Non-Ideality in Thymol + Menthol Type V Deep Eutectic Solvents
Nicolas Schaeffer, Dinis O. Abranches, Liliana P. Silva, Mónia A.R. Martins, Pedro J. Carvalho, Olga Russina, Alessandro Triolo, Laurent Paccou, Yannick Guinet, Alain Hedoux, and João A.P. Coutinho

ABSTRACT: The nonionic Type V deep eutectic solvent (DESs) thymol + menthol is experimentally and computationally studied aiming to clarify the relation between its liquid phase structure and its thermodynamic nonideality. $^1H$ NMR, Raman, and X-ray scattering analysis of the thymol + menthol system, supported by molecular dynamics simulations, show complex intermolecular interactions dominated by sterically hindered H-bonded clusters. For temperatures greater than or equal to room temperature, a quasi-linear evolution of the eutectic system properties between the pure compounds is observed, suggesting the absence of a magic stoichiometric composition in the eutectic solvent. However, temperature dependent Raman spectroscopy indicates a notable increase in thymol−menthol H-bonding as temperatures approach the eutectic point. This study shows that nonionic Type V DESs present an important temperature-dependent nonideality originating from the change in the intermolecular H-bonding with temperature. These findings have significant implications for the design and growing application of Type V DESs.

KEYWORDS: Alternative solvent, Characterization, Hydrogen-bonding, Temperature dependent, Nonionic eutectic solvent

INTRODUCTION

Recently, a new class of nonionic deep eutectic solvents (DESs), labeled as Type V DESs, in contrast to the ionic nature of Types I–IV, was identified. $^1$−$^3$ Type V DESs exhibit strong negative deviations from ideality, defined by the variation in the activity coefficient of the system, resulting in a significant depression of the melting point that in the case of the 1:1 thymol + menthol mixture is 60 K below that predicted for an ideal mixture. $^1$−$^4$ These nonionic DESs, which are often hydrophobic, appear as promising media for the solvent extraction of organic and metallic compounds presenting low viscosity while incorporating bioderived constituents. $^4$−$^7$ Certain properties of Type V DESs such as densities and Kamlet−Taft solvatochromic parameters vary monotonically and predictably with hydrogen-bond donor (HBD) and acceptor (HBA) selection as well as molar composition for a given mixture, allowing to tune the DES composition for specific applications. $^4$ Other properties such as the thermal stability and viscosity are dependent on the extent of the negative deviations from ideality for a given mixture and therefore are more difficult to extrapolate from the pure component data. $^4$ The viscosities of reported Type V DESs are typically in the range of 15−70 cP at 298 K, $^6$−$^7$ slightly above that of conventional organic solvents but significantly lower than comparable hydrophobic ionic liquids and DESs. $^9$ Importantly, solvent extraction of both apolar organic solutes and inorganic metal complexes in nonionic DESs was shown to be of comparable or superior efficiency relative to that in conventional and "unconventional" solvents such as hydrophobic ionic liquids. $^5$−$^8$, $^{10}$

Despite their potential, characterization of the condensed phase of Type V DESs beyond simple pairwise interaction of the HBD and HBA is still scarce. In this work, the molecular interactions of the prototypical Type V DES thymol + menthol are experimentally and computationally studied aiming to understand its liquid phase structure and its relation to nonideality. The system thymol + menthol is particularly interesting as, although both substances are structurally similar (structures shown in Figure 1), both compounds present severe negative deviations to thermodynamic ideality when mixed. Hydrogen bonding (H-bonding) in the mixture is followed by $^1H$ NMR and Raman spectroscopy as a function of eutectic composition as well as temperature. Additionally, the intermediate range order in the liquid phase structuring of the 1:1 thymol + menthol is probed by X-ray scattering. The experimental results are further complemented by molecular dynamic (MD) simulations.

Access

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Figure 1. Change in $^1$H NMR chemical shift of select highlighted protons ($\Delta \delta_i$) of thymol (circles) and menthol (squares) in the thymol + menthol eutectic as a function of composition at $T = 328$ K. A molar fraction of 1.0 corresponds to the pure individual component; all compositions are in the liquid state.

