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Improved concentration of citrus essential oil by solvent extraction with acetate ionic liquids

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ABSTRACT

Citrus essential oils have numerous applications in multiple sectors, including food, drink and personal care industries. Although mainly constituted by terpenes, the appealing characteristics of citrus essential oils are due to oxyterpenes and other derived oxygenated compounds. In fact, the presence of terpenes in the essential oil may lead to instability or loss of quality. Therefore, concentration of the oil in its oxyterpene compounds by removal of terpenes is desirable. The techniques currently in use for deterpenation of essential oils present a series of issues. In the search for better deterpenation processes, here the use of ionic liquids as solvents in liquid–liquid extraction is explored. In particular, the ionic liquids 1-ethyl-3-methylimidazolium acetate and 1-butyl-3-methylimidazolium acetate are investigated for their extraction of oxyterpene from a modelled citrus essential oil composed of limonene (terpene) and linalool (oxyterpene). The choice of the ionic liquids, in addition to other complementary characteristics, was based on a rationale of potential interactions that can be created preferentially with the linalool. The results show a great performance of these acetate-based ionic liquids, as compared to any other ionic or molecular solvent tested to date, for the concentration in oxyterpenes of the citrus essential oil.

1. Introduction

An essential oil is, in principle, the volatile fraction of the components of a plant or its parts, obtained by a physical separation process; although, depending on the nature of such process, the essential oil may also include certain non-volatile residues. At an industrial level, citrus essential oils are obtained from the corresponding fruits as co-products in the production of fruit juices. Typical processes for obtaining the essential oil include different versions of cold pressing, as well as distillation techniques (although the latter lead to oils of markedly lower quality), followed by downstream purification stages based on centrifugation or distillation [1]. Essential oils are the main responsible element for the characteristic aromas and flavours of plants.

Citrus essential oils find application in numerous areas. As aromatisers and/or flavouring agents, they are utilised in food and drink industries; in perfumery, cosmetics, soaps, and other cleaning and personal hygiene products; and to mask unpleasant flavours (e.g. certain medicines) and odours (e.g. in the textile, plastics, or paint industries). As a result of multiple biological activities, they can also be used in pharmaceutical and parapharmaceutical products, as well as in aromatherapy [2].

The dozens of components typically present in an essential oil can be categorised into terpenes, their oxygenated derivatives (oxyterpenes), and low molecular weight organic substances (aliphatic alkanes, alcohols, aldehydes, ketones, esters, acids), with non-volatile compounds (paraffins, waxes, etc.) being also present sometimes [3]. In essential oils of citrus fruit peels, the organoleptic characteristics are mainly due to the small proportion of oxygenated terpene derivatives and some other oxygenated compounds (alcohols, aldehydes, ketones, and esters) [4]. Although terpene hydrocarbons constitute over 95 % of these essential oils, they contribute little to the aroma and flavour [1]. In fact, the presence of the terpenes may give rise to problems associated with their insolubility in aqueous or alcohol solutions, or with their proneness to undergo oxidation (with subsequent evolution to resins); both of which result in the deterioration of the oil properties. The direct, non-deterpened oil may be preferable for some purposes, but in general the removal of terpenes is a desirable action that concentrates the oil in the more desirable components, increases its stability by slowing oxidation and resin formation, and increases its solubility in water, ethanol and other solvents used in food technology [5].

Deterpenation of essential oils at large scale is commonly carried out by vacuum distillation and/or extraction with aqueous alcohol or other solvents. The problem in the use of distillation is that the boiling point ranges of oxygenated compounds fraction are typically in between the boiling point ranges of different types

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of terpenes present [6]. As a consequence, deterpenation by distillation techniques needs to be combined with solvent extraction, or there is risk of loss of quality of the oil due to polymerisation and resinification reactions [7]. Regarding extraction with solvents, a few extractants that have been explored at a research level are the following: ethanol, methanol, and their aqueous solutions; and also ethyl acetate and acetone; among others [8–10]. Countercurrent liquid–liquid extraction is also a possibility with pentane being used as a second solvent along with diluted methanol or ethanol. Emerging technologies have also been tested, and for example membrane separation and supercritical fluid extraction are already in industrial use. Membrane separations afford a high quality product due to the operation at low temperatures, along with other concomitant advantages; but they present typical problems of membrane-based processes, such as tendency to clog and maintenance costs [1,11,12]. Extraction with supercritical fluids also avoids high temperatures and direct distillation processes in the deterpenation of essential oils, with CO_2 being the most commonly employed supercritical fluid, since it is non-toxic, non-flammable, and has a critical temperature of 31 °C; but again, problems inherent to supercritical fluid technologies, such as investment, safety, and operational costs, are a handicap [1,4,13–15].

