

Article

Extraction of Phenol as Pollutant from Aqueous Effluents Using Hydrophobic Deep Eutectic Solvents

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Abstract: Due to their toxicity and persistence in the environment, phenolic pollutants pose a serious threat to the ecosystem. In this work, the performance of hydrophobic deep eutectic solvents (HDESs) for phenol removal from aqueous effluents is thoroughly investigated using COSMO-RS screening followed by experimental validation. The screening results of 73 HDESs showed that the efficacy of phenol removal is significantly affected by chain length, functional groups, and aromaticity. Trioctylphosphine oxide (TOPO)-based HDESs were found to be the most effective HDESs for phenol elimination combined either with menthol (Men), 1-hexanol (Hex), Decanoic acid (DecA), or Thymol (Thy) all in 1:1 molar ratios. The better phenol elimination abilities of the selected HDESs were confirmed by experimental LLE data obtained at 298.15 K and 101 kPa. In fact, it has been found that there is a positive correlation between extraction efficiency and phenol content. For instance, at a phenol concentration of 7%, TOPO:Men had the highest extraction efficiency (96%). Moreover, the physicochemical properties of the selected HDESs, such as density, viscosity, FTIR, ¹HNMR, and TGA, were also measured. The results showed their high thermal stability and low water solubility, which makes them suitable for phenol extraction applications. This study shows that HDESs are capable of removing phenolic contaminants from aqueous effluents in a sustainable and efficient manner and that the selected TOPO-based HDESs are of particular interest for further research and application in phenol removal.

Keywords: HDES; phenol removal; liquid–liquid extraction; COSMO-RS screening; TOPO



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1. Introduction

Water pollution increased dramatically during the industrial revolution in the late 18th and early 19th centuries and remains a serious threat to human health and the environment. According to the World Health Organization (WHO), waterborne infections are on the rise as 80 percent of wastewater in developing countries is discharged untreated into water sources. Phenolic compounds containing hydroxylated aromatic rings are toxic, mutagenic, and carcinogenic, making them one of the deadliest substances, even at low concentrations [1–3]. The European Council Directive sets a limit of 0.5 g/L for phenolic content in drinking water, while in the Gulf region, the amount of phenolic compounds in industrial wastewater is limited between 20 and 200 mg/L [4,5]. WHO recommends a limit of 0.009 mg/L [6], while the United States sets its limit for pentachlorophenol in drinking water at 0.001 mg/L [7]. In Malaysia, the discharge of phenol into rivers is limited to concentrations of 0.001 mg/L upstream of the water intake and 1.0 mg/L downstream of the intake [8].

This is why many researchers have focused their work extensively on the removal of phenolic chemicals, and several approaches have been proposed. The major strategies can

be divided into three basic classes: (i) chemical, (ii) biological, and (iii) physical. First, the chemical removal approaches such as oxidative processes [9], electrochemical methods [10], photochemical methods [11], Fenton reagents [9], and irradiation [12] use a wide range of chemicals to remove phenolic compounds. However, despite their promising research results, these methods are not suitable for widespread application, especially in industry, because of the high cost of the chemicals and the large volumes of sludge generated.

Secondly, biological elimination methods are considered superior, both in terms of effectiveness and cost-benefit ratio [13]. Despite their efficiency and cost-effectiveness, biological elimination methods, such as biodegradation and bioremediation, have some limitations. These approaches depend on certain microbial strains, which may not be accessible in all environments [14]. The process is susceptible to being time consuming and sensitive to environmental conditions, such as temperature and nutrient availability [15]. Although biological removal methods are generally beneficial, their limitations should be considered, and the specific requirements of each situation evaluated.

Finally, various physical removal strategies have been used to remove phenolic compounds from wastewater. These approaches include membrane filtration [14,16], electrocoagulation [17], distillation [18], adsorption [14], liquid-liquid extraction (LLE), and ion exchange methods. Membrane filtration, such as reverse osmosis, offers remarkable advantages in terms of higher energy efficiency and lower operating costs. However, a major drawback of this process is the relatively limited lifetime of the membrane due to fouling by particles in the feed stream. Furthermore, the implementation of electrocoagulation treatment is very simple but is associated with significant sludge production and potential transfer of hazardous substances to the solid phase [12,19,20]. Distillation, especially the extractive distillation process, is mainly applicable to solutions with high phenol concentrations, as it requires significant energy input [14,21]. The adsorption process using activated carbon or other alternative adsorbents has proven to be a successful method for the removal of phenolic compounds [22]. However, it should be noted that this process requires expensive and complex regeneration of the adsorbent material [9,23,24]. The ion exchange method is usually easy to use and has readily available equipment to process large amounts of waste with low phenol concentrations [25]. However, it should be noted that the operating costs of this method are significantly higher, ranging from 50 to 100 times the cost of biological treatment, as shown by previous studies [26,27].

Liquid-liquid extraction (LLE) is a highly effective method for removing phenolic compounds from wastewater and outperforms other techniques such as membrane filtration and activated carbon adsorption [28]. It is also an environmentally friendly process that involves the regeneration of extractants, consumes less energy than distillation, and produces less sludge than electrocoagulation. While tributyl phosphate (TBP), cumene, and volatile organic compounds (VOCs) have shown promise in the removal of phenols, their use is associated with environmental and health risks, including toxicity and ozone layer depletion [29]. It is therefore essential to look for safer and more environmentally friendly solvents for this purpose.

However, the effectiveness of the extraction process depends heavily on the type of solvent used. The solvent must have high selectivity and capacity and a good distribution ratio with respect to the substance to be extracted in order to achieve efficient and cost-effective separation while minimizing the ratio of feedstock to solvent. The solvent must have hydrophobic properties and be easily regenerated. It is important to minimize the amount of solvent that is lost. Therefore, it is necessary to use a solvent with low vapor pressure and low volatility. In addition, it is important to consider favorable transport properties that facilitate solvent handling, such as density, viscosity, surface tension, and corrosiveness. In addition, the solvent for use in industry must comply with safety and environmental guidelines, including minimal toxicity and the absence of harmful effects on the environment. Finally, the solvent must be both cost-effective and readily available to be used on a large scale. Ionic liquids (ILs) and deep eutectic solvents (DESs) have proven their suitability as viable options for such a separation process.

Although ILs offer several benefits, their application is limited by significant drawbacks such as high toxicity, viscosity, and production costs. 1-butyl-3-methylimidazolium and other ILs have shown exceptional extraction capabilities, achieving up to 99.9% phenol removal [30]. Nevertheless, the wider use of ILs in industrial sectors is hindered by issues related to increased toxicity with longer alkyl chains, susceptibility to impurities affecting their physical and chemical properties, and the high cost of their synthesis and purification [31–33].

