

Proceeding Paper

Synthesis and Characterisation of Menthol-Based Hydrophobic Deep Eutectic Solvents [†]

Deborah O. Adeoye ^{1,2,*} , Zaharaddeen S. Gano ³, Omar U. Ahmed ⁴, Suleiman M. Shuwa ², Abdulazeez Y. Atta ², Samuel A. Iwarere ⁵ , Baba Y. Jubril ² and Michael O. Daramola ⁵¹ Nigerian Institute of Leather and Science Technology, Zaria P.M.B 1034, Kaduna State, Nigeria² Department of Chemical Engineering, Ahmadu Bello University, Zaria P.M.B 06, Kaduna State, Nigeria³ National Research Institute for Chemical Technology, Zaria P.M.B 1052, Kaduna State, Nigeria⁴ Department of Chemical and Petroleum Engineering, Bayero University, Kano P.M.B 3011, Kano State, Nigeria⁵ Sustainable Energy and Environment Research Group, Department of Chemical Engineering, Faculty of Engineering, Built Environment and Information Technology, University of Pretoria, Hatfield, Pretoria 0028, South Africa

* Correspondence: yawehst2006@gmail.com; Tel.: +234-9094726316

[†] Presented at the 27th International Electronic Conference on Synthetic Organic Chemistry (ECSOC-27), 15–30 November 2023; Available online: <https://ecsoc-27.sciforum.net/>.

Abstract: Hydrophobic deep eutectic solvents (HDESs) have found applications 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 or not they were hydrophobic as predicted.

Keywords: hydrophobic deep eutectic solvent; menthol; octanoic acid; decanoic acid; dodecanoic acid; moisture absorption capacity



Citation: Adeoye, D.O.; Gano, Z.S.; Ahmed, O.U.; Shuwa, S.M.; Atta, A.Y.; Iwarere, S.A.; Jubril, B.Y.; Daramola, M.O. Synthesis and Characterisation of Menthol-Based Hydrophobic Deep Eutectic Solvents. *Chem. Proc.* **2023**, *14*, 98. <https://doi.org/10.3390/ecsoc-27-16334>

Academic Editor: Julio A. Seijas

Published: 22 November 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Deep Eutectic Solvents (DESs) are alternative green solvents to ionic liquids. They are easy to prepare, have high purity, and are low-cost [1,2] which gives them an edge over ionic liquids. By definition, DESs are solvents composed of two or more components: a 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, the plasticising/fatliquoring of tanned leather, and the dyeing of plasticised leather [3]. In the open literature, many DESs researched are hydrophilic and, therefore, unstable in an aqueous environment, limiting their applications [4,5]. Due to its increasing number of applications, the concept of the synthesis of DESs is currently a subject of growing interest. It has further led to a recent investigation into the synthesis of hydrophobic deep eutectic solvents (HDESs).

The 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 the 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. Materials and Methods

Hydrophobic Deep Eutectic Solvent Synthesis

Menthol (99% assay) was purchased from Molychem, and octanoic acid (99% assay), decanoic acid (98% assay), and dodecanoic acid (99% assay) were 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 (in the molar ratios 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. 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 HDESs [6,7]. Fourier transform infrared (FTIR) spectra of the different terpenes and organic acids and the resultant HDESs from their combinations were determined to investigate and ascertain this interaction. Figure 1 shows a 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 in 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 and 3000 cm⁻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.

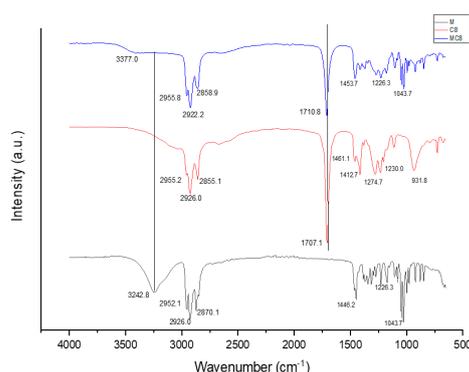


Figure 1. FTIR spectra for menthol, octanoic acid, and MC₈ HDES.

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 the HBD and HBA were maintained in the resulting HDESs (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 monoterpene and at the CO bands of organic acids, which signifies the interaction between the two components during the formation of HDESs [8–11].

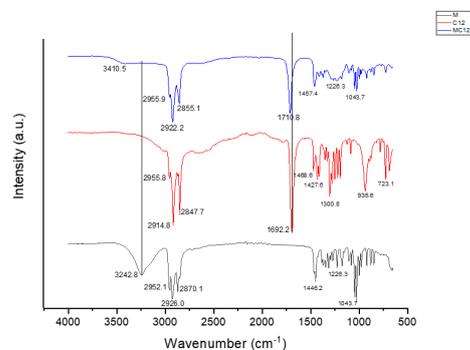


Figure 2. FTIR spectra for menthol, decanoic acid, and MC₁₀ HDES.