**METHODOLOGY**

**Chemicals.** ($\pm$)-Menthol (99.5 wt % purity) and thymol ($\geq$99.0 wt % purity) were obtained from Acros Organics. The menthol stereochromy is omitted in the manuscript. The samples were used as received from the supplier without further purification. Purity of the compounds was confirmed by $^1$H and $^{13}$C NMR spectra, GC-MS, and specific rotation. Thymol + menthol mixtures for varying thymol molar fraction ($\delta_{\text{thymol}}$) covering the full composition range (at 0.1 mol fraction intervals) were gravimetrically prepared using an analytic balance Mettler Toledo XP205. Samples were heated under ambient atmosphere with stirring at $T = 338$ K until a homogeneous liquid was formed and then stirred in the liquid state for more than 30 min. The mixtures were subsequently stored in sealed vials for measurement. The physical–chemical properties of the eutectic mixture including the solid–liquid equilibrium phase diagram and Kaml–Taft solvatochromic parameters across the full composition range as well as the viscosity (η = 57.88 mPa·s), density (ρ = 0.9365 g·cm$^{-3}$), and onset degradation temperature ($T_{\text{onset}} = 451.78$ K) at the eutectic composition ($\delta_{\text{thymol}} = 0.5$) were previously described. The water content of the mixture after extended exposure to air was previously reported and deemed negligible.

**Experimental Characterization.** Nuclear Magnetic Resonance (NMR) Analysis. A Bruker Avance 300 operating at 75 MHz was used to analyze the structures of pure liquid terpenes and their eutectic mixtures at 328 K with deuterated water (D$_2$O) as the solvent and tetramethylsilane as the reference placed in a coaxial insert.

**Raman Spectroscopy Analysis.** The Raman spectra of the thymol + menthol mixtures for varying molar composition as well as those of the pure compounds at 293 K were obtained using the InVia Renishaw Raman microscope equipped with a 514.5 nm laser source. Raman spectra were collected using an achromatic lens with an acquisition time of 120 s. The OH stretching spectra were normalized by the intensity of the CH stretching bands integrated between 2800 and 3150 cm$^{-1}$. The sample temperature was controlled by placing the sample in a THMS 600 Linkam temperature device. The temperature dependence of the OH stretching spectrum (2800–4000 cm$^{-1}$) was investigated for the 1:1 thymol + menthol mixture in the range 213–293 K. The spectra were deconvoluted in the region 3100–3700 cm$^{-1}$ using the Origin software package. The baseline was fitted using an exponential decay function and subtracted. The resulting area was deconvoluted into five Gaussian components.

**Small Angle X-ray Scattering (SAXS) Measurements.** The SAXS measurements were performed at the SAXBerlin Sapienza with a Xeuss 2.0 QZoom system (Xenocs SA, Sassenage, France), equipped with a microfocus Genix 3D X-ray source ($\lambda = 0.1542$ nm), a two-dimensional Pilatus 3 R 300K detector which can be placed at variable distance from the sample. Calibration of the scattering vector Q range, where $Q = (4\pi \sin \theta)/\lambda$, 20 being the scattering angle, was performed using a silver behenate standard. Measurements with different sample–detector distances were performed so that the overall explored Q range was 5.0 nm$^{-1} < Q < 30.0$ nm$^{-1}$. The sample was loaded into disposable quartz capillaries with nominal thickness 2.0 mm and sealed with hot glue before placing it in the instrument sample chamber at reduced pressure (~0.2 mbar). The beam size was defined through the two-pinhole collimation system equipped with scatterless slits to be 0.25 mm x 0.25 mm. The two-dimensional scattering patterns were subtracted for the dark counting and, then, masked, azimuthally averaged, and normalized for transmitted beam intensity, exposure time, and subtended solid angle per pixel, by using Fox Trot software developed at SOLEIL. The one-dimensional S(Q) vs Q profiles were then subtracted for the capillary contribution. Measurements on thymol--menthol 1:1 were conducted at ambient temperature (ca. 293 K), and the sample was maintained as liquid and homogeneous during the whole length of the experiment.

