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Hydrophobic Deep Eutectic Solvents for Ethanol, Propan-1-ol, and Propan-2-ol Recovery from Aqueous Solutions

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Abstract: Separating hydroalcoholic mixtures remains a significant challenge in engineering. Liquid–liquid extraction has emerged as an appealing alternative method, because it avoids the need for the large energy inputs, volatile organic compounds, and high pressures that are typically required by other separation processes. This study explores the use of hydrophobic deep eutectic solvents (HDESs) composed of terpenes and 10-undecenoic acid as extraction agents for the liquid–liquid separation of hydroalcoholic mixtures composed of alcohols (ethanol, propan-1-ol, and propan-2-ol) and water. The water content in the solvents studied was notably low, reflecting their hydrophobic nature. For the dried HDES samples, the water content ranged from 553 to 4901 ppm. In contrast, the water-saturated samples exhibited higher water contents, ranging from 7250 to 20,864 ppm. The HDES based on thymol, DL-menthol, and L-menthol displayed a eutectic point at an $x_{terpenes}$ of approximately 0.67. These mixtures maintained a liquid state up to a mole fraction of terpenes around 0.75. In contrast, the HDES composed of carvacrol, fenchyl alcohol, and α-terpineol exhibited their eutectic point at an $x_{terpenes}$ near 0.5. Notably, these mixtures remained in a liquid state across the entire composition range studied. The 2:1 molar ratio (HBA:HBD) presented the best values for extracting alcohols, reaching 34.04%, 36.59%, and 39.78% for ethanol, propan-2-ol, and propan-1-ol, respectively. These results show that HDES can be applied to overcome issues with existing extraction solvents, increasing the separation efficiency and making the process eco-friendly.

Keywords: hydroalcoholic mixtures; hydrophobic deep eutectic solvents; terpenes

1. Introduction

In contemporary engineering and technological development, green chemistry and sustainability are pivotal influences. The primary challenge lies in finding sustainable and environmentally friendly alternatives to toxic volatile organic chemicals that still meet the necessary chemical and physical requirements [1–5]. In this pursuit, alternative solvents have garnered significant attention due to their benign nature, ease of recycling, and reduced potential for contaminating both the final product and the environment. Among these alternatives, deep eutectic solvents (DESs) have emerged as a leading focus in the quest for green solvents that can effectively solvate a broad range of solutes [6–8].

DESs are renowned for their tunable and versatile physicochemical properties, mainly due to the vast array of available hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs). This adaptability allows DESs to be tailored to meet specific application requirements, earning them the name of design solvents [9–12]. Generally, DESs are formed by combining two constituents, typically an HBD and an HBA, which interact through hydrogen bonding to create a liquid with unique properties. This formation results in a

lower melting point for the DES compared to its pure constituents, attributed to the charge delocalization facilitated by the hydrogen bonds [13,14].

Most synthesized DESs are water-miscible, which restricts their use to applications involving water-soluble targets [15,16]. To overcome this limitation, hydrophobic deep eutectic solvents (HDESs) were introduced in 2015. The pioneering work by Kroon's group [9] and Marrucho's team [17] marked the development of HDESs. Kroon's research focused on HDESs composed of quaternary ammonium salts and decanoic acid, while Marrucho's team developed HDESs using DL-menthol combined with various carboxylic acids. Both types of HDESs demonstrated an ability to form a stable hydrophobic phase when mixed with water, highlighting their significant potential for extracting hydrophobic compounds from aqueous solutions. This hydrophobic characteristic expands their applicability, particularly in separating and purifying non-water-soluble substances from aqueous media.

Terpenes have shown great promise as sustainable and low-cost components for preparing hydrophobic solvents due to their low water solubility. Among these, menthol and thymol, which are monoterpenoids, are widely used in various industrial processes and commercial products. Their incorporation into hydrophobic deep eutectic solvents (HDESs) has garnered significant interest. Several studies have highlighted the efficacy of HDESs composed of terpenes and other components [18–20]. For instance, Tereshatov et al. [21] demonstrated that HDESs based on menthol (a terpene) and lauric acid (a carboxylic acid) successfully extracted indium from aqueous solutions. Florindo et al. [22] achieved up to 80% extraction of neonicotinoids from water using HDESs formed by menthol and natural acids. Similarly, Van Osch et al. [23] used terpene-based HDESs to remove riboflavin (vitamin B2) from aqueous environments. The interactions between terpenes and fatty acids in HDESs have been explored through molecular dynamics studies. These studies reveal that strong hydrogen bonds form between the hydroxyl (OH) group of terpenes and the carboxylate oxygen atom of fatty acids, often showing an angular probability distribution of around 150–180 °C [24–27].

Regarding toxicity, Nejrotti et al. [28] reported that the toxicity of HDESs can be attributed to the synergistic interactions within the supramolecular structure of the eutectic mixture, such as hydrogen bond networks and charge delocalization. These interactions change the intrinsic characteristics of the starting materials, leading to different properties in the resulting HDES. Marchel et al. [29] further described that HDESs based on terpenes and fatty acids frequently exhibit antimicrobial activity. This effect is due to the interaction with bacterial cell walls: in Gram-negative bacteria, the presence of lipopolysaccharides in the outer membrane inhibits the fatty acids from penetrating to the inner cell membrane. Conversely, in Gram-positive bacteria, the fatty acids can more easily pass through the cell wall and disrupt the inner membrane, leading to cell destabilization or dissolution. The type of microorganisms used in toxicity studies significantly influences the outcomes. Research has studied a variety of microorganisms, including *E. coli*, *S. aureus*, *P. aeruginosa*, *B. subtilis*, *B. cereus*, *C. perfringens*, *A. niger*, *C. albicans*, and *S. cerevisiae* [29–31]. These works provide insights into how HDESs can selectively target and affect different microbial species.