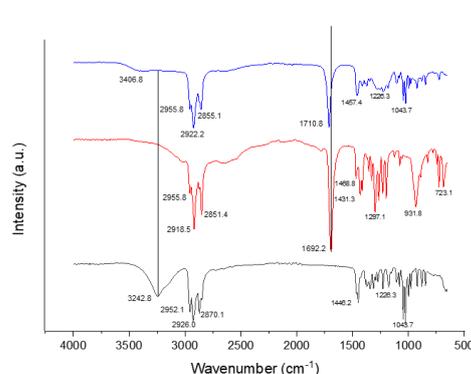


Figure 3. FTIR spectra of menthol, dodecanoic acid, and MC₁₂ HDES.

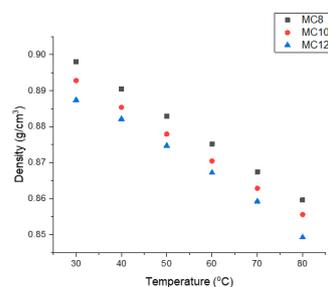


Figure 4. Density–temperature graph for menthol-based HDESs.

In FTIR, one of the factors that influence peak intensity is concentration. A shift in peak position usually depicts an electron distribution in the molecular bond that has 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

3.2.1. 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 HDESs ranged between 0.8493 and 0.8981 kg/L. All HDESs revealed a linear decrease in density with a consistent increase in temperature. According to Francisco et al., densities of menthol-based HDESs were between 0.890 and 0.925 kg/L. Hydrophobic deep eutectic solvents have been reported to possess lower densities than water [12]. The density of a deep eutectic solvent reveals a temperature-dependent behaviour,

which decreases linearly with increasing temperature [8,11–13]. Moreover, density depends on the choice of hydrogen bond donor, and the molar ratio [14–18].

3.2.2. Viscosity

Viscosities of the prepared HDESs were observed to be temperature-dependent. They decreased linearly with corresponding temperature increases. In Figure 5, the viscosity profile of menthol-based HDESs increased from MC₈ to MC₁₂, i.e., MC₈ < MC₁₀ < MC₁₂, and was between 9 and 18 mPa.s. The results above align with results obtained from previous work [12]. 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) [13].

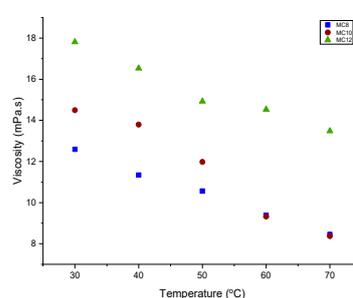


Figure 5. Viscosity–temperature graph for menthol-based HDESs.

The viscosity of a eutectic mixture is affected by the nature of its components [11,14], their molar ratio [16], the temperature [8,19–24], and the water content [10,11,18,24,25]

3.2.3. 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 HDESs 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 [9,19,26]. The surface tension of all HDESs was observed to be <30 mN/m, and, as exemplified in previous works, decreased with increasing temperature.

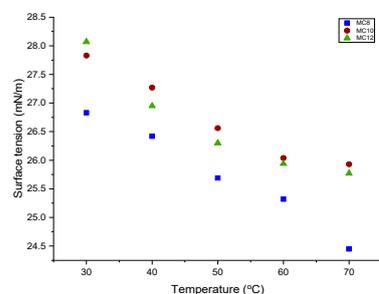


Figure 6. Surface tension–temperature graph for menthol-based HDESs.

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 h to see if the emulsion formed any phase separation. After 24 h, clear and distinctive phase separation was noticed

with water (the denser phase) seen at the bottom of the bottle and the HDESs (the less dense phase) on top, as seen in Figure 8.



Figure 7. HDESs in water immediately after agitation.

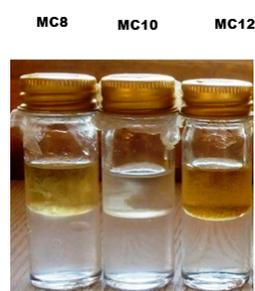


Figure 8. HDESs in water 24 h after agitation.

Figure 9 is a chart indicating the moisture content determined in each HDES after its interaction with water for 24 h. The HDESs MC₈, MC₁₀, and MC₁₂ had the following moisture contents: 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 did. It was also reported by Florindo et al. that an increase in the alkyl chain of the HBDs resulted in the increased hydrophobicity of the HDESs [12].