**Determination of the Vapor–Liquid Equilibrium (VLE).** VLE measurements of the thymol + menthol mixture were determined at 0.05 MPa, using an in-house isobaric microebulliometer. The apparatus was previously described and optimized in previous publications. Briefly, the equipment is composed by three sections: (a) a glass chamber containing approximately 8 mL of sample, placed inside an aluminum block sited on top of a heating and stirring plate; (b) a glass condenser at the top of the chamber where the temperature is kept constant by means of a thermostatic bath; and (c) a liquid injection system, pressure line connections, and temperature probes. The temperature of the liquid phase was measured with a type K thermocouple, with an uncertainty of 0.05 K. The temperature probe was previously calibrated by comparison with a NIST-certified Fluke calibration 1521 thermometer, with an uncertainty of 5 x $10^{-3}$ K. The pressure of the internal system was measured and kept constant using a Buechi vacuum pump (model v-700) and a Buechi pressure controller unit (model 728A) kept at 373 K and with an accuracy of 0.5%. During the measurements, the equilibrium was assumed to be reached when the temperature remained constant (with a temperature drift lower than 0.05 K·min$^{-1}$, for at least 5 min). The composition of the liquid phase was determined at 323 K using an Anton Paar Abbemat 5010 refractometer, with an uncertainty of 2 x $10^{-5}$ dN. Standards with compositions with an uncertainty of 1 x $10^{-3}$ g were used to determine a calibration curve at 323 K that, through error propagation, was able to allow the determination of the sample composition within ± 0.001 mol fraction.

**Modelling.** COSMO-RS. COSMO-RS is a quantum chemistry-based thermodynamics model that has been shown to accurately predict the solid–liquid equilibrium of the thymol/menthol system and, thus, its activity coefficients. To use the COSMO-RS model, the thymol and menthol molecules were first optimized by density functional theory (DFT) using the COSMO-BP-TZVP template available in the software TmoleX (TURBOMOLE). This template adopts a def-TZVP basis set for all atoms with the B-P86 functional and the COSMO solvation model (continuum with infinite permittivity). The molecular files obtained were used as input for the software COSMOtherm, which implements the model COSMO-RS using the BP_TZVP_19.erd parametrization.

The vapor–liquid equilibrium (VLE) of a system with a homogeneous liquid phase at a given temperature, $T$, is described by the following equation:

$$n_x P_x^n = P$$

(1)
where \( x_i \) is the mole fraction of generic component \( i \) in the liquid phase, \( \chi_i \) is its activity coefficient in the liquid phase, \( P^\circ_i \) is its component vapor pressure at temperature \( T_i \), and \( P \) is the total pressure of the system. In this work, the ideal VLE phase diagram of the thymol/menthol system was calculated using eq 1 and \( \gamma_i = 1 \). COSMO-RS was also used to predict the VLE phase diagram of the system by predicting \( \gamma_i \) at temperature \( T \) and composition \( x_i \). In both cases, the vapor pressures of pure thymol and pure menthol at different temperatures were calculated using the Antoine equation.

The solid–liquid equilibrium (SLE) of a eutectic-type system, where all components solidify into pure solid phases, is described by the following equation:

\[
\ln(x_i^S) = \frac{\Delta_{hi} \beta_i}{R} \left( \frac{1}{T_{mi}} - \frac{1}{T} \right)
\]

where \( T_{mi} \) is the melting temperature of generic component \( i \), \( \Delta_{hi} \beta_i \) is its enthalpy of fusion at temperature \( T_{mi} \), and \( R \) is the ideal gas constant.

In this work the ideal SLE phase diagram of the thymol/menthol system was calculated using eq 2 by considering \( \gamma_i = 1 \). COSMO-RS was also used to predict the SLE phase diagram of the system by predicting \( \gamma_i \) at temperature \( T \) and composition \( x_i \). The melting temperatures of thymol and menthol are 323.5 and 315.7 K, respectively, and their enthalpies of fusion are 19.65 and 12.89 kJ/mol, respectively.