On the other hand, the application of DESs as environmentally friendly solvents in the extraction of contaminants from aqueous media has attracted considerable interest due to their low cost, ease of preparation, biodegradability, and renewability [31,34]. Nevertheless, a significant portion of DESs exhibit hydrophilic properties that make them unsuitable for use in aquatic environments and limit their practical applications [12,34]. To overcome these limitations, researchers have developed hydrophobic deep eutectic solvents (HDESs). The use of HDESs for the extraction of water-insoluble volatile organic compounds has been extensively explored, leading to their wide applicability in many fields. A comparison of extraction efficiencies for the removal of phenolic contaminants using VOCs, ILs, and HDESs can be found in the supporting information (Table S1).

In the study conducted by Sas et al. [35], the efficacy of various HDESs containing organic acids and either menthol or thymol in the extraction of phenolic compounds was investigated. Extraction efficiencies of over 80% were obtained for 2-chlorophenol and o-cresol and over 70% for phenol by using menthol-based DES. The improved extraction efficiency of menthol-based DES can be attributed to the cyclic structure of menthol, which provides a larger free volume compared to thymol-based DES. The extraction efficiency has been shown to be consistent with the hydrophobic sequence, with 2-chlorophenol showing the highest efficiency, followed by o-cresol and phenol.

In a separate study, Adeyemi et al. [36] performed an analysis using seven HDESs to extract chlorophenols from water. The results of their study showed that the HDESs exhibited favorable extraction performance for the chlorophenols studied. The extraction efficiencies for all chlorophenols studied were over 94% under ideal conditions. The extraction efficiency of alcanoic acid-based HDESs was generally found to be better than that of thymol-based HDESs. This difference in performance may be explained by the greater polarity and better hydrogen-bonding capacity exhibited by alcanoic acids compared to thymol. In addition, An et al. [37] performed a study on the dispersive liquid–liquid microextraction technique for the analysis of chlorophenols in wastewater. The HDES consisting of methyltrioctylammonium chloride and octanoic acid exhibited good extractive properties as evidenced by the extraction efficiencies of 87.95%, 81.17%, and 79.18% for 4-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol, respectively.

In this work, more than seventy HDESs have been screened using the COSMO-RS predictive model by evaluating the activity coefficient at infinite dilution. Four of the best HDESs have been selected for experimental validation. In addition, some important physicochemical properties of these HDESs were also measured.

2. Materials and Methods

2.1. Materials

The chemicals used in this work are shown in Table 1. They were of high purity and were used without further purification. The DESs were prepared according to the procedure described by Abbott et al. [38]. The mixes were introduced into screw-capped containers and subsequently agitated in an incubating shaker that possessed temperature and speed regulation capabilities, operating at a temperature of 100 °C (± 0.1 °C) with a rotating speed of 200 rpm, until a homogenous mixture was formed. The Mettler Toledo balance, which has a precision of ± 0.0001 g, was utilized to accurately measure and prepare the necessary quantities for each component. The chemical structures of the HDES's components and phenols are presented in Table S2.

Table 1. List of chemicals.

Name	Formula	Cas Number	Supplier	M.W ¹	Purity (%)
TOPO ²	(Oct) ₃ PO	78-50-2	Thermo scientific (Japan)	386.6	99.0
1-hexanol	C ₆ H ₁₄ O	111-27-3	Fisher Scientific (UK)	102.17	99.0
Phenol	C ₆ H ₆ O	108-95-2	AnalaR (UK)	94.11	99.0
Menthol	C ₁₀ H ₂₀ O	89-78-1	Sigma–Aldrich (St. Louis, MO, USA)	156.27	≥95.0
Thymol	C ₁₀ H ₁₄ O	89-83-8	BDH Laboratory (UK)	150.22	≥99.0
Decanoic acid	C ₁₀ H ₂₀ O ₂	334-48-5	Sigma–Aldrich (Subang Jaya, Malaysia)	172.26	≥98.0
Naphthalene	C ₁₀ H ₈	91-20-3	Sigma–Aldrich (Taufkirchen, Germany)	128.17	≥99.0
Toluene	C ₇ H ₈	108-88-3	Scarlau (Barcelona, Spain)	92.14	≥99.0
Ethanol	C ₂ H ₆ O	64-17-5	Sigma–Aldrich (Taufkirchen, Germany)	46.07	≥99.8

Note: ¹ Molecular weight in g/mol, ² Trioctylphosphine oxide.

2.2. Extraction Experiments

In the current study, the efficiency of HDES in the removal of phenol from aqueous solutions with phenol concentrations of 1 to 7 wt% is investigated. HDES was added to the feed at a mass ratio of 1:1. The mixtures were stored in screw-capped and airtight vials. The mixture was then stirred at 200 rpm, 1 atm atmospheric pressure, and 298.15 K ambient temperature in an incubator shaker. After stirring for two hours, we allowed the phases to settle for twenty-four hours to ensure that they had separated thoroughly. For the extraction of phenol from water, quantitative analysis was performed by gas chromatography (GC). Raffinate-phase and HDES-phase compositions were determined using a GC-2010 Pro (Shimadzu, Kyoto, Japan) equipped with a flame ionization detector (FID) and a HP-5 column (5% diphenyl/95% dimethylpolysiloxane, 30 m, 0.32 mm ID, 0.25 m df). Helium served as the carrier gas in a split mode. To prevent contamination of the column with non-volatile chemicals (i.e., the HDES ingredients), the GC liner was cleaned after each system analysis. The amount of TOPO in the aqueous solution that came into contact with the HDESs was measured using a high-performance liquid chromatography (HPLC) system with an automated sample injector. Table 2 lists the operating parameters for GC and HPLC. Each measurement was performed in triplicate, and average uncertainties were calculated. For GC analysis, naphthalene was employed as an internal standard. The selection of naphthalene as an internal standard is attributed to its thermal stability within the range of 300 to 400 °C [39]. The GC calibration curve is shown in the supporting information.

Table 2. Specifications of GC and HPLC.

HPLC	
Device	Shimadzu Prominence LC-20 HPLC System
Column	Zobrax Eclipse Plus C-18 column (250 mm, 4.6 mm, 5 µm), at 40 °C
Mobile phase	95% methanol and 5% water
Mobile phase flow rate	1 mL/min
Detector	Refractive-Index Detector (RID) at 40 °C
Injection volume	20 µL
GC	
Temperature of injector	593.15 K
Temperature of detector	593.15 K
Pressure of carrier gas	134.5
Carrier gas	Helium
Oven program	353.15 K for 2 min 353.15 K to 513.15 K Rate: 40 K/min

The extraction efficiency (E%) of phenol was evaluated using Equation (1).

$$E\% = \left(\frac{c_{phenol}^{initial} - c_{phenol}^{final}}{c_{phenol}^{initial}} \right) \times 100 \% \quad (1)$$

where $c_{phenol}^{initial}$ is initial phenol concentration in aqueous phase and c_{phenol}^{final} is the final phenol concentration in aqueous phase.