Due to their unique thermophysical properties, DESs and HDESs have been proposed as extractive agents in liquid–liquid separation processes of azeotropic mixtures [32]. Azeotropic mixtures are a problem for industrial processes due to the close boiling point between two compounds, such as ethanol and water [33–36]. Liquid–liquid extraction (LLE) is an effective method for separating azeotropic mixtures, offering significant advantages over traditional hydroalcoholic distillation. Unlike azeotropic distillation, which demands a high energy input due to the need for elevated pressures and temperatures, LLE operates under milder conditions and at a lower cost. The principle of LLE relies on the immiscibility of two liquid phases. In this process, a third component, known as the extracting agent, is introduced into the azeotropic mixture [37–39]. Some studies have reported the use of DESs for hydroalcoholic separation. Rodriguez et al. [40] used DESs based on choline chloride (ChCl) with glycolic acid (1:1) and lactic acid (1:2) to separate the ethanol–hexane

hydroalcoholic system. Oliveira et al. [38] investigated DESs consisting of ChCl + glycerol (1:2), levulinic acid (1:2), and ethylene glycol (1:2) as extracting solvents for separating ethanol from a hydroalcoholic mixture (ethanol + heptane). Sharepour et al. [32] studied ethanol separation from hexane using DESs formed by ChCl + malic or malonic acid (1:1). Most studies reported using ChCl-based DESs. To our knowledge, only the work by Haider et al. [33] applied HDESs to separate azeotropic mixtures (isopropanol from water). The authors used HDESs based on menthol + dodecanoic acid (2:1) or decanoic acid (1:1) and HDESs formed by fatty acids (decanoic acid + myristic acid (5:1) or palmitic acid (8:1) or dodecanoic acid (3:1)).

10-undecenoic acid has not yet been applied to HDES formation. Thus, the main aim of this work was to evaluate the potential of HDESs as extractor solvents in liquid–liquid extraction processes for separating ethanol, propan-1-ol, and propan-2-ol from aqueous hydroalcoholic mixtures. For this purpose, HDESs composed of 10-undecenoic acid (HBD) and terpenes (DL-menthol, L-menthol, carvacrol, terpineol, thymol, and fenchyl alcohol) as hydrogen acceptors were formed.

2. Materials and Methods

2.1. Materials

DL-menthol, L-menthol, thymol, carvacrol, alpha-terpineol, fenchyl alcohol, and 10-undecenoic acid were supplied from Merck group, Sigma-Aldric, São Paulo, Brazil. The alcohols (ethanol, propan-1-ol, and propan-2-ol) were acquired from Isofar, Rio de Janeiro, Brazil and Vetec, São Paulo, Brazil. The CAS number, catalog number, suppliers, and purity are depicted in Table 1.

Table 1. Name, molecular weight, water solubility, catalog number, CAS number, supplier, and purity [a] of chemicals used in this work.

HBA/HBD	Molecular Weight (g mol^{-1})	Water Solubility (mg L^{-1})	Catalog n°	CAS n°	Supplier	Purity [a]
10-undecenoic acid	184.27	7.37	124672	112-38-9	Sigma-Aldrich	98%
DL-menthol	156.27	420	W266507	89-78-1	Sigma-Aldrich	99%
L-menthol	156.27	490	PHR1116	2216-51-5	Sigma-Aldrich	≥99%
Carvacrol	150.22	1250	282197	499-75-2	Sigma-Aldrich	≥98%
Alpha-Terpineol	154.25	7100	432628	98-55-5	Sigma-Aldrich	≥96%
Thymol	150.22	900	T0501	89-83-8	Sigma-Aldrich	99%
Fenchyl alcohol	154.25	461	W248099	1632-73-1	Sigma-Aldrich	≥97%
Ethanol	46.06	totally miscible	1211	64-17-5	Isofar	99.5%
propan-1-ol	60.09	totally miscible	200-746-9	71-23-8	Vetec	99.5%
propan-2-ol	60.09	totally miscible	190764	67-63-0	Vetec	99.5%

[a] provided by supplier.

2.2. Hydrophobic Deep Eutectic Solvent (HDES) Preparation

To prepare all the hydrophobic deep eutectic solvents (HDESs), a precise method was employed involving the mixing of 10-undecenoic acid (acting as the hydrogen bond donor, HBD) with various hydrogen bond acceptors (HBAs). The HBAs used in this study included DL-menthol, L-menthol, carvacrol, terpineol, thymol, and fenchyl alcohol. The preparation followed a meticulous process, adapted from Ribeiro et al. [17], to ensure accuracy and consistency. The required amounts of each component were weighed using an analytical balance with a precision of ±0.0001 g. The mixtures were gently heated up to 50 °C while being continuously stirred with a magnetic stirrer. The stirring was maintained until each mixture became clear, transparent, and homogenous, indicating the formation of the HDES. Once a homogenous solution was achieved, the HDES was allowed to slowly cool to room temperature. The resulting liquids were then stored in their sealed glass vials to prevent contamination and moisture uptake. To assess the interaction of the HDES with water, binary mixtures of each HDES and water were prepared. These mixtures were vigorously shaken and then left to equilibrate for 24 h, allowing for thorough saturation. After the equilibration period, the HDES phase was carefully separated from

the mixture. The water content in both the dried and water-saturated samples of each HDES was measured using Karl Fischer titration, employing a Metrohm 831 Karl Fischer coulometer.

