Application and mechanism of carrier facilitated carbohydrate extraction from aqueous solution

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ABSTRACT

Recovery of carbohydrates from aqueous solution represents a problem due to their large, multivalent and flexible structure and their high hydrophilicity. Organic solvents as well as alternative solvents such as ionic liquids are able to extract carbohydrates from aqueous media by the aid of primary amines. The mechanism of the extraction process has been explored by using galactose and its corresponding O-methyl galactoside. The results indicate that the mechanism is based on formation of an adduct between the aldo-structure of the monosaccharide and the primary amine to provide a hemiaminal, which is extracted into the organic phase. The extraction rate can be influenced by variation of temperature, time, and the amount of amine and depends on the structure of the carbohydrate. The selectivity can also be tuned using different types of ionic liquids. This procedure opens the possibility to recover a carbohydrate selectively from a mixture of different carbohydrates.

1. Introduction

Carbohydrates are especially suitable feedstocks accessible in large amounts. For instance, glucose, an important raw material with a worldwide production of 5 million tons per year, is industrially produced by enzymatic hydrolysis of starch [1,2]. Apart from the application in food industry, carbohydrates are carbon sources for industrial fermentation and essential raw materials for the synthesis of sorbitol [1]. The widening use of bioraffineries necessitates effective tools for selective recovery of valuable compounds. Extraction is increasingly gaining interest in downstream processing due to its technical accessibility and high efficiency. Especially, if distillation is not feasible for non-volatile and/or thermal instable compounds, or the energy costs are too high, extraction processes constitute a viable alternative. Physical extraction can be easily applied when the compounds exhibit great differences of their solubility in water and suitable water non-miscible solvents. For neutral carbohydrates however, which are well soluble in water, no immiscible solvent is known which at the same time

shows good solubility for them. This can be overcome by adding a suitable reactant resulting in a carrier mediated or reactive extraction. In this paper we describe our findings on the selective carrier supported extraction of carbohydrates from aqueous solutions. Several research groups have reported the transport of carbohydrates from an aqueous media into an immiscible organic solvent facilitated by carrier like boronic acids [3–8] or mediated by methyl cholate carrier in a supported liquid membrane [9–12]. Recently Mehling et al. demonstrated the potential of micellar ultrafiltration for recovery of sugars from aqueous solutions by adding a surfactant and phenylboronic acid as carrier [8]. The addition of long-chain, aliphatic amines as carrier for ionizable compounds such as carboxylic or hydroxycarboxylic acids has also been described. Besides tertiary amines, which are effective extractants for separation of carboxylic acids from dilute fermentation solutions, organophosphoric derivates were applied as well [13–17].

In recent years, ionic liquids (ILs) have emerged as functional materials. They are usually composed of heterocyclic organic cations and various anions. Of great interest are their special dissolution properties as well as chemical and thermal stability, non-flammability and very low vapor pressure [18–24]. Depending on the structures of cations and anions, ILs can be hydrophilic or hydrophobic. All these properties make them attractive for many separation processes. The hydrophobic ionic liquids are able to form a biphasic system and can therefore be used for liquid–liquid

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Nomenclature

K_D	partition coefficient (–)	c_{solv}	carbohydrate concentration in the non-aqueous phase (mol L^{-1})
K_A	partition coefficient of component A (–)	S	selectivity (–)
K_B	partition coefficient of component B (–)	α	phase ratio (–)
c_{aq}	carbohydrate concentration in the aqueous phase (mol L^{-1})	c_0	initial sugar concentration (mol L^{-1})

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extraction [25–28]. The high solubility of carbohydrates in ionic liquids was already reported. MacFarlane et al. were able to dissolve glucose in high (>100 g L^{-1}) concentrations in ionic liquids containing the dicyanamide anion [29,30]. Park and Kimizuka reported the dissolution of glucose in different ILs based on the imidazolium cation [31,32]. Recent research suggests using ionic liquids based on dimethylguanidinium and imidazolium cations combined with acesulfame, thiocyanate, saccharine and acetate anions for solubility of carbohydrates [33]. Other authors described a method to extract the carbohydrates in low amounts directly (without any surfactants) from the aqueous solution [33,34].