2.3. Characterization Methods

The densities of HDESs were measured at a pressure of 101.3 KPa using an Anton Paar DMA 4100 M densimeter. The instrument has an accuracy of 0.1 kg/m³ and a reproducibility of 0.05 kg/m³. The standard uncertainties of the densities were calculated according to the approach described in the literature [40], taking into account the chemical precision. The viscosities of the DESs were measured using an Anton Paar Lovis 2000 M/ME viscometer (Austria), which had a relative accuracy of 0.005 and was set to a pressure of 101.3 kPa. To obtain the average values, the viscosities were calculated three times. The standard uncertainties were calculated using the given equation, assuming that the given values represent a triangular probability distribution [41]:

$$u(\eta) = \frac{\eta_+ - \eta_-}{\sqrt{6}} \quad (2)$$

Here, η_+ and η_- are the upper and lower limits of the measured values. The water content of the individual HDES was measured by Karl Fischer titration (Aquamax Karl-Fischer, GR Scientific Ltd., Halle, Germany).

The thermal properties of the HDESs were analyzed with the TGA/DSC 1 Star system from Mettler Toledo (Columbus, OH, USA). The thermograms were generated with a Mettler-Toledo TGA/DSC 1 STAR system. The temperature range was set to 25 to 400 °C, with a heating rate of 10 K/min. The measurements were performed under a controlled flow of synthetic air at a rate of 80 mL/min. A quantity of 2–5 mg of the sample was used for each run. A PerkinElmer Spectrum 100 FTIR spectrometer was used to analyze HDESs. The spectrometer used infrared light in the range of 500 to 4000 cm^{−1} to obtain the spectra of the samples. Proton nuclear magnetic resonance (¹HNMR) spectra were recorded using a JEOL RESONANCE spectrometer (model ECX-500 II, Tokyo, Japan). Chloroform was used as a solvent, and spectra were recorded at 24 °C.

2.4. COSMO-RS Software Utilisation

The use of the COSMO-RS (CONductor-like Screening MODEL for Real Solvents) is crucial for modeling the extraction process. By incorporating sensitivity testing, this predictive model is able to reduce the time and resources normally spent on the experimental process. Adeyemi et al. [36] illustrated the use of COSMOTermX and TMoleX software to describe the process by which chlorophenols were extracted from an aqueous solution with HDES. The mechanism is that the chlorophenols and HDES form hydrogen bonds and hydrophobic interactions. The authors also performed a comparative analysis between the COSMOTermX modeling results and the efficiency of 3-chlorophenol extraction. They found that the model provides a satisfactory prediction of chlorophenol extraction efficiency.

Trial and error is the most common method to find out which solvent is best suited for the extraction of certain compounds, especially when it comes to unidentified and under-researched solvents such as DESs. As a result, inadequate solvent selection may occur. This can lead to suboptimal solvent selection. Using the COSMO-RS software to identify the most effective DESs for extracting the desired compounds will undoubtedly save time, cost, and effort that would have been spent on a lengthy experiment.

The quantum chemistry program TURBOMOLE was used to calculate the molecular geometry of all constituents used in this study (i.e., water, phenol, and HDES constituent).

In this study, the BP86 level of density functional theory (DFT) and triple zeta valence potential with diffuse functions (TZVPD) were used as the basis set. Following this procedure, the “.cosmo” files were generated. The parameterization file BP_TZVPD_FINE_19.ctd was then used to import the .cosmo files into COSMOthermX version 19.0.5. The electroneutral methodology was implemented. In this method, each HDES is considered as three different compounds (cation, anion, HBD). Since HBD reduces the interaction energy between the salt cation and the anion by forming a complex with the salt halide anion in liquid form, HDES can be considered to consist of three different species in liquid form: cation, anion, and HBD [42].

The activity coefficients for phenol and water at infinite dilution (γ^∞) were calculated for each HDES. The values of γ^∞ were used to predict the capacity and selectivity of phenol in HDESs relative to water at infinite dilution (C^∞ and S^∞), as indicated in Equations (3)–(5), to determine the performance index (PI). In this study, 73 HDESs were investigated (Table 3).

$$C_{phenol}^\infty = \left(\frac{1}{\gamma_{phenol}^\infty} \right)_{DES \text{ phase}} \quad (3)$$

$$S_{\frac{phenol}{water}, max} = S_{\frac{phenol}{water}}^\infty = \left(\frac{\gamma_{water}^\infty}{\gamma_{phenol}^\infty} \right)_{DES \text{ phase}} \quad (4)$$

$$PI = C_{phenol}^\infty \times S_{\frac{phenol}{water}}^\infty \quad (5)$$

Table 3. List of HDESs screened.

No.	HBA	HBD	Ratio	Abbreviation
1	Benzoyltrifluoroacetone	Triphenyl phosphate	2:1	BTFA:TPP (2:1)
2	Decanoic acid	Lidocaine	2:1	DecA:Lid (2:1)
3			3:1	DecA:Lid (3:1)
4			4:1	DecA:Lid (4:1)
5	Dodecanoic acid	Octanoic acid	1:3	DdecA:OctA (1:3)
6		Decanoic acid	1:2	DdecA:DecA (1:2)
7		Nonanoic acid	1:3	DdecA:NonA (1:3)
8	Hydrocinnamic acid	Decanoic acid	1:1	HDCA:DecA (1:1)
9	Menthol	Aliquat 336	7:3	Men:Alq (7:3)
10		Lidocaine	5:5	Men:Lid (5:5)
11		ibuprofen	7:3	Men:Ibp (7:3)
12		Proton Sponge [®]	7:3	Men:PS (7:3)
13		Octanoic acid	1:1	Men:OctA (1:1)
14			1:2	Men:OctA (1:2)
15		Decanoic acid	1:1	Men:DecA (1:1)
16			1:2	Men:DecA (1:2)
17			1:3	Men:DecA (1:3)
18		methyl-2,4-pentanediol	2:1	Men:MPD (2:1)
19		1-decanol	2:1	Men:Dcl (2:1)
20		Salicylic acid	4:1	Men:SacA (4:1)
21		Propionic acid	1:1	Men:PrpA (1:1)
22		Formic acid	1:1	Men:FomA (1:1)
23	Methyl anthranilate	Lidocaine	9:1	MAT:Lid (9:1)
24		Ibuprofen	9:1	MAT:Ibp(9:1)
25		Proton Sponge [®]	9:1	MAT:PS (9:1)
26		Menthol	9:1	MAT:Men (9:1)
27	Methyltriocetylammmonium bromide	Octanoic acid	1:2	MTOAB:OctA (1:2)
28		Decanoic acid	1:2	MTOAB:DecA (1:2)

Table 3. Cont.