2.3. HDES Characterization

The DSC instrument used was a Shimadzu DSC-60 Plus, operated with the following parameters: Nitrogen (N_2) as purge gas, flow rate of 100 mL min^{-1}, a temperature range of $-100\ ^\circ$C to 100 $^\circ$C, and 10 $^\circ$C min^{-1} of heating rate. For each analysis, samples ranging from 2 to 10 mg of the mixtures were accurately weighed and placed in aluminum DSC pans. These pans were then hermetically sealed to prevent any vaporization of the samples during the measurement process. The uncertainty in the melting point temperature was better than $\pm 1\ ^\circ$C. This was determined by calculating the standard deviation from multiple consecutive measurements of the same sample.

Thermogravimetric Analysis (TGA) and Fourier Transform Infrared Spectroscopy (FTIR) were performed to characterize the thermal stability and molecular structure of the samples, respectively. The TGA instrument was a Shimadzu Model TGA-50 thermal analyzer, with the samples measured at a flow rate of 60 mL min^{-1}, and approximately 10 mg of each material was used for the analysis. Moreover, the temperature was ramped from 25 $^\circ$C to 900 $^\circ$C at a constant rate of 10 $^\circ$C min^{-1}. A Shimadzu IRTracer-100 FTIR spectrometer was used in transmittance mode, at a wavenumber range of 4000–600 cm^{-1}, with each sample being analyzed with 45 scans to ensure high-quality spectral data.

2.4. Liquid–Liquid Extraction

Hydroalcoholic solutions were prepared with a concentration of 10 wt% alcohol. To determine the optimal conditions for alcohol extraction (ethanol, propan-1-ol, and propan-2-ol), binary mixtures were prepared by varying the ratio of HDES (2:1, 1:1, and 1:2). The binary mixtures were stirred using a Thermomixer C (Eppendorf®, Hamburg, Germany) at 500 rpm for 24 h. This ensured thorough mixing and interaction between the HDES and the hydroalcoholic solution. After stirring, the mixtures were centrifuged at 4000 rpm for 15 min. The samples were then allowed to stand at room temperature for an additional 24 h to reach thermodynamic equilibrium. This ensured complete separation and proper phase formation.

The phases were carefully separated and meticulously collected to ensure accurate analysis. The focus was on quantifying the concentration of alcohols present in the HDES-rich phase (the top phase) after the separation process. The quantification was performed using gas chromatography–mass spectrometry (GC-MS). A Shimadzu QP2010 Ultra GC coupled to a mass spectrometer was employed for this analysis. A DB-5 capillary column (J&W Scientific, Folsom, CA, USA, 30 m × 0.25 mm id, 0.25 μm) was used for the separation. The column temperature was programmed from 60 $^\circ$C to 270 $^\circ$C at a rate of 10 $^\circ$C min^{-1} and kept at 270 $^\circ$C for 20 min. The injector was heated to 250 $^\circ$C and the detector to 290 $^\circ$C. Ultrapure helium was used as the carrier gas at a flow rate of 1.0 mL min^{-1}. Data acquisition was carried out using electron impact (70 eV). The samples were analyzed in scan mode, covering a mass range from 40 to 600 u. Samples were injected in spitless mode to maximize sensitivity. The injection volume was precisely controlled at 1 μL. The extraction efficiency of each alcohol was determined using Equation (1).

$$EE\% = \frac{m_{alcohol}^{HDES}}{m_{alcohol}^{HDES} + m_{alcohol}^{water}} \times 100 \tag{1}$$

where m_{EtOH}^{HDES} and m_{EtOH}^{water} are the alcohol mass in the *HDES* phase and water, respectively.

3. Results

3.1. HDES Characterization

HDESs are frequently highly viscous fluids compared to organic solvents and thus need to be used in solutions. Nevertheless, some studies reported in the literature on HDES formed using terpenes and fatty acid [24,41–45] showed variations between 11 and 300 mPa·s at room temperature, clearly overcoming one of the ESs' main disadvantages. Furthermore, in order to reduce the amount of extracting solvent used while maintaining its extraction properties and determine the hydrophobicity of the HDESs studied here, the water content (ppm) of the dry and water-saturated HDES was measured, as can be seen in Figure S1 in Supplementary Materials and Table 2. Molar ratios between HBA:HBD of 1:2, 1:1, and 2:1 were previously chosen, since this includes the liquid region for all the terpenes studied.

Table 2. Water contents (ppm) of hydrophobic deep eutectic solvents based on terpenes (HBA) and 10-undecenoic acid (HBD), dried and water-saturated and with different molar ratios at room temperature.

