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Screening of ionic liquids for efficient extraction of methylxanthines using COSMO-RS methodology

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ABSTRACT

The COSMO-RS methodology was used to perform a screening of ionic liquids as the most effective media for extraction of methylxanthines from natural sources. The computational methodology was validated based on the values of experimentally obtained extraction yields of caffeine from guarana seeds. A linear dependence between the extraction yields and computed thermodynamic activity coefficients of caffeine was found. A total of 23 cations and 38 anions commonly used in ionic liquids were used in the studies comprising a total of 874 ionic liquids. It was found that the ionic liquid based on the 1-dodecyl-3-methylimidazolium cation and tetraphenyl borate anion was responsible for the best extraction efficiency equal to 10.1 wt%, which is more than 50% higher than the best experimentally studied ionic liquid. Furthermore, the effectiveness of recyclability of methylxanthines from the aqueous solutions of ionic liquids was modeled. It was found that the partition coefficient values of caffeine are a good qualitative measure of re-extraction efficiency of the solvents. Since ionic liquids with high extraction efficiency have a strong affinity towards aqueous solutions, while those with high recyclability towards the organic phase it is indispensable to take both these steps into account when modeling the extraction process.

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1. Introduction

Methylxanthines are a very important and interesting group of pharmacologically active compounds, which belong to the broad alkaloids class. Among them, three are of special importance from the perspective of pharmacological applications, that is caffeine (1,3,7-trimethylxanthine), theobromine (3,7-dimethylxanthine) and theophylline (1,3-dimethylxanthine). These compounds can be found in a variety of plants as well as many different beverages, foods and medical preparations (Dolder et al., 2013). For example, caffeine can be found in coffee (*Coffea Arabica*), tea (*Thea sinensis*) or guarana (*Paullinia cupana*). Theobromine is most commonly found in cacao beans (*Theobroma cacao*) while theophylline can be found in modest concentrations in tea. However, very often all the above methylxanthines can coexist in a single plant and as a result in a prepared beverage or food which can therefore stand as a source of all the mentioned methylxanthines although with varying concentrations. Among the pharmacological activities of methylxanthines the stimulation of the central nervous system (CNS) is probably the most recognized one (Charles and Craig, 2004). Other pharmacological activities include cardiac stimulation, blood pressure increase, diuresis of kidneys, relaxation of smooth muscles, especially the bronchial smooth muscle, strengthening of the concentration of skeletal muscles and others like gastric acid secretion (Satoskar et al., 2015). Due to their activities, methylxanthines are used in medicine as CNS stimulants, migraine relief agents, diuretics, in acute left ventricular failure and in bronchial asthma (Satoskar et al., 2015). Interestingly, methylxanthines can also be used in applications exceeding the pharmacological ones, for example as natural pesticides or repellents (Nathanson, 1984; Hollingsworth et al., 2002).

Since the consumption of these naturally occurring alkaloids is very high, especially in the form of beverages and drugs, a large number of investigations was carried out in order to find effective ways of extracting methylxanthines and determining their concentration. An efficient and popular way of extracting caffeine from natural products is the use of supercritical carbon dioxide (Peker et al., 1992; Kim et al., 2008). The improvement of this technology involves the use of cosolvents in order to obtain higher extraction yields and these cosolvents include water, alcohols or esters (Bermejo et al., 2016; Kopcak and Mohamed, 2005; Tello et al., 2011; İçen and Gürü, 2010). Another way of methylxanthines extraction is the use of organic solvents, as well as their mixtures

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with water. Examples of such solvents include acetone, methanol, ethanol, ethyl lactate, chloroform and methylene chloride (Jun, 2009; Bermejo et al., 2013; Mumin et al., 2006; Hulbert et al., 1998). Microwave assisted extraction as well as high pressure extraction was also developed (Rahim et al., 2014; González-Nuñez and Cañizares-Macías, 2011; Villanueva Bermejo et al., 2015). Furthermore, the solid phase extraction (SPE) was likewise applied for the extraction of methylxanthines (Salinas-Vargas and Cañizares-Macías, 2014; Rodrigues et al., 2007). The determination of the concentration of methylxanthines can be performed with the use of high-performance liquid chromatography (Pura Naik, 2001; Bispo et al., 2002), ion chromatography (Chen and Wang, 2001), spectrophotometry (Khanchi et al., 2007) or gas chromatography (Sereshti and Samadi, 2014). The future development of extraction techniques must be focused on two different aspects. The first one is the improvement of extraction yields and processing time, while the second is related to the environmental safety and reduction of health hazards. This latter aspect involves finding replacements for volatile, flammable and toxic compounds.

Ionic liquids are a well-established alternative to standard solvents and it is not surprising that they have attracted attention in the context of extraction processes. Ionic liquids can be defined as melted salts, however the modern understanding of the term ionic liquid (IL) is restricted to salts that melt in room temperature. Ionic liquids have been the subject of many studies and their desirable properties were evaluated. Among these interesting properties one can mention their minimal volatility, at least at room temperature (HU, 2004; Welton, 1999), low flammability (Brennecke and Maginn, 2001), wide liquid range (Holbrey and Seddon, 1999), high thermal (Armand et al., 2009) and chemical (Anderson and Armstrong, 2003) stability. A very important advantage of ionic liquids is the adjustability of their physicochemical properties which can be achieved by changing the cation or anion of the liquid. This makes it possible to use ionic liquids for a variety of applications like analytical chemistry (Liu et al., 2010), electrochemistry (MacFarlane et al., 2007) or chemical engineering (Jenck et al., 2004). Ionic liquids are regarded as "eco-friendly"(Chen et al., 2015; Messali et al., 2013) which contributes to their widespread usage. As mentioned earlier, ionic liquids have been extensively used for extraction purposes. Interesting examples of such applications include the extraction of glycerin from palm oil-based biodiesel (Hayyan et al., 2010), separation of aromatic hydrocarbons from naphtha (Kareem et al., 2012), extraction of phenolic compounds from plant material (Dai et al., 2013), extraction of flavonoids (Bi et al., 2013), extraction of proteins (Xu et al., 2015) or the extraction of natural pigments (Xu et al., 2016).