No.	HBA	HBD	Ratio	Abbreviation
29	Methyltrioctylammonium chloride	Octanoic acid	1:2	MTOAC:OctA (1:2)
30	Tetrabutyl ammonium bromide	Thymol	1:2	TBAB:Thy (1:2)
31		Octanoic acid	1:2	TBAB:OctA (1:2)
32	Thenoyltrifluoroacetone	Triphenyl phosphate	2:1	TTFA:TPP (2:1)
33	Thymol	methyl-2,4-pentanediol	2:1	Thy:MPD (2:1)
34		1-decanol	2:1	Thy:Dcl (2:1)
35		Trioctylphosphine oxide	1:1	Thy:TOPO (1:1)
36		Decanoic acid	1:3	Thy:DecA (1:3)
37		Camphor	1:1	Thy:Cam (1:1)
38	Trioctylmethylammonium chloride	Methyl 4-hydroxybenzoate	1:1	TOMAC:MHB (1:1)
39			1:2	TOMAC:MHB (1:2)
40			2:1	TOMAC:MHB (2:1)
41		butyl 4-hydroxybenzoate	1:1	TOMAC:BHB (1:1)
42			1:2	TOMAC:BHB (1:2)
43			1:3	TOMAC:BHB (1:3)
44			2:1	TOMAC:BHB (2:1)
45		isobutyl 4-hydroxybenzoate	1:1	TOMAC:IBHB (1:1)
46			1:2	TOMAC:IBHB (1:2)
47			1:3	TOMAC:IBHB (1:3)
48			2:1	TOMAC:IBHB (2:1)
49		2-Ethylhexyl 4-hydroxybenzoate	1:1	TOMAC:EHHB (1:1)
50			1:2	TOMAC:EHHB (1:2)
51			1:3	TOMAC:EHHB (1:3)
52			2:1	TOMAC:EHHB (2:1)
53	Trioctylmethylammonium chloride	n-octyl 4-hydroxybenzoate	1:1	TOMAC:OHB (1:1)
54			1:2	TOMAC:OHB (1:2)
55			1:3	TOMAC:OHB (1:3)
56			1:4	TOMAC:OHB (1:4)
57			2:1	TOMAC:OHB (2:1)
58		Decanoic acid	2:1	TOMAC:DecA (2:1)
59			1:1	TOMAC:DecA (1:1)
60			1:2	TOMAC:DecA (1:2)
61		Ketoprofen	2:1	TOMAC:KTP (2:1)
62			1:1	TOMAC:KTP (1:1)
63			1:2	TOMAC:KTP (1:2)
64		Gemfibrozil	1:2	TOMAC:GFZ (1:2)
65			1:1	TOMAC:GFZ (1:1)
66	Trioctylphosphine oxide	Decanoic acid	1:1	TOPO:DecA (1:1)
67			1:1	TOPO:Men (1:1)
68			1:2	TOPO:Men (1:2)
69		Menthol	1:3	TOPO:Men (1:3)
70			1:4	TOPO:Men (1:4)
71			1:5	TOPO:Men (1:5)
72		1-hexanol	1:1	TOPO:Hex (1:1)
73		3,5-Di-tertbutylcatechol	1:1	TOPO:DTBC (1:1)

3. Results and Discussion

3.1. COSMO-RS Screening Results

When selecting an HDES for a separation process, it is crucial to consider capacity, selectivity, and performance index as essential attributes. Phenol selectivity is the measure of the phenol content in the extract phase relative to the raffinate phase. A higher selectivity

means a stronger interaction between the HDES and the phenol, reducing the need for multiple extraction steps and lowering investment costs. The term “capacity at infinite dilution” refers to the maximum amount of phenol that can be dissolved in the HDES. Using an HDES with a high capacity allows the use of a smaller amount of solvent, resulting in a smaller extraction column and lower operating costs.

Nevertheless, the PI effectively captures the combined influence of capacity and selectivity, making it a commendable statistic for assessing the overall efficiency of a solvent. A greater value of the PI indicates a more favorable balance between capacity and selectivity, hence enhancing the suitability of HDES for phenol removal in practical situations. This comprehensive parameter facilitates a detailed understanding, allowing for the identification of superior combinations of HDES that demonstrate outstanding potential in mitigating environmental concerns.

A comprehensive examination of the findings revealed a diverse array of values among the 73 HDESs in relation to the parameters under investigation. The study revealed a significant link between capacity and PI, as well as selectivity and PI. This finding emphasizes that HDES systems with higher capacity and selectivity tend to provide superior performance in the removal of phenols. The analysis conducted indicated an apparent trend in which HDESs containing higher-molecular-weight components and exhibiting balanced hydrogen bond acceptor–hydrogen bond donor ratios exhibited superior performance in terms of phenol removal effectiveness. The observed phenomenon can be ascribed to the capacity of HDES to establish stable and efficient interactions with phenolic compounds. The results of HDES screening in terms of capacity, selectivity, and PI are shown in Figures 1–3 and Table S3.

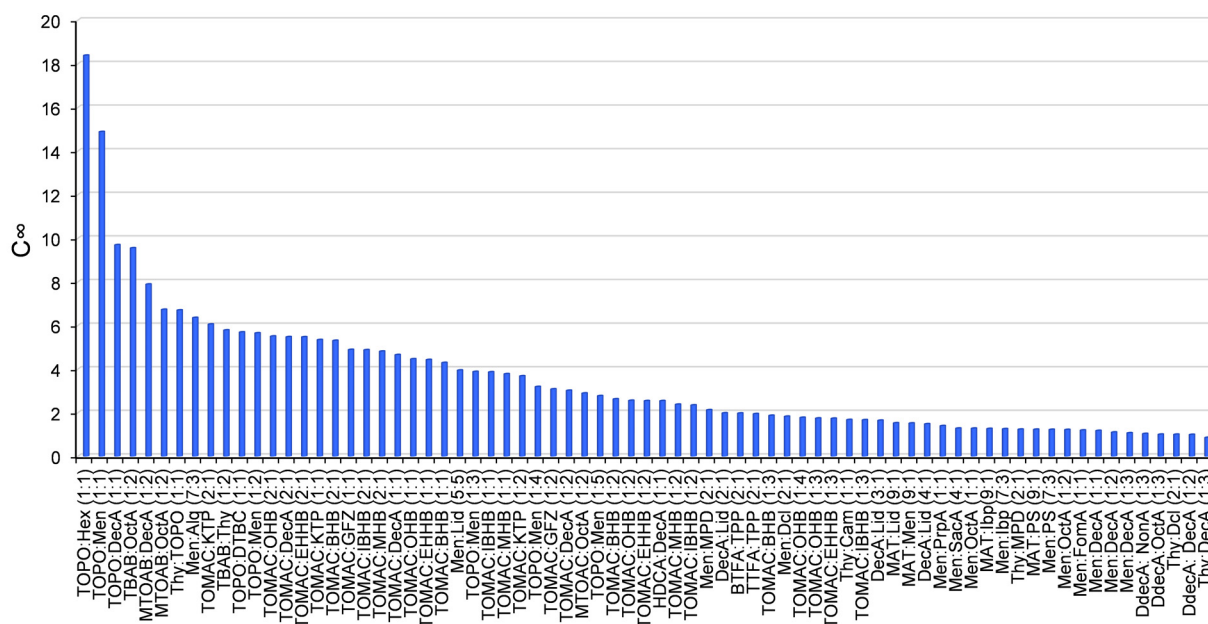


Figure 1. Capacity of HDESs at infinite dilution.