### RESULTS AND DISCUSSION

\(^1\text{H} \) NMR spectra of the thymol + menthol liquid phase covering the full composition range is presented in Figure S2, with the change in chemical shift of selected protons (\( \Delta \delta_{hi} \)) highlighted in Figure 1. Gradual addition of thymol to menthol results in a respective upshift and downshift of their proton chemical shifts relative to the pure compounds. The rise in \( \Delta \delta_{hi} \) of thymol in the presence of menthol is indicative of thymol protons in a less shielded environment, and their overall greater acidity with increasing menthol molar fraction (\( \chi_{\text{menthol}} \)), with the opposite being observed for menthol at increasing thymol molar fractions (\( \chi_{\text{thymol}} \)). The magnitude of \( \Delta \delta_{hi} \) is highly dependent on the proton position in each molecule with the hydroxyl proton presenting the largest \( \Delta \delta_{hi} \) values. An increase in H-bonding removes electron density from the local vicinity of the nucleus, making the nuclei less shielded with respect to the applied magnetic field. This is consistent with the formation of an intermolecular H-bonded network in the DESs liquid phase driven by the greater acidity of the phenolic hydrogen, making thymol an excellent HBD.\(^{1,38} \) The preferential nature of the thymol(oH)···(OH)menthol H-bond is evidenced by \( \Delta \delta_{hi} = 1.73 \) ppm of the thymol hydroxide for \( x_{\text{thymol}} = 0.5 \) and appears as the main driving force for the system nonideality. However, the observed \( \Delta \delta_{hi} \) is lower than \( \Delta \delta_{hi} = 4.10 \) ppm in the equimolar thymol + trioctylphosphine oxide mixture due to the greater Lewis basicity of the phosphine oxide bond compared to alcohols.\(^7 \) The downshift in the menthol hydroxide \( \Delta \delta_{hi} \) relative to its pure state with increasing \( x_{\text{thymol}} \) is attributed to the decrease in inter menthol H-bonding due to competing presence of the more acidic proton of thymol as HBD. Interestingly, the magnitude of \( \Delta \delta_{hi} \) for similarly positioned proton groups in thymol and menthol excluding the hydroxyl group does not follow identical trends; Figure 1. The nearest proton to the hydroxyl group in thymol exhibits the second greatest upshift but presents the smallest shift in menthol. Conversely, the thymol ring hydrogen in the para position from the hydroxyl group displays the smallest \( \Delta \delta_{hi} \) in accordance with resonance effects in the thymol aromatic ring, but the second largest in menthol. This suggests that relative to the interactions in their pure liquid state, H-bonding is reinforced for thymol molecules in the thymol + menthol DESs while additional dispersive interactions combined with H-bonding stabilize menthol molecules.

Reduction of the thymol + menthol system to simple binary interactions, thymol–menthol vs the pure compounds with themselves, provides only a partial picture considering H-bonded liquids can assemble into extended H-bonding networks and oligomers.\(^{40} \) Small angle X-ray scattering (SAXS) analysis of the liquid 1:1 thymol + menthol DESs \((T = 293 \text{ K})\) in Figure 2 clearly shows the presence of a prepeak at 6.0 nm\(^{-1}\), corresponding to the distance of 1.05 nm \((-2\pi/6.0 \text{ nm}^{-1}\)) appearing much before the standard peak associated to neighbor alkyl moieties at 12.5 nm\(^{-1}\).\(^{41} \) Such prepeaks are commonly observed in covalent and ionic glasses or melts\(^{42} \) and more unexpectedly in certain molecular "fragile" glass-forming liquids including alcohols as well as ionic liquids.\(^{43-46} \) The existence of the prepeak is usually interpreted as evidence of an intermediate-range order (the length is greater than the first shell of neighboring molecules) due to the existence of H-bond-induced heterogeneities or clusters. Contrary to H-bonded liquids with reduced packing constraints like glycerol or methanol, steric exclusion between the ring of menthol and/or thymol prevents formation of a continuous H-bond network resulting instead in smaller H-bonded clusters presenting a hydroxyl rich core and an alkyl rich exterior.\(^{43} \) Changes in the eutectic components can potentially lead to the formation of ordered clusters in the liquid phase.