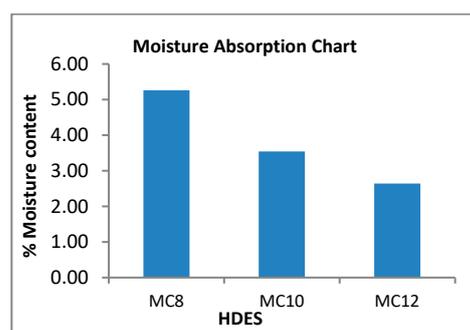


Figure 9. Percentage moisture content graph for HDESs (test for hydrophobicity).

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. Conclusions

Three 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 those of 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 HDESs.

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 and 0.925 kg/L. All densities were found to decrease with an increase in temperature. The viscosity of the HDESs was found to be <20 mPa.s and decreased with an increase in temperature. Similarly, 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 and 5.26%. It was observed that the degree of hydrophobicity increased with an increase in the alkyl chain of the organic acids (HBDs).

Author Contributions: Conceptualization, D.O.A.; Methodology, D.O.A., Z.S.G. and A.Y.A.; validation, D.O.A., Z.S.G. and A.Y.A.; formal analysis, D.O.A. and Z.S.G.; investigation, D.O.A.; resources, D.O.A., Z.S.G. and A.Y.A.; data curation, D.O.A.; writing—original draft preparation, D.O.A.; writing—review and editing, D.O.A., Z.S.G., O.U.A., S.M.S., A.Y.A., S.A.I., B.Y.J. and M.O.D.; visualization, D.O.A.; supervision, Z.S.G. and A.Y.A.; project administration, A.Y.A. and B.Y.J.; funding acquisition, Z.S.G. All authors have read and agreed to the published version of the manuscript.

Funding: This project was partly funded by National Research Institute for Chemical Technology under the project number FGN/AB2021/ERG30122610.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Supporting data available on request.

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

References

1. Francisco, M.; Van Den Bruinhorst, A.; Kroon, M.C. Low-transition-temperature mixtures (LTTMs): A new generation of designer solvents. *Angew. Chem.-Int. Ed.* **2013**, *52*, 3074–3085. [[CrossRef](#)] [[PubMed](#)]
2. Paiva, A.; Craveiro, R.; Aroso, I.; Martins, M.; Reis, R.L.; Duarte, A.R.C. Natural deep eutectic solvents-Solvents for the 21st century. *ACS Sustain. Chem. Eng.* **2014**, *2*, 1063–1071. [[CrossRef](#)]
3. Abbott, A.P.; Alaysuy, O.; Antunes, A.P.M.; Douglas, A.C.; Guthrie-Strachan, J.; Wise, W.R. Processing of leather using deep eutectic solvents. *ACS Sustain. Chem. Eng.* **2015**, *3*, 1241–1247. [[CrossRef](#)]
4. Passos, H.; Tavares, D.J.P.; Ferreira, A.M.; Freire, M.G.; Coutinho, J.A.P. Are Aqueous Biphasic Systems Composed of Deep Eutectic Solvents Ternary or Quaternary Systems? *ACS Sustain. Chem. Eng.* **2016**, *4*, 2881–2886. [[CrossRef](#)]
5. Silva, N.H.C.S.; Pinto, R.J.B.; Freire, C.S.R.; Marrucho, I.M. Production of lysozyme nanofibers using deep eutectic solvent aqueous solutions. *Colloids Surf. B Biointerfaces* **2016**, *147*, 36–44. [[CrossRef](#)] [[PubMed](#)]
6. Ali, H.H.; Ghareeb, M.M.; Al-Remawi, M.; Tal-Akayleh, F. New insight into single phase formation of capric acid/menthol eutectic mixtures by Fourier-transform infrared spectroscopy and differential scanning calorimetry. *Trop. J. Pharm. Res.* **2020**, *19*, 361–369. [[CrossRef](#)]
7. Zhang, Q.; De Oliveira Vigier, K.; Royer, S.; Jérôme, F. Deep eutectic solvents: Syntheses, properties and applications. *Chem. Soc. Rev.* **2012**, *41*, 7108–7146. [[CrossRef](#)]
8. Kareem, M.A.; Mjalli, F.S.; Hashim, M.A.; Alnashef, I.M. Phosphonium-based ionic liquids analogues and their physical properties. *J. Chem. Eng. Data* **2010**, *55*, 4632–4637. [[CrossRef](#)]
9. Nunes, R.J.; Saramago, B.; Marrucho, I.M. Surface Tension of dl -Menthol: Octanoic Acid Eutectic Mixtures. *J. Chem. Eng. Data* **2019**, *64*, 4915–4923. [[CrossRef](#)]
10. Shah, D.; Mjalli, F.S. Effect of water on the thermo-physical properties of Reline: An experimental and molecular simulation-based approach. *Phys. Chem. Chem. Phys.* **2014**, *16*, 23900–23907. [[CrossRef](#)]
11. D'Agostino, C.; Harris, R.C.; Abbott, A.P.; Gladden, L.F.; Mantle, M.D. Molecular motion and ion diffusion in choline chloride-based deep eutectic solvents studied by 1H pulsed field gradient NMR spectroscopy. *Phys. Chem. Chem. Phys.* **2011**, *13*, 21383–21391. [[CrossRef](#)] [[PubMed](#)]