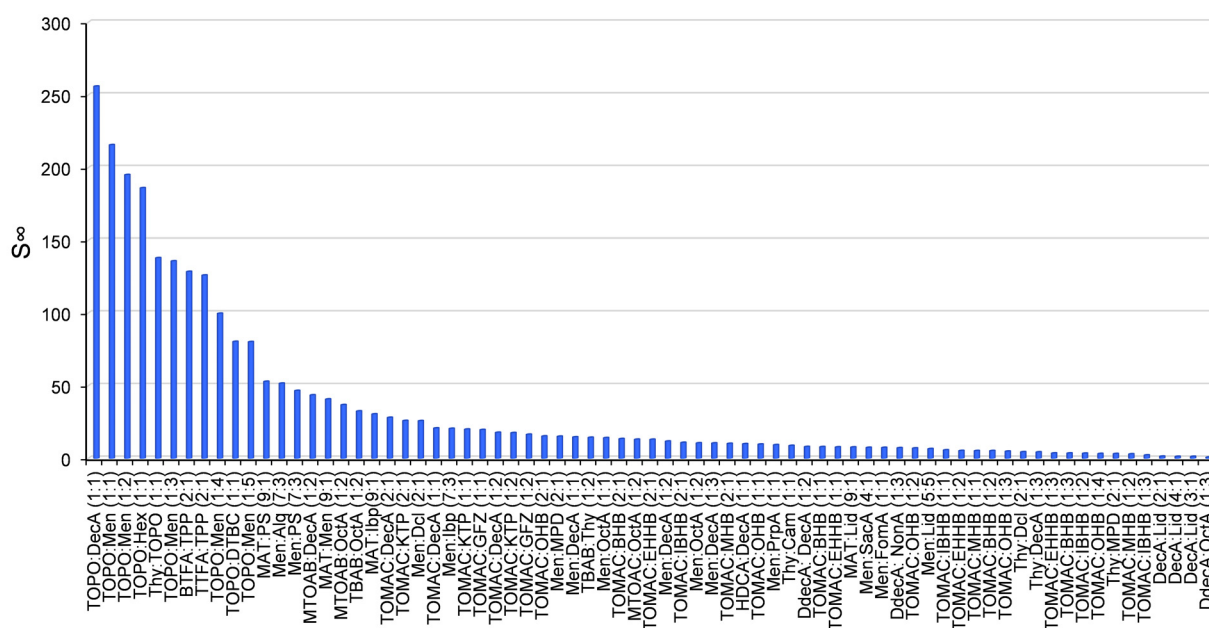


Figure 2. Selectivity of HDESs at infinite dilution.

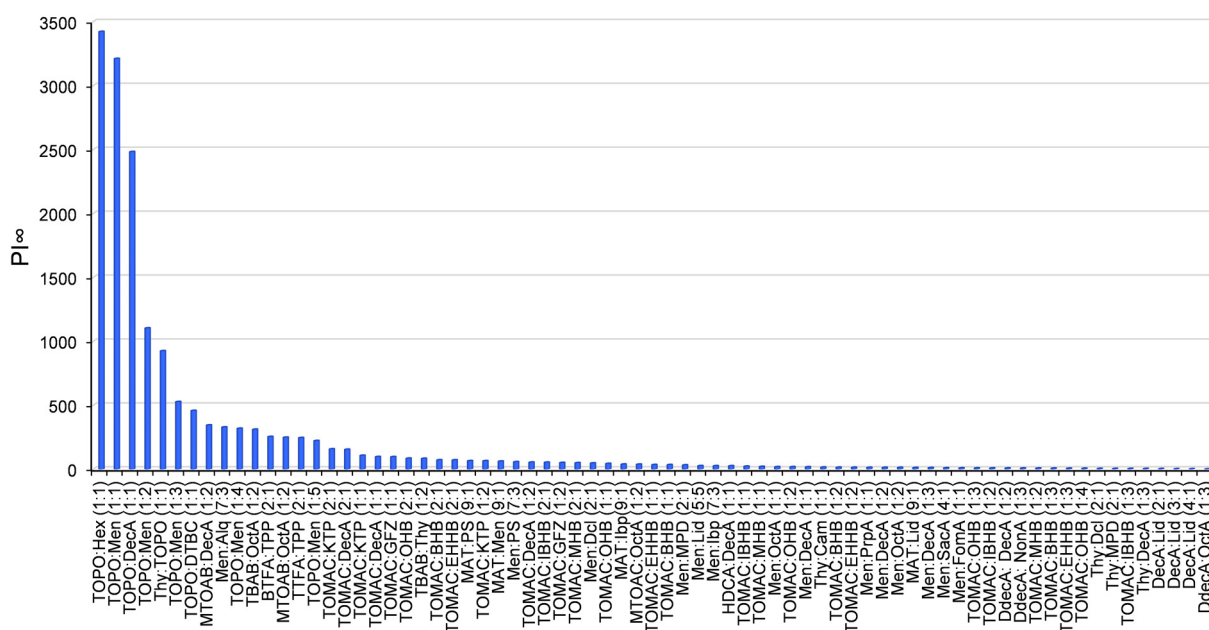


Figure 3. Performance index of HDESs at infinite dilution.

It can be seen from Figures 1–3 that the selection of HBA and HBD is crucial in the formation of HDESs. HBAs and HBDs that possess larger molecular weight and complex structures exhibit a tendency to generate HDESs that possess superior capacity and selectivity towards phenols. This phenomenon can be attributed to the enhanced interaction between these HBAs and HBDs and phenol molecules. An example of a notable outcome is the combination of TOPO with DecA in a 1:1 molar ratio, resulting in a significantly high PI value of 2483.17. It can also be observed that the molar ratio has a noticeable effect on the effectiveness of phenol removal. For instance, a change in the molar ratio of the DecA:Lid HDES results in a decrease in the PI from 3.01 to 2.04. This pattern suggests that the solvent's affinity for phenol may be improved by a larger ratio of HBA to HBD. Effective extraction depends on the solvent's polarity and, consequently, its affinity

towards phenol molecules, which are influenced by the intricate balance between the HBA and HBD components in the HDES.