In the last years, a new approach to the deterpenation of essential oils by solvent extraction has been considered, with the use of ionic liquids instead of conventional volatile solvents [8,16]. Ionic liquids are salts that can be used as solvents at the typical operation temperature ranges in liquid–liquid extraction processes, given their low melting point [17]. Since they are integrally constituted by ions, they have a practically negligible volatility at the usual process conditions, and often they also exhibit other interesting properties for their use as solvents: wide liquid range, thermal stability, chemical stability, non-flammability, and great ability to solvate a wide variety of compounds [17,18]. Moreover, their properties can be tuned to an important extent by judicious selection and tailoring of the chemical structures of their constitutive ions [17]. This appealing characteristic has led to the coinage of the term ‘designer solvents’, although applications of ionic liquids in the present moment go far beyond their mere use as solvents [18,19]. Still, their typical set of properties render them very interesting as neoteric solvents in reaction and separation processes, and specifically they can lead to the reconsideration of current solvent extraction processes, as well as envisioning of new ones [20]. For the particular case of deterpenation of essential oils, a series of ionic liquids were tested for the separation of compounds in a simplified, modelled citrus essential oil consisting of a mixture of limonene (a representative terpene) and linalool (a representative oxyterpene) [8,16,21,22]. Although different structural features in the constitutive ions were explored, seeking an optimisation of the ionic liquid to carry out the target separation, the results were only partially successful at best: some of the ionic liquids showed a high separation power of the terpene and the oxyterpene, but at the same time the low solubilities of the extracted oxyterpene would imply the need of prohibited amounts of solvent for the implementation of the extraction unit at an industrial scale.

It is the ability to carry out separations according to chemical type, rather than according to physical characteristics (such as vapour pressure), which often makes solvent extraction a so attractive separation technique [23]. In this regard, the main structural difference between limonene and linalool is the presence, in the latter, of a hydroxyl group (see chemical structures in Fig. 1). This functional group, contrary to the structural features in limonene, is susceptible of establishing hydrogen bonding with a suitable hydrogen bond acceptor. Thus, a possibility to improve the extracting performance of ionic liquids as extracting solvents in the separation of limonene and linalool could be the use of ionic liquids with a strong capacity to act as hydrogen bond acceptors. Apart from functional groups appended to the cationic core, the ability to accept hydrogen bonding in an ionic liquid is often connected with the basic character of its anion. Therefore, two ionic liquids containing the acetate anion, with a strong basic character, were considered herein: 1-ethyl-3-methylimidazolium acetate ($[C_2mim][OAc]$) and 1-butyl-3-methylimidazolium acetate ($[C_4mim][OAc]$). Their chemical structures are shown in Fig. 1. In addition to a potentially improved deterpenation of the essential oil and to the general ionic liquid advantages aforementioned, these ionic liquids present further favourable characteristics for their use in the proposed extraction process: moderately low toxicity, relatively low viscosity as compared to other ionic liquids, and the potential to be produced at a competitive cost upon adequate scale up of its production.

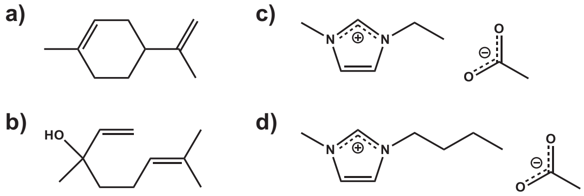

Fig. 1. Chemical structures of the components of the modelled citrus essential oil, and of the ionic liquids tested as extracting solvents for deterpenation: (a) limonene, (b) linalool, (c) $[C_2mim][OAc]$, (d) $[C_4mim][OAc]$.

In this work, the analysis of the suitability of $[C_2mim][OAc]$ and of $[C_4mim][OAc]$ as solvents for the deterpenation of citrus essential oil has been carried out through the experimental determination of the liquid–liquid equilibrium of each ionic liquid with limonene and linalool. The results have been compared not only with previously tested ionic liquids for the same separation, but also with the benchmark molecular solvents in the state-of-the-art. Moreover, a thermodynamic correlation of the liquid–liquid equilibrium data has been carried out, to facilitate their treatment and implementation in process simulation software.

2. Experimental

2.1. Materials

Citrus essential oil was simulated as the mixture of two representatives of its main types of components: the terpene limonene and the oxyterpene linalool. *R*-(+)-limonene was supplied by Sigma–Aldrich with a nominal purity of 97 wt%, and (±)-linalool was purchased from SAFC with a nominal purity of $\geq$97 wt%. Both chemicals were used as received, without further purification.

The ionic liquid $[C_2mim][OAc]$ was purchased from Iolitec with a nominal purity of >95 wt%. The ionic liquid $[C_4mim][OAc]$ was purchased from Fluka with a nominal purity of $\geq$95 wt%. Both ionic liquids were purified for 48 h under high vacuum (<0.1 mbar), while continuously stirred and heated at ca. 70 °C, to remove residual volatile compounds that might be present. The chemical identity and absence of major impurities for the purified ionic liquids was verified by proton and carbon nuclear magnetic resonance (^1H and ^{13}C NMR) spectrometry.

The content in water (a relevant impurity that can particularly affect the properties and performance of ionic liquids [24]) of the substances used in this work was determined by Karl-Fischer titration in a MetrOhm 737 KF coulometer. These values are reported in Table 1, along with the corresponding CAS numbers and with experimentally determined values of density and refractive index (measured with an Anton Paar DMA 5000 and an ATAGO RX-5000 refractometer, respectively), at 298.15 K. These experimental values are compared in Table 1 with literature values published by other authors [25–29]. The fair comparison observed constitutes