HBA (Molar Ratio)	Dried (ppm)	Saturated (ppm)	Log P (HBA)
Carvacrol (1:2)	2149 ± 109	$16{,}859 \pm 84$	
Carvacrol (1:1)	1438 ± 84	$10{,}068 \pm 109$	3.08
Carvacrol (2:1)	780 ± 45	$12{,}497 \pm 168$	
Terpineol (1:2)	3511 ± 118	$19{,}566 \pm 142$	
Terpineol (1:1)	2069 ± 92	$13{,}062 \pm 107$	2.79
Terpineol (2:1)	987 ± 67	$15{,}089 \pm 168$	
Thymol (1:2)	1278 ± 127	$13{,}008 \pm 227$	
Thymol (1:1)	934 ± 96	7250 ± 284	3.20
Thymol (2:1)	797 ± 36	$10{,}018 \pm 360$	
Fenchyl (1:2)	4901 ± 126	$20{,}864 \pm 106$	
Fenchyl (1:1)	2763 ± 68	$15{,}648 \pm 141$	2.71
Fenchyl (2:1)	1168 ± 33	$18{,}713 \pm 136$	
DL-menthol (1:2)	1373 ± 97	$11{,}154 \pm 70$	
DL-menthol (1:1)	866 ± 36	7607 ± 175	3.28
DL-menthol (2:1)	631 ± 38	8795 ± 136	
L-menthol (1:2)	701 ± 68	$12{,}919 \pm 328$	
L-menthol (1:1)	629 ± 30	8868 ± 136	3.28
L-menthol (2:1)	553 ± 27	$10{,}160 \pm 282$	

The HDESs had water contents ranging from 553 ± 117 ppm to 4901 ± 226 ppm for dried and 7250 ± 284 ppm to $19{,}566 \pm 142$ ppm for water-saturated, indicating much lower contents compared to traditional hydrophilic ESs based on choline chloride (ChCl). Florindo et al. [46] reported the water content of water-saturated deep eutectic solvents formed by a salt, choline chloride, and several organic diacids, with values between 140,000 and 190,000 ppm, and monoacids, such as clavulanic acid, with a water content near 100,000 ppm. Furthermore, looking at the molar ratio variation for each dried ES, it is clear that the water content decreases as the amount of terpene is increased (1:2 > 1:1 > 2:1). In contrast, for water-saturated ES, the 1:1 molar ratio showed the lowest water content, and a higher amount of C_{11} acid displayed the highest water contents. This behavior was found in all the ES studies.

The octanol–water coefficient, log P, seems to influence the water content for the dried ES of each terpene. The water content (fixed molar ratio) decreased as the hydrophobicity of the terpenes increased, following the following order (log P in parenthesis): L-menthol (3.28) ≈ DL-menthol (3.28) < thymol (3.20) < carvacrol (3.08) < alpha-terpineol (2.79) < fenchyl (2.71). Regarding the water-saturated HDES, a similar behavior to that mentioned above was observed, except for the thymol-based HDES, which had the lowest water content. Thus, it is suggested that the hydrophobicity of the terpenes played a fundamental

role in the water content values for these dried and water-saturated HDESs. In contrast to hydrophilic DESs, log P can be a good predictor for low-ionicity HDESs. Deepika et al. [47] found water contents of 34,000 to 40,000 ppm for water-saturated HDESs composed of thymol and C_{10} acid at different molar ratios. Florindo et al. [22] demonstrated that the hydrogen bonds responsible for HDES formation are partially broken, and the compounds solubilize in the aqueous phase according to their individual water-solubility. Mjalli and Ahmad [48], Pandey and Pandey [49], and Silva et al. [50] observed through molecular dynamics (MD) studies that adding water to hydrophilic ESs based on choline chloride results in an increase in hydrogen bonds between the HBD and water molecules. In contrast, Paul et al. [51] demonstrated using MD that the hydrogen bonds between HBAs and HBDs are the dominant force and play a crucial role in the interactions with water and, consequently, in the water contents. Shishov et al. [52] observed that in many cases, HDES stability is dependent on the molar ratio between its forming constituents. In addition, a high-water content can benefit the solvent's extractive properties, since it can increase hydrogen bonds with the target solute. Thermophysical properties, such as density and viscosity, are also important properties for characterizing solvents. Some studies have described these properties for HDESs based on terpenes and fatty acids. Ribeiro et al. [17], Florindo et al. [22,46,53], and Martins et al. [45] demonstrated that in these new HDESs, both dried and water-saturated, the density decreases linearly with temperature, while the viscosity decreases exponentially. The authors also observed a very small influence of water on these thermophysical properties, which was due to the high hydrophobicity of these new HDESs.

The solid-liquid phase diagrams measured for the mixtures studied in this work using differential scanning calorimetry (DSC) allowed the melting temperatures (*Tm*) to be measured in the molar ratio ranges in which the HDESs remained liquid at room temperature and could therefore be used as solvents. The experimental diagrams of mixtures of terpenes (L-menthol, DL-menthol, thymol, carvacrol, alpha-terpineol, and fenchyl) and 10-undecenoic acid are displayed in Figure 1. The *Tm*s found for the HDESs studied are L-M:C_{11} (1 °C), DL-M:C_{11} (−4 °C), T:C_{11} (−11 °C), C:C_{11} (−33 °C), A-T:C_{11} (−17 °C), and F:C_{11} (−25 °C), validating their use as solvents at room temperature. These systems showed phase behavior characterized by a single eutectic point.
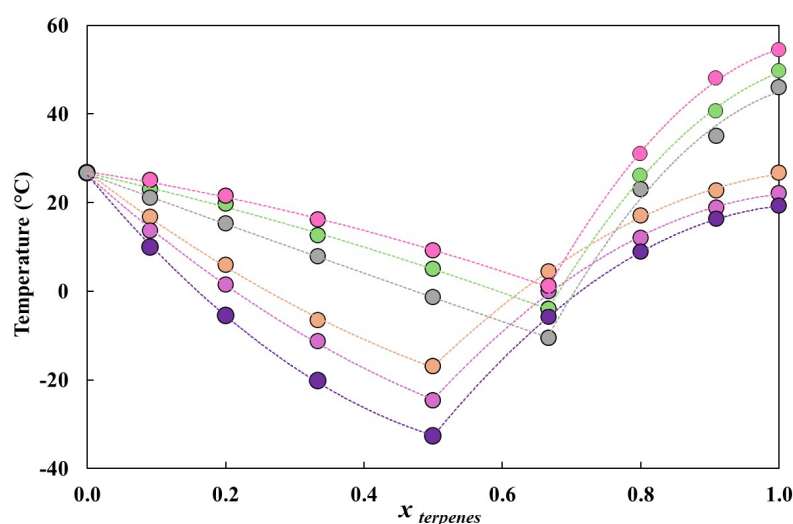

