

Proceeding Paper

Synthesis and Characterization of Menthol-Based Hydrophobic Deep Eutectic Solvents

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Abstract: Hydrophobic Deep Eutectic Solvents (HDESs) have found application in water purification in recent years. The extent of their stability in aqueous media determines whether they are suitable materials for water purification or if they end up constituting a greater pollution load to the water they are to purify. This work sought to prepare HDESs from a monoterpene (menthol), and three long-chain organic acids (octanoic acid, decanoic acid, and dodecanoic acid). The physicochemical characteristics of the prepared HDESs were investigated. Thereafter, their moisture absorption capacity and stability in an aqueous medium were determined to ascertain whether they were hydrophobic as predicted

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1. Introduction

Deep Eutectic Solvents (DESs) are alternative green solvents to ionic liquids. They are easy to prepare, have high purity, and have low cost [17,24], which gives them an edge over ionic liquids. By definition, DESs are solvents composed of two or more components: Hydrogen Bond Donor (HBD) and Hydrogen Bond Acceptor (HBA) generally associated via hydrogen bonding or complexation which produces a liquid whose melting point is lower than that of the individual components. This hydrogen bond interaction gives rise to a unique chemical entity with a lower melting point than its precursors. Interestingly, some DESs have been proven at a laboratory scale to be applicable in leather manufacturing processes such as chrome tanning, vegetable tanning, plasticizing/fatliquoring of tanned leather, and the dyeing of plasticized leather [2]. In the open literature, many DESs researched are hydrophilic and, therefore, unstable in an aqueous environment, limiting their applications [25,30]. Due to its increasing number of applications, the concept of synthesis of DESs is currently the subject of growing interest. It has further led to a recent investigation into the synthesis of hydrophobic Deep Eutectic Solvents (HDESs).

Synthesis of HDESs can be achieved by using water-insoluble components. Properties such as density, viscosity, surface tension, and melting/freezing point depend on the HDES structure, while moisture absorption capacity and thermal stability determine

appropriate application options. This paper sought to investigate the fundamental physicochemical properties of three (3) non-ionic HDESs prepared from monoterpene and long-chain saturated organic acids.

2.0. Materials and Methods

2.1. Hydrophobic Deep Eutectic Solvents Synthesis

Menthol (99% assay) was purchased from Molychem, Octanoic acid (99% assay), Decanoic acid (98% assay), and Dodecanoic acid (99% assay) from Loba Chemie. Binary mixtures of monoterpene (menthol) and carboxylic acids (octanoic acid, decanoic acid, and dodecanoic acid) were prepared by weighing each component using a Mettler Toledo analytical weighing balance (ME 204E) and adding them into glass vessels (at the molar ratios as contained in Table 1). The solid mixtures were melted while stirring on a magnetic stirrer hot plate at 80°C until a homogeneous liquid mixture was obtained and cooled to room temperature.

Table 1. Composition of different hydrophobic Deep Eutectic Solvents.

HBA	HBD	Abbreviation	Mole Ratio	Physical appearance
Menthol	Octanoic acid	MC ₈	1:1	Pale yellow liquid
	Decanoic acid	MC ₁₀	1:1	Colourless liquid
	Dodecanoic acid	MC ₁₂	1:1	Golden yellow liquid

3.0. Results and Discussion

3.1. Fourier Transform Infrared of HDESs

The hydrogen bond is the primary intermolecular interaction between terpenes and organic acids in the formation of HDES [10,31](Ali et al., 2020; Zhang et al., 2012). Fourier Transform Infrared (FTIR) spectra of the different terpenes and organic acids and the resultant HDES from their combinations were determined to investigate and ascertain this interaction. Figure 1 shows cascaded spectra of menthol (M), octanoic acid (C₈), and MC₈. C₈ served as the HBD with a characteristic carbonyl stretching band (C=O) at 1707.1 cm⁻¹, while M was the HBA with a representative OH stretching band at 3242.8 cm⁻¹. The spectrum for MC₈ indicated a shift of the OH band in menthol to 3377 cm⁻¹, while the C=O band also reflected a shift in its wavelength to 1710.8 cm⁻¹. Both precursors had characteristic alkane C-H stretching bands between 2840–3000cm⁻¹, which was also reflected in MC₈. These shifts and intensity changes reflect the impact of the hydrogen bond between the hydrogen in the carboxyl moiety of the octanoic acid, and the oxygen in the OH of menthol, which resulted in the formation of MC₈.