In our previous study [35] we reported the screening of a large number of organic solvents for carrier-facilitated extraction of different mono- and disaccharides. From the number of tested amines cyclooctylamine and 2-aminooctane turned out to be superior carriers, both with respect to extraction efficiency as well as their handling. Here, we report our results from using these primary amines and selected hydrophobic ionic liquids for selective extraction of carbohydrates in high concentrations from an aqueous phase including the possibility for recovery. Differences between ionic liquids and organic solvents as extracting agent are shown for the separation of disaccharides. The influence of different parameters like temperature, time and amine to sugar ratio is investigated. Finally, an examination and comparison of the underivatized galactose and its corresponding *O*-methyl galactoside offer an insight in the extraction mechanism of carbohydrates with primary amines, which clearly differs from the extraction using phenylboronic acid as carrier [8,36]. An exemplary recovery process (1-stage reextraction) is shown with high galactose concentration to demonstrate the feasibility and reversibility of the proposed reaction between the carrier amine and the carbohydrate.

2. Experimental

2.1. Reagents

D-Glucose, L-rhamnose, methyl *tert*-butyl ether (MTBE) and 2-aminooctane were obtained from Merck (Darmstadt, Germany) and D-tagatose from Sigma–Aldrich (Buchs, Switzerland). D-Fructose, D-galactose, cellobiose, D-mannose and D-ribose were purchased from Fluka (Buchs, Switzerland). Lactose was obtained from Fisher Scientific (Leicester, England). Methyl α-D-galactopyranoside was purchased from Fluka while the corresponding methyl β-D-galactopyranoside was synthesized by a procedure of Hönig et al. in two steps [37]. Butanol and *n*-hexane were acquired from Baker (Deventer, Netherlands), toluene from Acros (Geel, Belgium) and DMSO-d$_6$ from Chemotrade (Leipzig, Germany). The carrier cyclooctylamine was provided by Evonik Industries (formerly Degussa, Düsseldorf, Germany). The ionic liquid [BMIM][NTf$_2$] was prepared in close analogy to a method described by Eckstein et al. [38]. [OMPy][BF$_4$] was provided by Lonza (Visp, Switzerland), BMIMCl and Li[NTf$_2$] were obtained from Solvent Innovation (Cologne, Germany), now part of Merck, Darmstadt. Deionized water was used in all experiments.

2.2. Extraction with organic solvents and preferred hydrophobic ionic liquids

2.2.1. Partition coefficients of mono- and disaccharides

In general, the organic solvent and the ionic liquids were saturated with water before performing the extraction. The amount of water present is shown in Fig. SI-8. However, there was no correlation between the water content and the extraction rates. The carrier-solvent phase was a mixture of organic solvent or ionic liquid and primary amine. The aqueous phase was prepared by dissolving carbohydrates in water. 500 µL of the aqueous phase containing the carbohydrate and 500 µL of the organic phase containing the carrier (phase ratio of 1, v/v) were mixed in a temperature-controlled shaker at 1000 rpm (Thermo mixer comfort, Eppendorf, Hamburg, Germany) at different temperatures and times. The vessels were then transferred to a centrifuge (Hettich Micro 22 R, Tuttlingen, Germany) and spun at 10,000 rpm for 2 min in order to separate the two phases. Samples were taken from the aqueous phase, diluted and monitored by HPLC. For recovery experiments the extraction was performed accordingly: 500 µL of the loaded organic phase were mixed with 1000 µL of aqueous strip solution (phase ratio of 0.5, v/v). The phases were mixed in a temperature-controlled shaker and centrifuged for phase separation. Once again the aqueous phase was separated from the organic phase and monitored by HPLC. All experiments were carried out in triplicate; the mean value and the standard deviation were calculated. The partition coefficients (K_D) and the selectivity (S) were calculated according to Eqs. (1) and (2):

$$K_D = \frac{c_{solv}}{c_{aq}} \tag{1}$$

$$S_B^A = \frac{K_A}{K_B} \tag{2}$$

2.2.2. Extraction of methyl glycosides

The extraction procedure of the *O*-methyl galactoside was conducted similarly to the determination of partition coefficients of mono- and disaccharides (Section 2.2.1).

2.2.3. Sugar recovery – batch operation mode

The experiments for extractive sugar recovery were performed in a glass vessel with a volume of 250 mL using an initial carbohydrate concentration of 0.5 mol L^{-1}. For extraction experiments 100 mL of the aqueous phase containing the carbohydrate were added to 100 mL of the organic phase containing the carrier. The phases were stirred with a pitched blade impeller at 600 rpm. The extraction was conducted at 30 °C for 30 min. Samples were taken from the aqueous phase, diluted and monitored by HPLC. For recovery of the carbohydrate from the organic phase the two phases were separated. The organic phase containing the carbohydrate-carrier adduct was added to 100 mL of a fresh aqueous strip solution (1-stage reextraction). The conditions and procedures were as described above. After separating and sampling the aqueous phase was evaporated. The received syrup was dried under