Figure 1. Experimental solid–liquid phase diagram for hydrophobic deep eutectic solvents (HDESs) based on terpenes (HBA) and 10-undecenoic acid (C_{11}) using DSC to visualize *Tm*s: C:C_{11} (●), F:C_{11} (●), A-T:C_{11} (●), T:C_{11} (●), DL-M:C_{11} (●), and L-M:C_{11} (●).

Although the melting point depressions are relatively small and near those predicted, in many cases, assuming an ideal liquid phase allows for the formation of liquid mixtures at room temperature while the starting compounds are solid [23,54,55]. Therefore, the

molecular interactions established in the mixture are similar to and of the same strength as those present in the liquid phases of the initial components (hydrogen bonds between hydroxyl groups of a similar nature) [5,19,56].

The terpene diagrams based on DL- and L-menthol with 10-undecenoic acid demonstrated the presence of minor negative deviations from ideality for high concentrations of the respective terpenes. Furthermore, it can also be observed that from $x_{\text{menthol}} \approx 0.75$, it was no more possible to form a solvent in the liquid state. This conclusion corroborates other studies reported in the literature, which show SLE phase diagrams forming liquid mixtures of solvents based on terpenes [17,22,44,46,47,53,57]. In relation to thymol, slight positive deviations from ideality were noted for high terpene concentrations and a liquid range up to $x_{\text{thymol}} \approx 0.75$. Concerning carvacrol, alpha-terpineol, and fenchyl, slight positive deviations from ideality were noted for high terpene concentrations and a net range throughout the molar composition. This behavior was also found by Abranches et al. [58], who reported the characterization of HDESs formed by thymol and fatty acids (C_8, C_{10}, and C_{14} acids). In fact, this result is consistent with the main structural difference between thymol and other terpenes. Thymol is a weaker hydrogen acceptor than menthols, carvacrol, fenchyl, and terpineol [59]. In addition, other studies have been reporting behavior similar to that found in this work [24,43,47,60].

The HDESs formed by fenchyl alcohol, terpineol, and carvacrol showed a sharp depression in their Tm when compared to their initial constituents. Moreover, there were no negative deviations from ideality, thus proving the formation of their respective eutectic solvents over the complete composition range. This behavior is in agreement with other studies that have examined these terpenes with other HBDs [60–64]. It is important to emphasize that none of these studies reported the formation of 10-undecenoic acid-based HDESs.

All HDESs based on terpenes and 10-undecenoic acid and their individual components were characterized by FTIR and TGA in a 2:1 molar ratio to evaluate the hydrogen bonding formed during their synthesis, as shown in Figure 2. The FT-IR spectrum of pure terpenes displayed a large band at 3268 to 3156 cm^{-1} assigned to the O-H bond, while the C-H stretching vibrations were observed at 2947 to 2861 cm^{-1}. Other characteristic bands at 2451 cm^{-1} and 2367 cm^{-1} are attributed to the stretching vibrations of the C-H bond, and an absorption at 1223 to 1262 cm^{-1} is attributed to the C-O bond. Furthermore, the absorptions at 1365 cm^{-1} and 1454 cm^{-1} are attributed to the bending of the C-H bonds of the CH_3 (methyl) and CH_2 (methylene) groups, respectively. 10-undecenoic acid showed characteristic regions attributed to C-H bonds at 2911 to 2946 cm^{-1}. For the C=O stretching bond, a strong absorption is displayed between 1694 and 1777 cm^{-1}, and the C-O interaction is observed in the 1286 to 1302 cm^{-1} band. This acid's characteristic unsaturated C=C bond was seen in the 898 to 917 cm^{-1} region. Additionally, the bands at 1458 cm^{-1} and 1412 cm^{-1} corresponded to the C-C bonds of the hydrocarbon chain.

The successful formation of HDESs through the formation of hydrogen bonds due to the extension of the O-H band was confirmed by FTIR analysis. This phenomenon is due to a reduction in the force constant caused by the transfer of protons through the hydrogen bonding of the components, resulting in a widening of the peak [43,65]. A widening of the C=O band was also observed for all HDESs. These variations suggest an increase in the electronic density of the carbonyl oxygen, which can be attributed to the formation of hydrogen bonds between its components [66,67]. Therefore, the broadening of the O-H and C=O bands confirmed the hydrogen bond formation between the terpenes and the 10-undecenoic acid, thus confirming the successful formation of HDESs, corroborating some studies that have reported the formation of HDESs based on terpenes and fatty/carboxylic acids [24,41–44,64–67].