Figure 2 represents spectra of menthol, decanoic acid (C₁₀) and MC₁₀ HDES. C₁₀ being the HBD, showed a characteristic carbonyl stretching band (C=O) at 1692.2 cm⁻¹, while MC₁₀ showed a shift in the OH band in menthol to 3406.8 cm⁻¹ and a corresponding shift in the C=O band to 1710.8 cm⁻¹. The alkane C-H stretching bands reflecting in the HBD and HBA were maintained in the resulting HDES (MC₁₀). In Figure 3, the HBD for MC₁₂ was dodecanoic acid (C₁₂) with an initial C=O band at 1692.2 cm⁻¹. The menthol OH band shifted from its initial wavelength to 3410.5 cm⁻¹ while the C=O band in C₁₂ experienced a slight backward shift to 1710.8 cm⁻¹ as reflected in MC₁₂. The resulting spectra in Figures 2–4 when compared with previous related works reflect similar shifts at the OH band of the monoterpene and the CO bands of the organic acids; which signifies the interaction between the two components during the formation of HDESs [19,22,26].

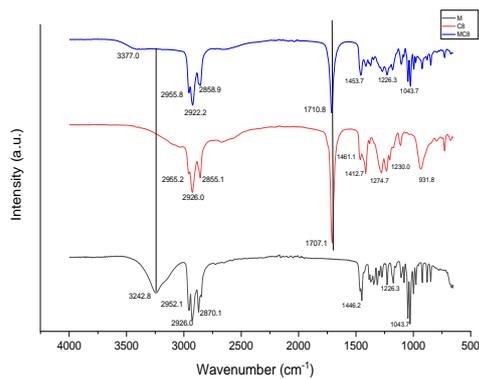


Figure 1: FTIR Spectra for Menthol, Octanoic acid, and MC₈ HDES

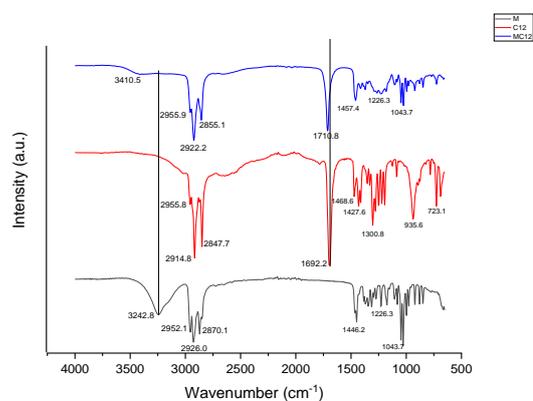


Figure 2: FTIR spectra for Menthol, Decanoic acid, and MC₁₀ HDES

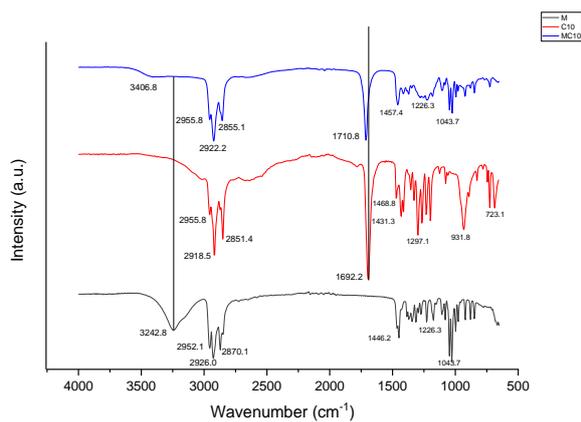


Figure 3: FTIR spectra of Menthol, Dodecanoic acid, and MC₁₂ HDES

In FTIR, one of the factors that influence peak intensity is concentration. A shift in peak position usually depicts electron distribution in the molecular bond that had changed. Therefore, the various peak shifts observed in the spectra of the HDESs can be attributed to the intermolecular hydrogen bonding between the HBDs and HBAs.