The four HDESs including TOPO:Men, TOPO:Thy, TOPO:Hex, and TOPO:DecA (all at 1:1 molar ratio) demonstrated significantly higher PI values compared to other HDESs in the study, making them superior candidates for further investigation in phenol removal applications. While TOPO:DecA showed superior selectivity (Figure 2), suggesting a higher specificity towards phenol over water, TOPO:Men and TOPO:Hex, in particular, displayed high capacity values, reflecting their ability to dissolve larger quantities of phenols. The carboxylic acid group in decanoic acid may have contributed to TOPO:DecA's high PI by promoting hydrogen bonding with phenols. The high PI seen in the TOPO:Men system may be attributed to a synergistic interaction between capacity and selectivity, which might potentially be ascribed to the chemical interactions occurring among TOPO:Men HDES and phenol. Similarly, TOPO:Hex has a high PI value, indicating enhanced phenol elimination effectiveness, probably due to the longer alkyl chain encouraging favorable interactions. TOPO:Thy demonstrated substantial PI, indicating favorable interactions with phenol molecules, most likely owing to thymol's aromatic ring promoting π - π interactions.

The chosen HDESs have a combination of favorable attributes such as a balanced molar ratio, a high PI, and diverse molecular structures. They have the potential to provide critical insights into the mechanics of phenol extraction, necessitating additional experimental investigation. The subsequent experimental screening attempts to confirm the computational findings and elaborate on the fundamental factors governing phenol extraction efficiency.

3.2. Characteristics of HDESs

The physical properties of HDESs, including viscosity, density, and water content, are listed in Table 4. The viscosity and density of HDESs were measured at a temperature of 298.15 K and an atmospheric pressure of 101.3 kPa. Density and viscosity are essential properties of any solvent, as they influence the mass transfer processes and thus the usability for certain purposes. The viscosity and density data measured in this work showed good agreement with literature data. At 298.15 K, the viscosities of all HDESs were <70 mPa·s. These values are much lower than those of some conventional hydrophilic DESs [42,43], ILs [44], and some categories of HDESs [45]. Van Osch et al. [46] reported viscosities of 17 HDESs that ranged from 20 to 86,800 mPa·s. The authors also suggested that viscosities as low as 100 mPa·s are suitable for industrial applications.

Table 4. Water content, densities (ρ)s and viscosities (η) of the prepared HDESs at temperature $T = 298.15$ K and pressure $p = 101.3$ kPa.

HDES	Water Content (%)	η (mPa·s)	ρ (Kg/m ³)	η (mPa·s)	ρ (Kg/m ³)
		This Work		Literature Data	
TOPO:Men	0.078	43.16	877.6	NA	NA
TOPO:Hex	0.112	23.35	862.1	NA	NA
TOPO:Thy	0.097	68.39	898.1	69.93 [47]	898.0 [47]
TOPO:DecA	0.083	44.26	877.9	44.11 [47]	881.0 [47]

The effect of temperature on viscosity and density of all the prepared HDESs was also investigated in this study. The influence of temperature on viscosity for all HDESs prepared in this work is depicted in Figure S1. The figure illustrates that the viscosity of all HDESs reduces as temperature rises. At any temperature, TOPO:Thy has the highest viscosity. The viscosity of a mixture can be greatly influenced by the intermolecular interactions among its constituent components. An increase in intermolecular forces might result in an increased viscosity. Thymol possesses an aromatic ring and a hydroxyl group, which enables it to partake in stronger van der Waals interactions and hydrogen bonding in comparison to the other ingredients, leading to a higher viscosity. The effect of temperature on the density of

all the prepared HDESs is shown in Figure S2. As the temperature increases, the density of all HDES decreases.

It is useful to quantify the degradation of HDESs. Thermograms were measured in order to assess the degradation temperatures of HDESs. The weight loss of HDESs is seen as a function of temperature. As shown in Figure 4, the degradation temperature values appear to be less than those previously noted for HDESs that are based on decanoic acid and quaternary ammonium salt. It is hypothesized that these reduced values do not symbolize deterioration but rather suggest the sublimation or evaporation of the HDES elements. Constituents with a prominent odor such as menthol and thymol can undergo sublimation. These findings underscore that the degradation temperature and volatility significantly hinge on the constituents. This critical factor should be taken into account when constructing a DES for a specific use, applying to both hydrophilic and hydrophobic DESs.

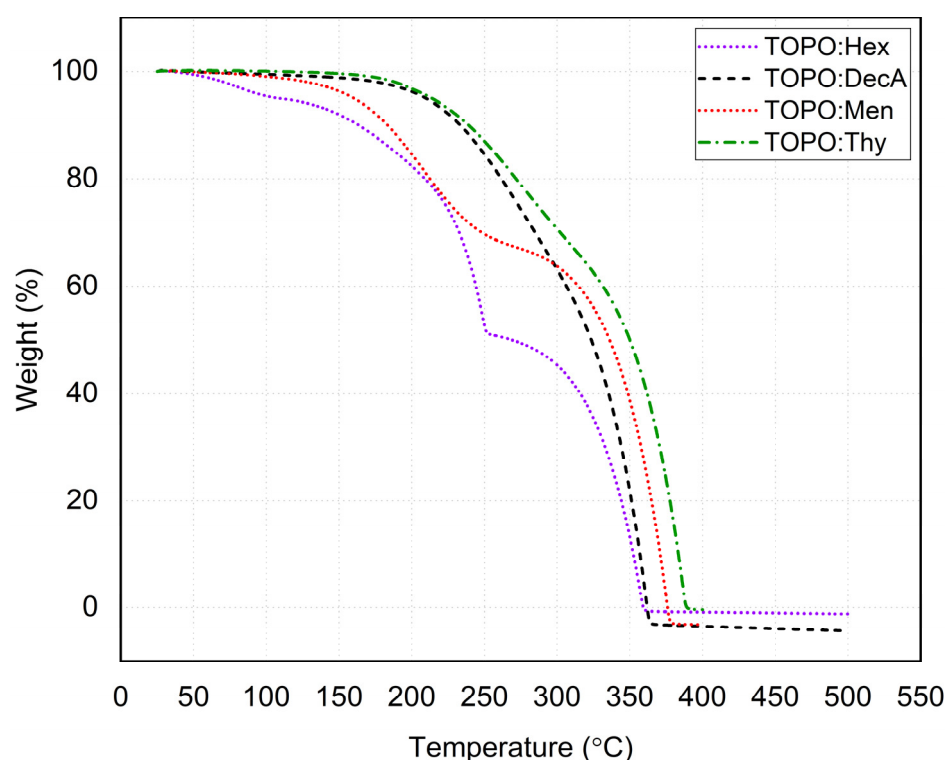


Figure 4. TGA analysis of all HDESs prepared in this work.

