraction studies for glucose, and glucose-fructose, lactose-sucrose, fructose-lactose mixtures (1:1 wt.) from an aqueous solution to the IL. This study was complemented with different hydrophobic ILs. (Figure 1)

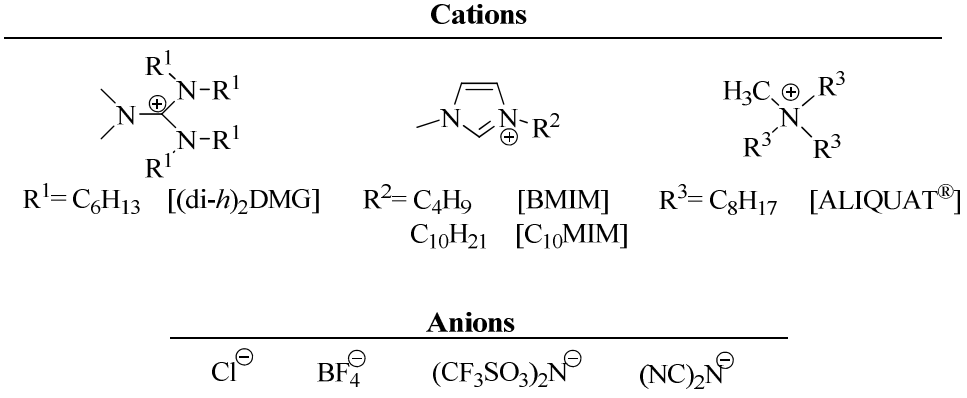

Figure 1. Ionic Liquids used for the extraction of carbohydrates from aqueous solutions.

The extraction method is simple: the sugar is dissolved in the aqueous solution, and mixed with the hydrophobic IL for one week. Then the two phases are separated and was added

dichloromethane to the organic layer in which sugar dissolved in the IL. The carbohydrate precipitates immediately. Following filtration and washing with dichloromethane the sugar recovered shows no trace of IL. On the other hand, after evaporation of dichloromethane, the IL is recovered without any traces of carbohydrates, and can be recycled for, at least, three times.

Results and discussion: It was possible to extract glucose (from an initial concentration of 500 mg/mL in the aqueous phase) in a range of 4.23 to 1.29 wt. %, using the ILs described on Figure 1.

Table 1. Extraction of a mixture of carbohydrates from an aqueous phase (500 mg/mL) to different hydrophobic ILs.

Mixture of carbohydrates extracted	Ionic Liquid		Quantity extracted (wt. %)	Selectivity [a] (wt. %)
Glucose/Fructose (G/F – 50:50 wt.%)	[(di-*h*)$_2$DMG]	[DCA]	5.78	71.6G/28.4F
	[Aliquat®]	[Cl]	2.31	80.2G/19.2F
		[DCA]	7.22	69.2G/30.8F
	[$P_{6,6,6,14}$]	[Cl]	1.68	82.5G/17.5F
		[DCA]	5.22	77.8G/22.2F
Sucrose/Lactose (S/L – 50:50 wt.%)	[(di-*h*)$_2$DMG]	[DCA]	1.52	53.8S/46.2L
	[Aliquat®]	[Cl]	3.76	-S/-L
		[DCA]	3.73	48.8S/51.2L
	[$P_{6,6,6,14}$]	[Cl]	2.83	-S/-L
		[DCA]	2.42	55.1S/44.9L
Fructose/Lactose (F/L – 50:50 wt.%)	[(di-*h*)$_2$DMG]	[DCA]	6.84	51.9F/48.1L
	[Aliquat®]	[Cl]	2.02	-F/-L
		[DCA]	1.08	54.6F/45.4L
	[$P_{6,6,6,14}$]	[Cl]	1.37	-F/-L
		[DCA]	2.68	47.3F/52.7L

a – ratios determined by ^{1}HNMR.

When a mixture of two o monosaccharides was used (glucose/fructose), ILs based on dicyanamide anions could extract a larger quantity than ILs with chloride as anion (Table 1). All the five hydrophobic ILs tested can extract this mixture with relative selectivity, extracting a higher amount of glucose than fructose. When a mixture of two disaccharides (sucrose and lactose) is extracted from an aqueous phase the cation influence the quantity extracted. With the IL based on [(di-h)$_2$DMG] cation a small amount of the mixture is extracted, increasing with ILs based on [$P_{6,6,6,14}$] cation (either with dicyanamide or chloride as anion). ILs based on [Aliquat®] cation can dissolve the biggest amount of the mixture of disaccharides (sucrose/lactose), although with almost no selectivity.

Conclusions: Additionally to the dissolution of carbohydrates studies it was also possible to describe a simple method for the extraction of carbohydrates, where hydrophobic ILs can extract directly carbohydrates from an aqueous solution without the need of a surfactant, or a buffer solution in the aqueous phase. Hydrophobic ILs can extract a large quantity of glucose from an aqueous solution. It is important to noted that ILs contains large amount of water, since they are saturated, which should play an important role in the observed

partitions. Although some selectivity in the partition studies was observed, indicating that the water amount of the IL is not a determining factor for the carbohydrate extraction.

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