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Liquefying flavonoids with terpenoids through DES formation

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PURPOSE OF THE ABSTRACT

Flavonoids are polyphenolic organic compounds naturally found in multiple plants, having important functions to its development, and being highly sought after for their favourable biochemical and antioxidant effects as well as many health benefits they provide [1?3]. One of the ways to extract those compounds is using (Deep) Eutectic Solvents (DES) as the extraction media [2,4,5]. Moreover, DES are tuneable solvents that can be designed to become a greener (less-toxic and more sustainable) alternative for extraction and many other purposes [6?8]. The classification of a deep eutectic mixture is due to negative deviations to the ideal thermodynamic behaviour resulting in melting temperature being lower than ideality [9], primarily through intermolecular hydrogen bonds between hydrogen bond donors (HBD) and acceptors (HBA) [9?11]. Strongly interacting DES can be obtained using non-ionic compounds as HBA and HBD, which are classified as type V, and previous works suggested that they could be formulated using HBA, such as alcohols, ketones or amines, and phenolic compounds acting as HBD [11,12]. Additionally, HBA can provide even stronger interactions if they are not able to form hydrogen bonds with itself (also referred as lone HBA [12]).

In this work, the focus is the design of DES for the extraction of flavonoids from plant matrices. The two most commonly used compounds to prepare type V DES are thymol and menthol [13?16]. The compounds selected as representatives of flavonoids present in plants were flavone, flavanone, and (-)-hesperetin. The solid-liquid equilibria (SLE) phase diagrams of the mixtures of thymol and menthol with the flavonoids were experimentally measured using an automatic melting point glass capillary device or by Differential Scanning Calorimetry (DSC) (Figure 1). Complementarily, the SLE phase diagrams were predicted using the computational method Conductor-like Screening Model for Real Solvents (COSMO-RS) [17], in order to provide insights on the molecular interactions in these systems and to evaluate the ability of the model to design DES.

Negative deviations from ideality were observed on thymol systems with either flavone or flavanone, both being lone HBA flavonoids, thus forming non-ionic Type V DES. On the other hand, the menthol systems with those compounds showed mostly positive deviations to ideality. Both systems with hesperetin also showed in positive deviations, probably due to it possessing both HBD and HBA groups, thus being able to form more favorable

hydrogen bonds with itself than with thymol or menthol. COSMO-RS satisfactorily predicted the behavior of the solid-liquid phase diagram of the studied systems, allowing to evaluate the impact of the different contributions to the intermolecular interactions.

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FIGURES

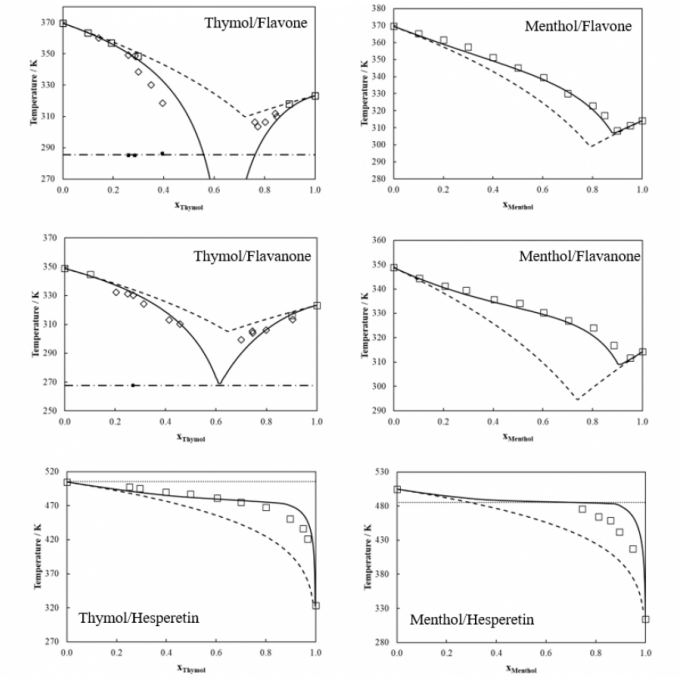

FIGURE 1

Solid-liquid phase diagrams of binary mixtures composed of thymol or menthol and flavonoids

FIGURE 2

KEYWORDS

deep eutectic solvents | solid-liquid equilibria | flavonoids | COSMO-RS

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