Intermolecular interactions between the constituent substances are responsible for the formation of eutectic mixtures. Therefore, we have performed FTIR and ^1H NMR analyses of the pure HDESs to understand the interactions between HBD and HBA. For instance, the FTIR spectra of TOPO:Men are depicted in Figure 5. The FTIR spectra of TOPO:Men have a prominent peak at 3356 cm^{-1} , situated within the O-H stretching frequency range of both TOPO and menthol. This observation suggests the occurrence of hydrogen bonding between these two constituents, hence verifying the formation of the HDES complex. The alteration in frequency of the O-H stretching vibration in HDESs might perhaps be associated with the establishment of hydrogen bonds between the O-H group of TOPO and the hydroxyl group in menthol. This interaction leads to a reduction in the strength of the O-H bond, thereby causing a displacement towards lower frequencies. The FTIR spectra of the other three HDESs are presented in the supporting information. The structure and purity of HDESs can be characterized by ^1H NMR spectroscopy. Different functional groups in HDESs can be identified and characterized by examining the proton signals in the NMR spectra. The ^1H NMR spectra of the TOPO:Men HDES are exhibited in Figure 6 while the

^1H NMR spectra of the other three HDESs are provided in the supporting information and confirm the presence of all components.

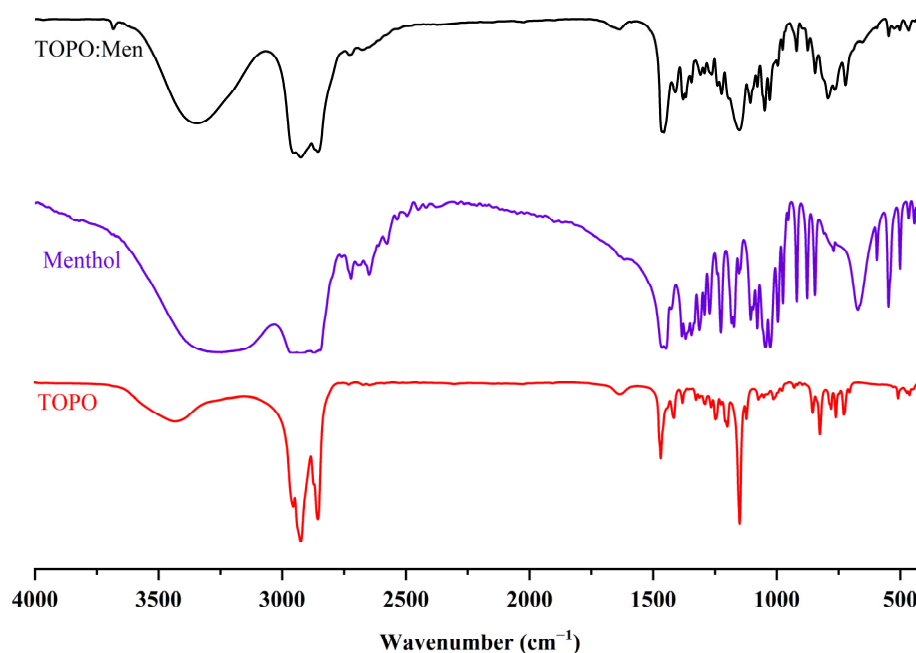


Figure 5. FTIR analysis of TOPO:Men HDES and its individual components.

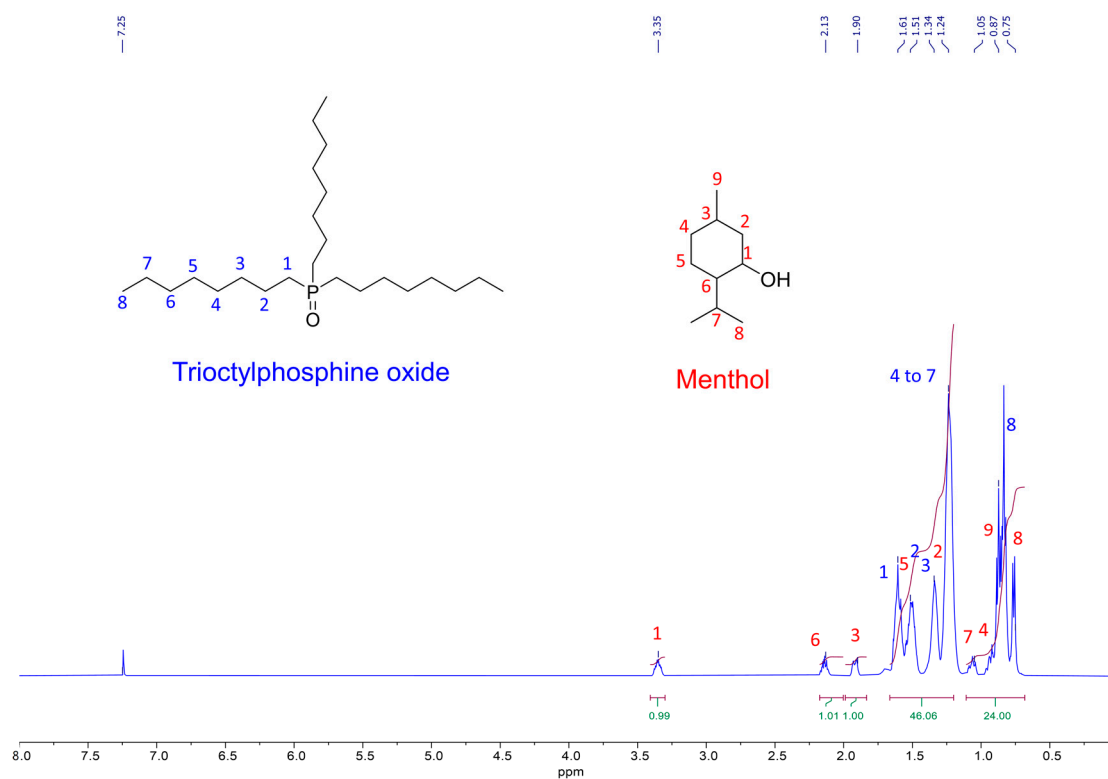


Figure 6. ^1H NMR spectra of TOPO:Men HDES. The peak around 7.25 is the peak of chloroform.

The ^1H NMR analysis has been used in order to certify the purity of the HDES prepared with the specified molar ratio. It also proves that only physical interactions are involved, without any chemical reaction.

3.3. Liquid–Liquid Extraction

The experimental LLE data for ternary systems was investigated at a temperature of 298.15 K and a pressure of 101 kPa to assess the effectiveness of HDESs in extracting phenol from wastewater. The obtained LLE data are reported in Table 5 and the extraction efficiency is shown in Figure 7. The experimental results indicate that as the concentration of phenol is varied from 1% to 7%, there is a slight rise in the phenol composition in the water-rich phase, but the phenol concentration in the HDES-rich phase experiences a significant increase. This observation suggests that the affinity of phenol towards HDESs becomes stronger as the concentration of phenol increases. This suggests the hydrophobic characteristics of phenol, as it tends to favor the HDES phase over the aqueous phase. Furthermore, with a rise in the concentration of phenol, both the distribution ratio and the selectivity exhibit an upward trend across all the HDESs. This suggests that higher phenol concentrations lead to improved extraction efficiency. The observed correlation between improved efficiency and increasing phenol content indicates that higher concentrations of phenol are favorable to more effective extraction. The observed phenomenon may be attributed to the increased driving force for mass transfer that occurs at higher phenol concentrations.