Evaluating the thermal stability of HDESs is essential, since it allows for the decomposition or phase change of the solvent to be determined. The thermograms represent the weight loss of an HDES as a function of the temperature and are shown in Figure 3. The thermograms showed that all the HDESs were degraded entirely in the temperature range

from 120 to 250 °C. All thermograms show a weight reduction in a single step. This means that the interaction between the two DES precursor molecules is significant, which results in a one-step decrease [65]. Moreover, L-menthol-based HDESs have a lower degradation temperature due to the higher volatility of menthol. The difference between the DL- and L-menthol thermograms can also be seen. Despite being polymorphic, the racemic mixture (DL-menthol) showed a slower drop in weight than the pure isomer. This demonstrates that these stereoisomers have different properties, exhibiting distinct behaviors in the formation of an HDES [68].
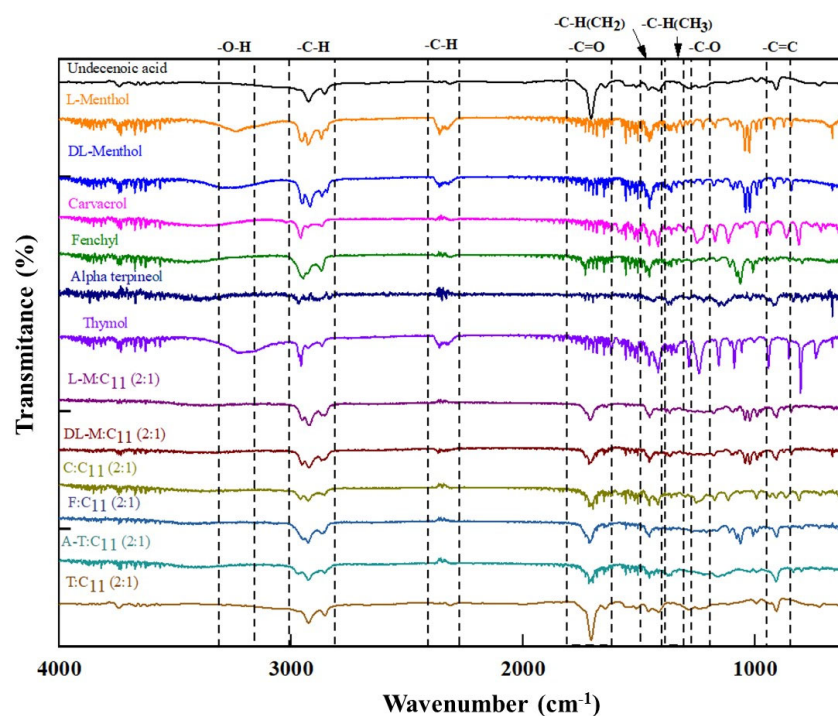
Figure 2. FT-IR spectra of hydrophobic deep eutectic solvents (HDESs) based on terpenes (HBA) and 10-undecenoic acid (C_{11}) and their individual components.
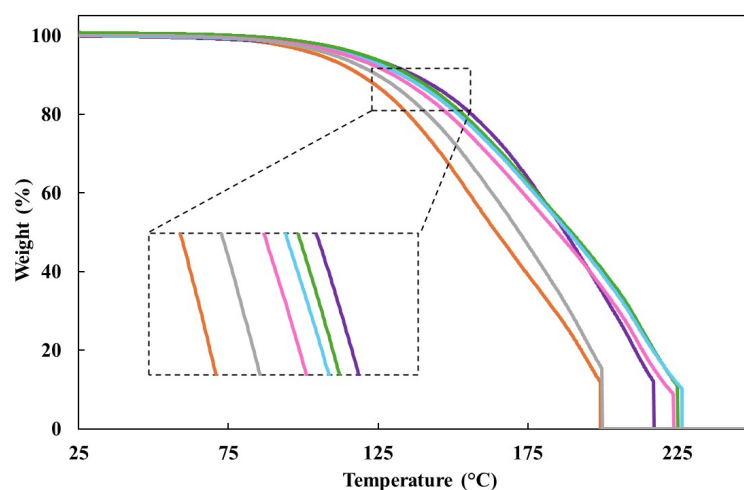
Figure 3. Thermograms of the hydrophobic deep eutectic solvents (HDESs) based on terpenes (HBA) and 10-undecenoic acid (C_{11}) using TGA analysis: C:C_{11} (•), F:C_{11} (•), A-T:C_{11} (•), T:C_{11} (•), DL-M:C_{11} (•), and L:C_{11} (•).

Compared to other previously reported HDESs formed by decanoic acid and quaternary ammonium salts, the T_{deg} values are lower. Thus, it is suggested that these lower

T_{deg} values do not show degradation, reflecting the sublimation/evaporation of the HBA components [9,23,54]. Components such as menthol, thymol, and carvacrol, among others, have an intense odor and are known to have the ability to sublimate [33]. These results suggest that the degradation temperature, volatility, and thermal stability depend highly on the precursor molecules. This is important to consider when designing an HDES for a particular application. Duque et al. [65], Haider et al. [33], and Van Osch et al. [23] reported similar thermogram behaviors in their characterization studies of hydrophobic HDESs based on terpenes.