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promote additional intermediate range ordering of the liquid phase. For example, small angle neutron scattering (SANS) of the thermodynamically ideal mixture of menthol + decanoic acid\(^3\) suggests the presence of weakly interacting micellar-like spherical aggregates.\(^47\)

The H-bonding in the thymol + menthol system was further probed at different molar compositions by Raman spectroscopy in the 2600–4000 cm\(^{-1}\) region, shown in Figure 3A. For increased clarity, the spectra in the OH stretching (\(\nu(\text{OH})\)) region were deconvoluted into Gaussian-shape components based on the dominant peaks of the pure compounds, with selected examples presented in Figure 3B. Due to the difficulty in the unequivocal assignment of spectral distributions to specific H-bonded species in the undiluted eutectic, this was not attempted here. Rather, the Raman \(\nu(\text{OH})\) spectrum was analyzed in terms of different contribution depending on their involvement in the H-bond formation, namely into \(\alpha, \beta, \gamma,\) and \(\delta\) OHs.\(^{48,49}\) “Free” hydroxyl groups not involved in hydrogen-bonding, corresponding to \(\alpha\) and \(\beta\) OHs, were detected at around 3620 cm\(^{-1}\) in the studied system and correspond to the gray band in the deconvoluted spectra in Figure 3B.\(^{50}\)

Terminal proton-donating OH bonds, with lone pairs of the O atom not involved in hydrogen bonds (\(\gamma\) OH), only partially contribute to the H-bonded network through dimer formation. The corresponding band is detected at approximately 3540 cm\(^{-1}\) and identified by the orange band in the deconvoluted spectra. Finally, proton accepting and donating \(\delta\) OHs detected at lower wavenumbers are responsible for the

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**Figure 2.** X-ray scattering profile of the liquid 1:1 thymol + menthol DESs (\(T \approx 293\) K).

**Figure 3.** (A) Raman spectra of liquid thymol and crystalline menthol and their liquid binary mixtures in the OH stretching region at \(T = 293\) K. (B) Deconvoluted Raman spectra for three different \(X_{\text{thymol}}\) concentrations in the range 3100–3700 cm\(^{-1}\); the red line corresponds to the deconvolution fit. (C) H-bond distribution in the MD simulations of the thymol + menthol system for varying \(X_{\text{thymol}}\) (\(T = 330\) K; 400 molecules). H-bonding analysis\(^5^7\) was performed with geometric criteria for weak (full bars; \(r \leq 0.35\) nm, angle \(\leq 90^\circ\)) and medium (pattern bars; \(r \leq 0.30\) nm, angle \(\leq 30^\circ\)) H-bonds. The radius was defined as the H–O distance between two components and the angle as O–H–O. Simulation composition and H-bond numbers are summarized in Table S1.

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\(^{3}\) See reference \(\text{[3]}\).

\(^{47}\) See reference \(\text{[47]}\).

\(^{48}\) See reference \(\text{[48]}\).

\(^{49}\) See reference \(\text{[49]}\).

\(^{50}\) See reference \(\text{[50]}\).
formation of intrachain OH bonds resulting in the formation of H-bonded aggregates (green and blue bands in the deconvoluted spectra).

The large gap in the melting and crystallization temperature of thymol provides sufficient longevity to the metastable liquid state, allowing study of the full range of composition on the thymol side of the thymol + menthol phase diagram at room temperature.¹ The Raman spectra of metastable liquid thymol, i.e. noncrystalline, covers a wide wavenumber range (3200–3650 cm⁻¹) but is dominated by the γ ν(OH) band at 3530 cm⁻¹ confirming thymol as an excellent H-bond donor but poor H-bond receptor. This in turn restricts the formation of larger hydrogen bonded oligomers and is consistent with the limited self-association of the structurally similar phenol in aprotic organic solvents.³⁴ Additionally, the free OH band is clearly observable at 3620 cm⁻¹. Compared to thymol, menthol as a classical alcohol can act both as an H-bond donor and acceptor in equal measure, promoting a more efficient H-bonding.³⁵ Classical MD simulations of the pure thymol and menthol condensed phase at 330 K confirm the lesser number and weaker average energy of H-bonds in thymol (ΔG = 10.5 kJ·mol⁻¹) compared to that in liquid menthol (ΔG = 21.4 kJ·mol⁻¹), Figures S3 and 3C. Addition of thymol in menthol induces the breaking of strong H-bond molecular associations and vice versa for addition of menthol in thymol, with observation of persistent free OH groups not involved in molecular associations even at low thymol molar fractions (xthymol = 0.2 in Figure 3B). Results indicate that the thymol + menthol DESs structural organization involves three types of molecular associations, menthol–menthol via stronger H-bonds, thymol–thymol via weaker H-bonds, and thymol–menthol via mixed strength bonding, characterized by the δ OH stretching band (green) around 3400 cm⁻¹. Decreasing xthymol in the eutectic mixture results in the linear decrease in the deconvoluted area of the γ ν(OH) band (orange) of thymol but in the increase of the δ OH stretching band (green), Figure S4.