3.2. Physicochemical properties

i. Density

Density is a crucial property of solvents that greatly influences dissolution, reaction and separation processes, determining their viability. From experimental data obtained and captured in Figure 4, the density of all menthol-based HDES ranged between 0.8493–0.8981 kg/l. All HDESs revealed a linear decrease in density with a consistent increase in temperature. According to [16], densities of Menthol-based HDES were between 0.890–0.925 kg/l. Hydrophobic deep eutectic solvents have been reported to possess lower densities than water [16]. The density of a deep eutectic solvent reveals a temperature-dependent behaviour, which decreases linearly with increasing temperature [11,15,19,28]. Moreover, density depends on the choice of the hydrogen bond donor [(Andrew P. Abbott, Barron, et al., 2007; Andrew P. Abbott, Harris, et al., 2007; Cui et al., 2017; C. Florindo et al., 2014; García et al., 2015), and the molar ratio (Andrew P Abbott et al., 2011).

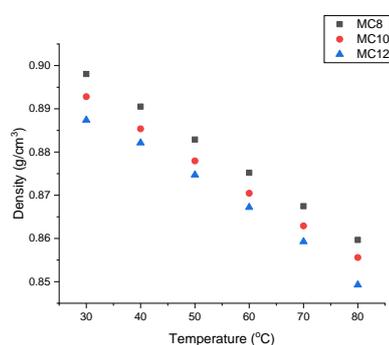


Figure 4: Density-temperature graph for Menthol based HDESs

i. Viscosity

Viscosities of the prepared HDESs were observed to be temperature-dependent. It decreased linearly with corresponding temperature increases. In Figure 5, the viscosity profile of menthol-based HDES increased from MC₈ to MC₁₂, i.e. MC₈ < MC₁₀ < MC₁₂, and was between 9–18 mPa.s. The results above align with results obtained from previous work (Catarina Florindo et al., 2019). Also, from the results obtained, it was observed that an increase in the alkyl chain of the carboxylic acid (HBD) resulted in the corresponding rise in the viscosities of the HDESs. Noteworthy is the extraordinarily low viscosities (<20 mPa.s) of HDESs based on fatty acids combined with menthol and thymol. These overcame one of the significant drawbacks of hydrophilic DES, where for example, a viscosity of 859.45 mPa.s was attained for ChCl: urea (1:2) (Shekaari et al., 2017)

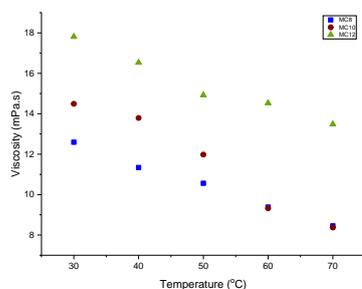


Figure 5: Viscosity-temperature graph for Menthol based HDESs

The viscosity of a eutectic mixture is affected by the nature of its components (Andrew P. Abbott, Barron, et al., 2007; D'Agostino et al., 2011), their molar ratio (Andrew P Abbott et al., 2011), the temperature (A. P Abbott et al., 2004; Andrew P. Abbott et al., 2003, 2006; Andrew P Abbott et al., 2004; Dai et al., 2015; Kareem et al., 2010), and the water content (D'Agostino et al., 2011; Dai et al., 2015; Du et al., 2016; C. Florindo et al., 2014; Shah & Mjalli, 2014).

i. Surface Tension

Surface tension is an essential property since it is highly dependent on the intensity of the intermolecular forces taking place between the hydrogen bond donor and the hydrogen bond acceptor. It also determines the suitability of HDES in interfacial processes in which mass transfer occurs. In Figure 6, the surface tension of MC₈, MC₁₀, and MC₁₂ was within 24.0–28.5 mN/m. The surface tension of the HDESs was also temperature dependent as it decreased with increasing temperature. Studies have shown that surface tension decreases linearly with increasing temperature (García et al., 2015; Lapeña et al., 2019; Nunes et al., 2019). The surface tension of all HDES was observed to be <30mN/m, and as exemplified in previous works, decreased with increasing temperature.