3.2. Alcohol Separation from Hydroalcoholic Mixtures

The HDESs formed in this study were applied to separate hydroalcoholic mixtures composed of alcohols (ethanol, propan-1-ol, or propan-2-ol) and water. Figure 4 shows the extraction efficiency of the alcohols for the HDES phase at different molar ratios. The separation efficiency is associated with the transport capacity of the solute (alcohols) from the solvent (HDES). The ideal extracting solvent should have high extraction values, since high selectivity values usually lead to a few steps in the process [34,37]. Figure 4a illustrates the alcohol extraction efficiency values using HDESs at a molar ratio of 2:1, which ranged from $26.58 \pm 1.79\%$ to $34.04 \pm 1.56\%$, while propan-2-ol and propan-1-ol ranged from $26.96 \pm 1.34\%$ to $36.59 \pm 1.66\%$ and $27.39 \pm 1.29\%$ to $39.78 \pm 1.46\%$, respectively. The terpenes' ability to separate alcohols from water followed the order of DL-menthol (3.28) $\approx$ L-menthol (3.28) < thymol (3.20) < carvacrol (3.08) < terpineol (2.79) < fenchyl (2.71). It can clearly be seen that the terpenes' hydrophobicity has a strong influence on the extraction of the alcohols, since it coincides with the terpenes' log P values (in parentheses). In relation to the 1:1 molar ratio (Figure 4b), the same behavior was observed as reported above, following the same trend as the separation performance of terpenes based on their hydrophobicity. However, the extraction efficiency values were lower compared to the 2:1 molar ratio HDES, reaching a maximum of $27.77 \pm 0.98\%$, $29.01 \pm 1.65\%$ and $32.23 \pm 1.44\%$ for ethanol, propan-2-ol, and propan-1-ol, respectively. These results suggest that the HBA acts as the driving force in the alcohol partitioning, since there was a decrease in the extraction values when the amount of 10-undecenoic acid in the mixture was increased. Figure 4c exhibits the extraction efficiency values of the alcohols in the hydroalcoholic mixtures for the HDESs formed using a 1:2 molar ratio (HBA:HBD). Slight variations in the extraction values were observed, reaching a minimum and maximum value for ethanol of $19.25 \pm 1.89\%$ and $22.97 \pm 1.56\%$, respectively, while for propan-2-ol and propan-1-ol, a minimum of $20.09 \pm 1.63\%$ and $19.69 \pm 1.51\%$ and a maximum of $23.41 \pm 2.01\%$ and $23.96 \pm 1.00\%$, respectively, were found. This behavior could be explained by the lower amount of HBA in the mixture, and consequently, the influence of the hydrophobicity of these compounds on the extractions was reduced. Furthermore, 10-undecenoic acid has a higher influence on this molar ratio, since it is the majority compound in the mixture and common to all the HDESs studied, corroborating the low variation in the extraction values. Nevertheless, this molar ratio had the lowest extraction values compared to the other molar ratios studied, even though 10-undecenoic acid had a log P of 3.89, corroborating the suggestion that the hydrophobicity of the HBA is of fundamental importance for the separation of alcohols from water.

The separation behavior of the alcohols was closely aligned with their hydrophobicity, as predicted by their log P values. Thus, the separation efficiency increased with the alcohol's log P value: ethanol (-0.14) < propan-2-ol (0.28) < propan-1-ol (0.35). This trend highlights the strong influence of hydrophobicity in determining the effectiveness of alcohol separation in HDES systems.
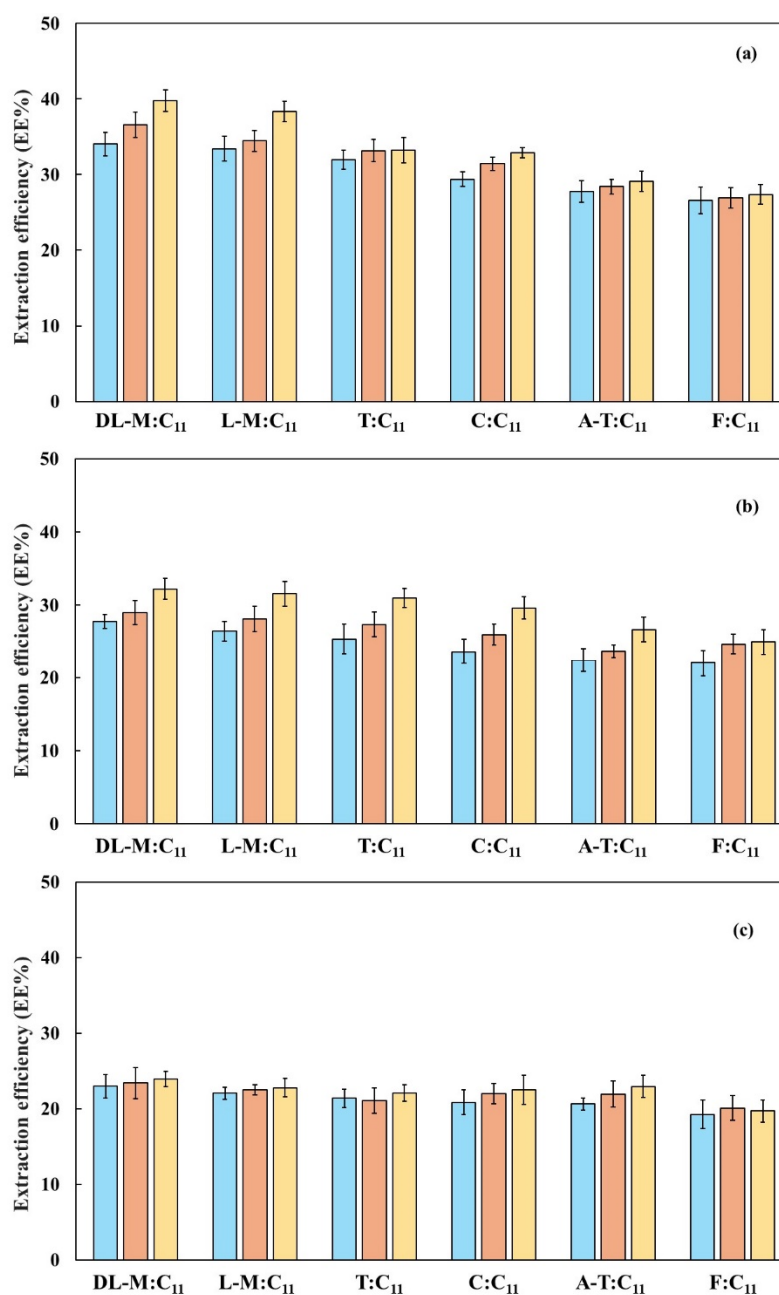
Figure 4. Extraction efficiencies of ethanol (■), propan-2-ol (■), and propan-1-ol (■) using hydrophobic deep eutectic solvents based on terpenes and 10-undecenoic acid at different molar ratios (HBA:HBD): (**a**)—2:1; (**b**)—1:1; (**c**)—1:2.