Figure 1 in the Supporting Information (SI) shows that the MD-derived X-ray scattering pattern² demonstrates the experimental structural features shown in Figure 2, thus providing support to the ability of the chosen potential to reproduce structural features of the thymol + menthol mixture. RDF analysis and the derived coordination numbers obtained from MD simulations of the thymol + menthol system for three molar ratios (xthymol of 0.25, 0.50, and 0.75) indicate the thymol(H)···(O)menthol H-bond as the predominant short-range (≤0.2 nm) H-bond interaction followed by intermenthol H-bonding for all compositions, Figure S5. This is consistent with the more stable interaction of the thymol–menthol pair in the liquid phase by 5.2 kJ·mol⁻¹ relative to menthol–menthol as determined by DFT in the COSMO solvation continuum.² Extending the geometry criteria for H-bond to include an HBD–HBA distance and a D–H–A angle characteristic of weak (r ≤ 0.35 nm, angle ≤ 90°) and medium (r ≤ 0.30 nm, angle ≤ 30°) H-bonding reveals a variable H-bond distribution between thymol–menthol, thymol–thymol, and menthol–menthol dependent on the eutectic composition, Figure 3C. Increasing xthymol results in a decrease in the total number of H-bonds of the system driven by the reduction in menthol–menthol interaction, the dominant H-bond at lower xthymol due to the competing nature of the stronger thymol–menthol hydrogen bond as also shown in Figure 1. At higher xthymol composition, the eutectic solvent is characterized by thymol–menthol H-bonding even in the presence of excess thymol molecules. The number of thymol–menthol H-bonds presents a maximum for equimolar composition. The H-bond criteria does not appear to influence the overall H-bond distribution trend in the studied systems, Figure 3C. However, a sharper decrease in menthol–menthol H-bond numbers is observed for stronger H-bonds (r ≤ 0.30 nm, angle ≤ 30°) as thymol (xthymol = 0.25) is added to pure menthol, in line with the Raman spectra in Figures 1 and 3 indicating a reduction in menthol–menthol H-bonding associations with increasing thymol content. A 3D spatial density function (SDF) plot of
the 1:1 thymol + menthol system projecting the most probable configurations of the various system components is presented in Figure S6. The SDF plot clearly shows the presence of the menthol hydroxide group in both HBD and HBA configurations. In contrast, the spatial localization of the thymol hydroxide group surface around the reference confirms thymol’s primary contribution as an HBD. Furthermore, while menthol molecules adopt a “head-on” arrangement to maximize H-bonding, the thymol surface surrounding the menthol alkyl regions suggests additional dispersive interactions in addition to H-bonding. This is in accordance with the important Δδ_{H} downshift in the menthol ring proton with increasing x_{thymol} in Figure 1 as well as the reported perpendicular T shaped organization of aromatic compounds with π–π interactions.

It is well-known that temperature exerts a strong influence on H-bonded systems, with the extent of H-bonding decreasing with temperature increase. 46,55,66 The temperature dependence of the Raman ν(OH) spectrum for thymol + menthol at a fixed composition (x_{thymol} = 0.5) was followed from room temperature to just above its glass transition temperature of ∼210 K. 1 This composition was selected as it presents the largest liquidus regime with temperature, permitting the study for a wider temperature range. The raw Raman spectra are available in Figure S7, and the deconvoluted spectra are presented in Figure 4. It is clearly observed that the contribution of the lower energy α/β and γ ν(OH) bands decrease for lower temperatures while the higher energy δ ν(OH) bands increase, Figure S8. Most notably, the free hydroxyl band of thymol fully disappears at 213 K, indicating the formation of strong intermolecular H-bonding association at the expense of weak H-bonding associations and free OH groups with decreasing temperature. Figure 4 emphasizes the important temperature dependency of Type V eutectics, affecting both the total number of H-bonds in the mixture as well as their strength. This is further confirmed by MD simulations of the liquid thymol + menthol system for x_{thymol} = 0.5 at different temperatures from 233 to 453 K, Figure S9. A decrease in the number of H-bonds in the system is observed as well as shift in the H-bonded population from higher ordered oligomers to monomers and dimers with temperature increase.