12. Florindo, C.; Branco, L.C.; Marrucho, I.M. Quest for Green-Solvent Design: From Hydrophilic to Hydrophobic (Deep) Eutectic Solvents. *ChemSusChem* **2019**, *12*, 1549–1559. [[CrossRef](#)] [[PubMed](#)]
13. Shekaari, H.; Zafarani-Moattar, M.T.; Mohammadi, B. Thermophysical characterization of aqueous deep eutectic solvent (choline chloride/urea) solutions in full ranges of concentration at T = (293.15–323.15) K. *J. Mol. Liq.* **2017**, *243*, 451–461. [[CrossRef](#)]
14. Abbott Andrew, P.; Barron, J.C.; Ryder, K.S.; Wilson, D. Eutectic-based ionic liquids with metal-containing anions and cations. *Chem. A Eur. J.* **2007**, *13*, 6495–6501. [[CrossRef](#)] [[PubMed](#)]
15. Abbott Andrew, P.; Harris, R.C.; Ryder, K.S. Application of hole theory to define ionic liquids by their transport properties. *J. Phys. Chem. B* **2007**, *111*, 4910–4913. [[CrossRef](#)]
16. Abbott Andrew, P.; Harris, R.C.; Ryder, K.S.; Agostino, C.D.; Gladden, F.; Mantle, M.D. Green Chemistry Glycerol eutectics as sustainable solvent systems. *Green Chem.* **2011**, *13*, 82–90. [[CrossRef](#)]
17. Cui, Y.; Li, C.; Yin, J.; Li, S.; Jia, Y.; Bao, M. Design, synthesis and properties of acidic deep eutectic solvents based on choline chloride. *J. Mol. Liq.* **2017**, *236*, 338–343. [[CrossRef](#)]
18. Florindo, C.; Oliveira, F.S.; Rebelo, L.P.N.; Fernandes, A.M.; Marrucho, I.M. Insights into the synthesis and properties of deep eutectic solvents based on cholinium chloride and carboxylic acids. *ACS Sustain. Chem. Eng.* **2014**, *2*, 2416–2425. [[CrossRef](#)]
19. García, G.; Aparicio, S.; Ullah, R.; Atilhan, M. Deep eutectic solvents: Physicochemical properties and gas separation applications. *Energy Fuels* **2015**, *29*, 2616–2644. [[CrossRef](#)]
20. Abbott Andrew, P.; Capper, G.; Davies, D.L.; Rasheed, R.K.; Tambyrajah, V. Novel solvent properties of choline chloride/urea mixtures. *Chem. Commun.* **2003**, *1*, 70–71. [[CrossRef](#)]
21. Abbott, A.P.; Boothby, D.; Capper, G.; Davies, D.L.; Rasheed, R. Deep Eutectic Solvents Formed Between Choline Chloride and Carboxylic Acids. *J. Am. Chem. Soc.* **2004**, *126*, 9142–9147. [[CrossRef](#)] [[PubMed](#)]
22. Abbott Andrew, P.; Capper, G.; Davies, D.L.; Rasheed, R.K. Ionic Liquid Analogues Formed from Hydrated Metal Salts. *Chem. A Eur. J.* **2004**, *10*, 3769–3774. [[CrossRef](#)] [[PubMed](#)]
23. Abbott Andrew, P.; Capper, G.; Gray, S. Design of improved deep eutectic solvents using hole theory. *ChemPhysChem* **2006**, *7*, 803–806. [[CrossRef](#)] [[PubMed](#)]
24. Dai, Y.; Witkamp, G.J.; Verpoorte, R.; Choi, Y.H. Tailoring properties of natural deep eutectic solvents with water to facilitate their applications. *Food Chem.* **2015**, *187*, 14–19. [[CrossRef](#)]
25. Du, C.; Zhao, B.; Chen, X.B.; Birbilis, N.; Yang, H. Effect of water presence on choline chloride-2urea ionic liquid and coating platings from the hydrated ionic liquid. *Sci. Rep.* **2016**, *6*, 29225. [[CrossRef](#)]
26. Lapeña, D.; Lomba, L.; Artal, M.; Lafuente, C.; Giner, B. The NADES glyceline as a potential Green Solvent: A comprehensive study of its thermophysical properties and effect of water inclusion. *J. Chem. Thermodyn.* **2019**, *128*, 164–172. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.