The large number of possible cation–anion combinations that constitute a ionic liquid makes it impractical to study experimentally all of them. However, *in silico* modeling can be a valuable tool in the screening stage enabling a rational selection of the most promising systems. This can involve modeling both the properties of a single ionic liquid (García et al., 2015a; Barycki et al., 2016) or the properties of a whole system containing the solute in IL (García et al., 2015b; Biniaz et al., 2016). The most obvious advantage of such preliminary step is a significant environmental impact due to saving of both energy and chemicals that would be otherwise spent without rationalized guidance. In this study an attempt was made to correlate the thermodynamic parameters describing ionic liquid properties with experimental values of extraction yields and to apply such method for prediction of the extraction potential of other ionic liquids.

Table 1 – Names and adopted codes of cations and anions constituting the ionic liquids analyzed in this study.

Anions

(A1) tetraphenyl borate; (A2) tetrachloroalumanuide; (A3) bis((trifluoromethyl)sulfonyl)amide; (A4) diphenyl phosphate; (A5) hexafluoroantimonate; (A6) octyl sulfonate; (A7) hexafluorophosphate; (A8) saccharinate; (A9) trifluoro methane sulfonate; (A10) thiocyanate; (A11) perchlorate; (A12) dicyanamide; (A13) tosylate; (A14) dibutyl phosphate; (A15) iodide; (A16) trifluoro acetate; (A17) tetrafluoroborate; (A18) methyl sulfate; (A19) hydrogen sulfate; (A20) butanoate; (A21) isobutyrate; (A22) bromide; (A23) diethylphosphate; (A24) N,N-dimethylcarbamate; (A25) lactate; (A26) nitrate; (A27) dimethyl phosphate; (A28) dimethyl phosphate; (A29) methane sulfonate; (A30) carbonate; (A31) acetate; (A32) methyl carbonate; (A33) chloride; (A34) hydroxide; (A35) fluoride; (A36) methyl phosphonate; (A37) sulfate; (A38) phosphate

Cations

(C1) 1-dodecyl-3-methylimidazolium; (C2) 1-decyl-3-methylimidazolium; (C3) 1-methyl-3-octylimidazolium; (C4) 1-butyl-2,3-dimethylimidazolium; (C5) 1-hexyl-3-methylimidazolium; (C6) 1-benzyl-3-methylimidazolium; (C7) 1,3-diethoxyimidazolium; (C8) 1-butyl-3-methylimidazolium; (C9) 1,3-bis(cyanomethyl)imidazolium; (C10) 1-methyl-3-propylimidazolium; (C11) 1-allyl-3-methylimidazolium; (C12) 1,2-dimethyl-3-propylimidazolium; (C13) 1,3-bis(3-cyanopropyl)imidazolium; (C14) 1-(3-cyanopropyl)-3-methylimidazolium; (C15) 1-methyl-3-vinylimidazolium; (C16) 1-methylimidazolium; (C17) 1-butyl-1-methylpyrrolidinium; (C18) 1-ethyl-3-methylimidazolium; (C19) 1-ethyl-2,3-dimethylimidazolium; (C20) 1-hydroxyethyl-3-methylimidazolium; (C21) 1,3-dimethylimidazolium; (C22) 1,2,3-trimethylimidazolium; (C23) 1-(2-hydroxyethyl)-3-methylimidazolium

2. Materials and methods

The experimental results of caffeine extraction from guarana seeds were taken from the study of Claudio et al. (2013). These data include the extraction yields of caffeine removed from guarana seeds with the use of six different ionic liquids as well as the recovery of caffeine from aqueous solutions of these ionic liquids using different organic solvents. These results were used for the purpose of validation of the proposed computational methodology of both extraction and re-extraction. After the validation step the list of ionic liquids constituents was extended up to 23 cations and 38 anions. All these ions are common components of a variety of practically useful ionic liquids (Ghandi, 2014; Plechkova and Seddon, 2008). The list of the considered ions can be found in Table 1 along with their codes. The interest was also extended towards extraction characteristics of other xanthine derivatives such as theobromine and theophylline, the structures of which are schematically presented in Fig. 1. Furthermore, an extensive analysis of 263 solvents from the Everything Added to Food in the United States–Generally Recognized as Safe (EAFUS–GRAS) list (U.S. Food Drug Administration, 2017) was conducted for screening of the most efficient solvent for highest recovery of xanthine derivatives from aqueous solutions of ionic liquids.

The COSMO-RS (Conductor like Screening Model for Real Solvents) (Klamt and Schüürmann, 1993; Klamt, 2011) approach was applied in this study for computing from first principle the values of chemical potentials of molecules in liquid solutions. Based on these data other thermodynamic properties such as vapor pressure, activity coefficients or solubility can be estimated. The COSMO-RS model was successfully used to study interactions of organic solvents with ionic liquids (Navas et al., 2009; Kurnia and Coutinho, 2013), as well as water–ionic liquid systems (Khan et al., 2014; Khan et al., 2016) and has been found to be a valuable tool for selecting ionic liquids for desired specific tasks (Anantharaj and

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