The thymol + menthol system presents complex intermolecular interactions dominated by sterically hindered H-bonding clusters with additional dipolar and van der Waals contribution. Results in Figures 1 and 3 obtained at room temperature or greater indicate the quasi-linear evolution of the eutectic system properties between the pure compounds. This suggests the absence of a magic stoichiometric composition in the eutectic solvent, 57 although small differences in the dominant H-bond interaction with composition (Figure 3C), namely the thymol–menthol H-bond, are observed. Rather, Figure 4 shows a notable increase in H-bonding as temperatures approach the eutectic solid–liquid equilibrium (SLE) conditions driven by the greater inclusion of thymol in H-bonded clusters. It is therefore proposed that the nonionic Type V DESs present a significant temperature-dependent nonideality originating from the change in the intermolecular H-bonding with temperature. To validate this hypothesis, the isobaric VLE of thymol + menthol at p = 500 mbar was estimated using the conductor like screening model for real solvent model (COSMO-RS) 19,20 due to its accurate prediction of the isothermal activity coefficients as well as the glass transition temperatures were taken from refs 1 and 4.
a systematic change with temperature in line with the shift in the ν(OH) profile of the eutectic in Figure 4.

■ CONCLUSIONS

To summarize, thymol + menthol are complex H-bonded solutions presenting a strong thermodynamic nonideality primarily conferred by the dominant intermolecular H-bond between the DESs component relative to their self-interaction. Furthermore, the extent of nonideality is defined by the temperature dependence of H-bonding aggregation in the mixture, this phenomenon being reinforced with decreasing temperature. For experimental temperatures sufficiently high, moderate to negligible deviations from ideality are observed. Most importantly, the presented findings have significant implications for design and application of Type V DESs, allowing the latter to be considered as quasi-ideal for solutions presenting a strong thermodynamic nonideality between the DESs component relative to their self-interaction.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.0c07874.

Additional molecular dynamic, COSMO-RS, 1H NMR, and Raman spectroscopy characterization of the thymol + menthol eutectic as a function of the eutectic molar ratio, temperature, H-bond cluster population, and isothermal activity coefficients (PDF)

■ AUTHOR INFORMATION

Corresponding Author
João A.P. Coutinho — CICECO–Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-1933 Aveiro, Portugal; orcid.org/0000-0002-3841-743X; Email: jcoutinho@ua.pt

Authors
Nicolas Schaeffer — CICECO–Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-1933 Aveiro, Portugal; orcid.org/0000-0002-0747-2532

Dinis O. Abranches — CICECO–Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-1933 Aveiro, Portugal; orcid.org/0000-0003-0097-2072

Liliana P. Silva — CICECO–Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-1933 Aveiro, Portugal; orcid.org/0000-0002-6656-1920

Mônica A.R. Martins — CICECO–Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-1933 Aveiro, Portugal; orcid.org/0000-0003-0748-1612

Pedro J. Carvalho — CICECO–Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-1933 Aveiro, Portugal; orcid.org/0000-0002-1943-0006

Olga Russina — Laboratorio Liquidi Ioni, Istituto Struttura della Materia, Consiglio Nazionale delle Ricerche, (ISM-CNR), 00133 Rome, Italy, Department of Chemistry, University of Rome Sapienza, 00185 Rome, Italy

Alessandro Triolo — Laboratorio Liquidi Ioni, Istituto Struttura della Materia, Consiglio Nazionale delle Ricerche, (ISM-CNR), 00133 Rome, Italy

Laurent Paccou — Univ. Lille, CNRS, INRAE, Centrale Lille, UMR 8207–UMET–Unité Matériaux et Transformations, F-59000 Lille, France

Yannick Guinet — Univ. Lille, CNRS, INRAE, Centrale Lille, UMR 8207–UMET–Unité Matériaux et Transformations, F-59000 Lille, France

Alain Hedoux — Univ. Lille, CNRS, INRAE, Centrale Lille, UMR 8207–UMET–Unité Matériaux et Transformations, F-59000 Lille, France

Complete contact information is available at:
https://pubs.acs.org/10.1021/acssuschemeng.0c07874

Notes
The authors declare no competing financial interest.

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