



Enhanced extraction of antioxidants from aqueous solutions by ionic liquids



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ABSTRACT

In this work, the extraction behavior of the three antioxidants, gallic acid (GA), vanillic acid (VA) and syringic acid (SA) by a series of hydrophobic ionic liquids (ILs) was investigated. The experimental results indicated that the extraction ability of the ILs highly depended on their chemical structures and the hydrophobicity of the three acids. For the ILs with perchlorate (ClO_4^-) as anion, the introduction of hydroxyl group on the cation improved significantly the extraction ability of ILs for GA. For the extraction of VA and SA, the hydrophobic interaction between ILs and VA or SA should also be considered. Thermodynamic analysis confirmed that hydrogen bonding was the main driving force underlying the transfer of the three acids from water to the IL phase. The three acids and ILs could be recovered and recycled, respectively by taking the advantage of pH dependence of the extraction efficiencies. These results suggested the ILs containing perchlorate anion exhibited potential applications in extraction of the three antioxidants from aqueous phase.

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1. Introduction

Free radicals and other reactive oxygen species produced through natural human physiological processes can interact with biomacromolecules such as, NDA and proteins leading to cell damage and thus have a deleterious effect on living organisms [1–3]. Antioxidants are molecules that can scavenge free radicals before biomacromolecules are damaged. Therefore, antioxidants are widely used as ingredients in food [1,4–6], medicine [6–8] and cosmetic industry [5,9,10]. Gallic acid (GA), vanillic acid (VA) and syringic acid (SA) are all antioxidants and commonly exist in natural sources, such as wood, flowers, fruits, vegetables and mushrooms [8,11,12]. A separation procedure is usually required during the production processes of the three acids and the conventional solvents such as, acetone [13] and ethyl acetate [14,15] are usually used. However, these solvents are highly volatile, irritant and flammable. The development of environmentally benign solvents is thus of importance.

Ionic liquids (ILs) are molten salts with melting points around room temperature. They have been widely regarded as

environmentally benign solvents due to their unique properties, such as poor volatility, nonflammability and high thermal stability. Recently, the applications of ILs in separation field have also attracted much attention of scholars. Three excellent works have reported the use of IL-based aqueous two-phase systems (ATPS) which are composed of two immiscible aqueous phases, IL-rich and inorganic-salt-rich phases to extract GA, VA and SA [16–18]. Cláudio et al. investigated the extraction behavior of GA with IL-based ATPS. It was found that Na_2SO_4 -based ATPS had better extraction efficiency; the neutral form of GA preferentially entered the IL-rich phase, whereas the gallate anions tended to enter the salt-rich phase [16]. Subsequently, Cláudio and coworkers used GA, VA and SA as model compounds to study the extraction efficiencies of the IL-based ATPS and to evaluate the efficacy on the IL recyclability and reusability. The three acids could be extracted into the IL-rich phase of $\text{Na}_2\text{SO}_4 + \text{IL}$ ATPS. After extraction, another ATPS composed of IL and Na_2CO_3 was used to perform the back-extraction of the three acids from IL-rich phase, accomplishing the reuse of IL [17]. Another work from the same research group used ILs to tune the polarity of ATPS composed of polyethylene glycol (PEG) and Na_2SO_4 . The additions of ILs enhanced the extraction efficiencies. As far as the effects of the IL chemical structures were concerned, the ATPS system containing CH_3CO_2^- or

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Cl⁻-based ILs exhibited better extraction efficiency as compared to the ILs with tosylate ([TOS]⁻), SCN⁻ and [N(CN)₂]⁻; furthermore, the ATPS containing imidazolium-based ILs had higher extraction efficiencies for the three acids than those containing piperidinium- and pyrrolidinium-based ILs because imidazolium was aromatic cation with high tendency to form hydrogen bonds with the three acids [18].

Despite the remarkable progress made in the extraction of GA, VA and SA, there are still several problems worthy of further study: (I) although, ATPS are undoubtedly good techniques for extraction, a large amount of organic compounds are usually used in order to form the organic-rich phase [16,17]. (II) The extraction mechanism of ATPS is complex and not well understood. (III) Some ATPS tend to form intensive and stable emulsions leading to long phase separation time [19]. Generally, the use of hydrophobic ILs in separation processes is preferable to the IL-based ATPS because the hydrophobic IL-based extraction is easy to operation and only consumes a small number of ILs [20,21]. Therefore, in this work, a series of hydrophobic ILs with different chemical structures were selected and the aims of this work were to investigate the relationship between the extraction ability and the IL chemical structures and to explore the driving forces underlying the extraction processes of GA, VA and SA.

2. Experimental

2.1. Materials

N-Benzylimidazole (98%) was obtained from Alfa Chem., Ltd. (Berkshire, UK). Potassium hexafluorophosphate (99%), 6-chloro-1-hexanol (98%), sodium tetrafluoroborate (98%) and sodium perchlorate monohydrate (99%) were obtained from Energy Chemical Co. (Shanghai, China). Gallic acid (GA, 99%), vanillic acid (VA, 98%), syringic acid (SA, 98%), *n*-octanol (99%), 1-bromohexane (99%), 1-bromoheptane (98%), 1-bromooctane (98%), *N*-methylimidazole (99%), hydrogen peroxide (H₂O₂, 30%, GR), catalase from bovine liver (3500 units mg⁻¹), activated carbons (200 mesh) and methanol (chromatographic grade) were obtained from Aladdin Reagent Co. (Shanghai, China). Sodium azide (NaN₃, ≥99%) was obtained

from Kuer Chemical Co. (Beijing, China). Lithium bis(trifluoromethanesulfonyl)imide (99.9%, LiNTf₂) was obtained from Maya Reagent Co. (Jiaying, China). Reichardt's dye (RD, 90%) and 4-nitroaniline (NA, ≥99%) were obtained from sigma-Aldrich Co., (St. Louis, MO, USA); *N,N*-diethyl-4-nitroaniline (DENA, 97%) was purchased from Fluorochem Ltd., (Hadfield, UK).