According to Xu and Liu [69], lower-chain alcohols have a better affinity for aqueous phases due to the higher formation of hydrogen bonds. According to Fong et al. [70], an increase in the number of carbons in the alcohol structure (aliphatic or branched) decreases the free energy and consequently increases the hydrophobicity. Lo et al. [71] demonstrated that a branched-chain alcohol (propan-2-ol) has lower intermolecular forces (hydrogen and hydrophobic bonds) than propan-1-ol. This phenomenon is attributed to the branched-chain structure of the propan-2-ol isomer, which provides the steric hindrance that reduces the acting force. These studies in the literature corroborate the results of the present study, since it seems that the hydrophobicity of the solutes and solvents plays a crucial role in separating these hydroalcoholic mixtures. Oliveira et al. [38] studied the separation of ethanol from heptane using DESs based on choline chloride (ChCl) with glycerol, levulinic

acid, or ethylene glycol. The authors demonstrated that these DESs achieved high selectivity that was superior to other alternative solvents, such as imidazolium-based ionic liquids. Sharepour et al. [32] reported hydrophilic DESs based on ChCl and malonic or malic acid (1:1) in the study of the separation of ethanol from hexane with a maximum extraction of 35%. Peng et al. [72] described that the addition of DESs composed of ChCl and urea was able to break the hydroalcoholic point of the mixture formed by ethanol and water. Xu et al. [73] evaluated the ability to separate azeotropic mixtures of propan-2-ol and water using DESs consisting of methyl trioctyl ammonium chloride and 1-hexanol or 1-decanol. The authors found selectivity values of 12 for DESs based on 1-hexanol and 17 for 1-decanol. Haider et al. [33] demonstrated the ability of HDESs composed of DL-menthol with C_{10} or C_{12} to separate 2-propanol from water, with selectivity values reaching 70. This study did not report the solute extraction efficiency values. Verma and Banerjee [74] studied the extraction of alcohols from water using HDESs based on tetramethylammonium (HBA) and decanoic acid, with lower distribution values than found by us. Furthermore, when compared to other alternative solvents, such as phosphonium-based ionic liquids [75], the HDESs studied in this work also showed better propan-1-ol extraction values from azeotropic mixtures with water ($\approx$34% extraction efficiency for DL-M:C_{11} HDES and $\approx$20% for trihexyltetradecylphosphonium tetracyanoborate—[P_{66614}][TCB]). Therefore, in this study, the high capacity through remarkable values of alcohol extraction from azeotropic mixtures with water using hydrophobic DESs based on terpenes and 10-undecenoic acid is evident.

4. Conclusions

This work studied low-viscosity hydrophobic eutectic solvents based on terpenes and 10-undecenoic acid to separate hydroalcoholic mixtures of alcohols (ethanol, propan-1-ol, and propan-2-ol) and water. Different molar ratios (2:1, 1:1, and 1:2) were studied in the extraction of alcohols. The 2:1 molar ratio (HBA:HBD) exhibited better values for extraction efficiency of alcohols, reaching 34.04, 36.59, and 39.78 for ethanol, propan-2-ol, and propan-1-ol, respectively. For the 1:1 molar ratio, values of 27.77, 29.01, and 32.23 for ethanol, propan-2-ol, and propan-1-ol, respectively, were observed. The terpenes with the highest hydrophobicity showed the highest extraction results in the following order: DL-menthol $\approx$ L-menthol < thymol < carvacrol < terpineol < fenchyl. Thus, it is suggested that the HBA's hydrophobicity proved to be the main driving force for the remarkable separation values of the alcohols. The 1:2 ratio showed the lowest extraction values and similar values between the HDESs. This behavior could be explained by the lower amount of HBA in the mixture and, consequently, a higher influence of 10-undecenoic acid (common to all HDES). The data obtained in this study show that HDESs can also be viewed as easier, cheaper, and greener alternatives to traditional solvents in the separation of ethanol–water hydroalcoholic mixtures.

Conflicts of Interest: The authors declare no conflicts of interest.

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