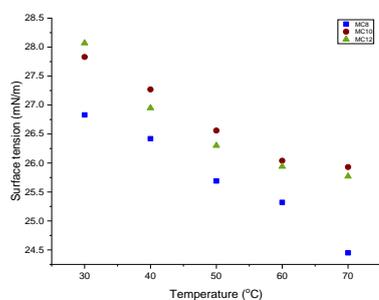


Figure 6: Surface tension-temperature graph for Menthol based HDESs

3.3. Hydrophobicity test

Figure 7 shows the image of the HDESs immediately after agitation. An oil-in-water emulsion-like mixture was observed. The samples were left for 24 hours to see if the emulsion formed any phase separation. After 24 hours, clear and distinctive phase separation was noticed with water (more dense phase) seen at the bottom of the bottle and the HDES (less dense phase) being on top, as seen in Figure 8.

Figure 7. HDESs in water immediately after agitation.

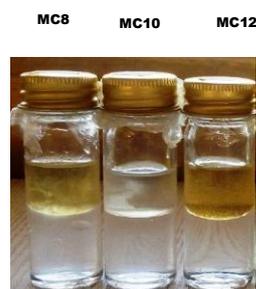


Figure 8. HDESs in water 24 hours after agitation.

Figure 9 is a chart indicating the moisture content determined in each HDES after its interaction with water for 24 hours. The HDESs MC₈, MC₁₀, and MC₁₂ had the following moisture content 5.26%, 3.54%, and 2.64% respectively. It could be seen that thymol-based HDESs had less moisture absorption capacity than their menthol-based counterparts. It was also reported by (Catarina Florindo et al., 2019), that an increase in the alkyl chain of the HBDs resulted in increased hydrophobicity of the HDESs.

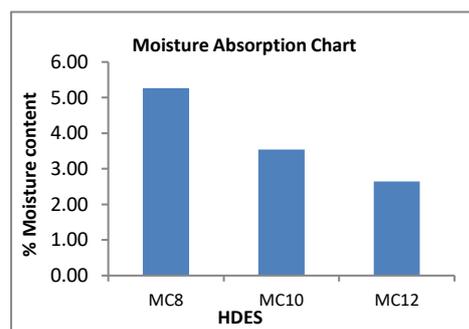


Figure 9. Percentage Moisture content graph for HDESs (Test for hydrophobicity).

It is highly recommended to determine the chemical stability of deep eutectic solvents that find applications in aqueous environments to ascertain that there is no contamination of the water phase with the DES and no loss of the DES structure due to water absorption. The ability of an HDES to maintain its structure and not lose its integrity in the presence of water is of enormous importance.

4.0. Conclusion

Three (3) hydrophobic deep eutectic solvents from menthol and long-chain organic acids were successfully prepared, all in a ratio of 1:1. All were liquids at room temperature, with MC₈ having a pale yellow colour, MC₁₀ being colourless and MC₁₂ having a golden yellow colour. The prepared HDESs were characterized using FTIR, and the spectra revealed remarkable shifts in the O-H stretching bands and C=O stretching bands of the HDESs compared with their precursors. The changes in the OH stretching bands and C=O stretching bands resulted from the intermolecular hydrogen bond formed between the starting materials to give HDES.

Also, physicochemical analysis was carried out on the synthesized HDESs, which revealed their excellent characteristics. This better informs researchers on their best areas of application, potentially in the removal of recalcitrant aromatic contaminants in wastewater. The density of menthol-based HDESs was found to be between 0.890–0.925kg/l. All densities were found to decrease with an increase in temperature. The vis-

cosity of the HDESs was found to be <20 mPa.s and decreased with an increase in temperature. Similar to viscosity, the surface tension of HDESs also reduced with an increase in temperature and was observed to be <30 mN/m. Finally, the extent of moisture absorption into the matrix of the HDESs was determined to be between 2.64 to 5.26 %. It was observed that the degree of hydrophobicity increased with an increase in the alkyl chain of the organic acids (HBDs).

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