All the other chemicals are analytical grade unless stated otherwise. Ultrapure water (18.2 MΩ cm) produced by an Aquapro purification system (Aquapro International Co., Ltd., Dover, DE, USA) was used throughout the experiments. The ILs, 1-methyl-3-heptylimidazolium bis(trifluoromethanesulfonyl)imide ([C₇mim]NTf₂) and 1-methyl-3-benzylimidazolium bis(trifluoromethanesulfonyl)imide ([Bzmim]NTf₂) were synthesized by the procedures described in our previous work [20]. The synthetic procedures and characterization of 1-benzyl-3-(6-hydroxyhexyl)imidazolium tetrafluoroborate ([C₆OHBzim]BF₄), 1-benzyl-3-(6-hydroxyhexyl)imidazolium hexafluorophosphate ([C₆OHBzim]PF₆), 1-benzyl-3-(6-hydroxyhexyl)imidazolium perchlorate ([C₆OHBzim]ClO₄), 1-benzyl-3-(6-hydroxyhexyl)imidazolium bis(trifluoromethanesulfonyl)imide ([C₆OHBzim]NTf₂), 1-methyl-3-heptylimidazolium perchlorate ([C₇mim]ClO₄), 1-methyl-3-hexylimidazolium perchlorate ([C₆mim]ClO₄) and 1-methyl-3-octylimidazolium perchlorate ([C₈mim]ClO₄) are shown in the Supporting Information (SI). For clarity, the chemical structures of the ILs, GA, VA and SA are shown in Fig. 1; and the abbreviations and symbols used in this work are listed in Table S1 in the SI.

The pH values of the aqueous solutions were adjusted by phosphate buffers (0.10 mol L⁻¹) and measured by a PHS-3B digital pH-meter (Shanghai Leici Instrument Factory, Shanghai, China).

2.2. Measurements of GA, VA and SA

The concentrations of GA, VA and SA in aqueous solutions were determined by a high performance liquid chromatograph (HPLC, 1200 model, Agilent, Santa Clara, CA, USA) equipped with a variable-wavelength detector (VWD) and an autosampler. The separation column was an Amethyst C18-H column (4.6 mm × 150 mm, 5 μm, Sepax Technologies Inc., Newark, DE, USA). The mobile phase was the mixture of methanol and 0.10%

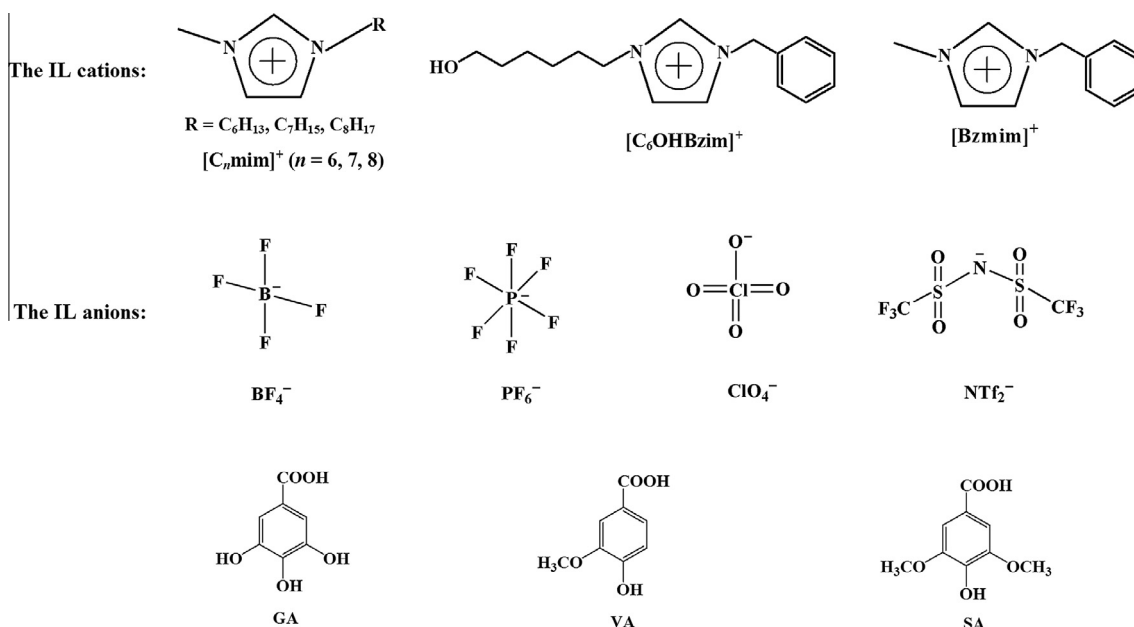


Fig. 1. Chemical structures of the IL cations, anions, GA, VA and SA.

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