The relationship between extraction efficiency and phenol concentration demonstrates a positive correlation across all HDESs, indicating an improvement in extraction efficiency as phenol concentration increases. The extraction efficiencies of TOPO:Men, TOPO:Hex, and TOPO:DecA were seen to be higher at elevated phenol concentrations in comparison to TOPO:Thy. At 7% phenol content, TOPO:Men exhibited the highest extraction efficiency (~96%). This indicates that the extraction efficiency is influenced by the type of HDES. The data clearly indicate that there is a notable variation in the composition of phases among various HDES. This observation implies that the selection of HDES has an impact on the equilibrium partitioning of phenol between the aqueous and DES phases. The interaction between phenol and the solvent, and therefore the extraction efficiency, may be influenced by the nature of the HDES. Table 5 indicates that the concentration of HDESs in the water phase is significantly low, underscoring the hydrophobic properties of HDES. This minimal presence may be attributed to slight solubility or dispersion of HDESs in the water phase.

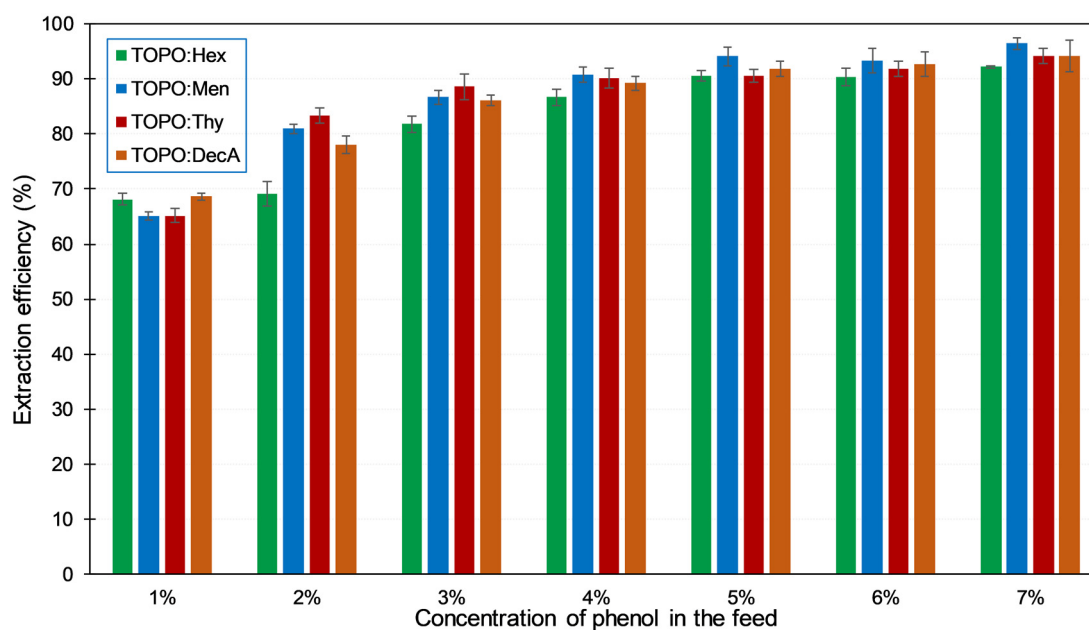


Figure 7. Effect of phenol concentration on the extraction efficiency of HDESs.

Table 5. Composition of the experimental tie-lines (mole fraction), phenol distribution ratio (D), and selectivity (S) for the ternary systems {water (1) + phenol (2) + HDES (3)} at 298.15 K and 101.325 kPa ¹.

Water-Rich Phase			HDES-Rich Phase			D	S
x'_1	x'_2	x'_3	x''_1	x''_2	x''_3		
{water (1) + phenol (2) + TOPO:Men (3)}							
0.9987	0.0007	0.0005	0.4707	0.0225	0.5068	30.7	65.1
0.9983	0.0008	0.0010	0.4576	0.0497	0.4927	64.8	141.3
0.9990	0.0008	0.0003	0.4478	0.0700	0.4822	91.3	203.6
0.9988	0.0007	0.0005	0.4376	0.0911	0.4712	128.0	292.2
0.9991	0.0006	0.0004	0.4235	0.1204	0.4561	208.0	490.7
0.9991	0.0008	0.0002	0.4148	0.1384	0.4467	178.2	429.2
0.9987	0.0005	0.0008	0.4034	0.1623	0.4344	331.1	819.7
{water (1) + phenol (2) + TOPO:Hex (3)}							
0.9978	0.0007	0.0015	0.5210	0.0192	0.4598	27.8	53.3
0.9974	0.0013	0.0013	0.5114	0.0372	0.4514	29.7	57.9
0.9978	0.0011	0.0012	0.4976	0.0633	0.4392	59.0	118.4
0.9981	0.0010	0.0009	0.4879	0.0815	0.4306	79.2	162.0
0.9985	0.0009	0.0006	0.4773	0.1014	0.4213	109.6	229.3
0.9975	0.0011	0.0014	0.4674	0.1201	0.4125	104.7	223.5
0.9982	0.0011	0.0007	0.4602	0.1337	0.4062	125.8	272.8
{water (1) + phenol (2) + TOPO:Thy (3)}							
0.9985	0.0007	0.0008	0.2270	0.0323	0.7406	43.7	192.2
0.9993	0.0007	0.0000	0.2185	0.0686	0.7128	105.4	482.2
0.9989	0.0007	0.0004	0.2108	0.1014	0.6877	153.4	726.8
0.9991	0.0008	0.0001	0.2048	0.1273	0.6679	169.5	827.3
0.9987	0.0009	0.0004	0.1978	0.1570	0.6452	170.3	859.6
0.9988	0.0009	0.0003	0.1905	0.1883	0.6213	200.5	1051.6
0.9986	0.0008	0.0006	0.1847	0.2130	0.6023	270.7	1463.9
{water (1) + phenol (2) + TOPO:DecA (3)}							
0.9989	0.0007	0.0005	0.3136	0.0388	0.6477	58.7	187.1
0.9988	0.0009	0.0003	0.3053	0.0642	0.6305	74.1	242.3
0.9988	0.0008	0.0004	0.2953	0.0949	0.6098	118.1	399.6
0.9989	0.0008	0.0003	0.2881	0.1170	0.5950	142.1	492.8
0.9987	0.0008	0.0005	0.2758	0.1547	0.5695	193.3	699.9
0.9988	0.0008	0.0004	0.2707	0.1703	0.5591	201.3	742.9
0.9991	0.0008	0.0001	0.2610	0.1999	0.5391	256.0	979.7

Note: ¹ Standard uncertainties: $u(x) = 0.013$, $u(T) = 0.5$ K, $u(P) = 1$ kPa.

The obtained LLE data are graphically rendered as triangular ternary diagrams in Figure 8. Figure 8 demonstrates that all ternary systems exhibit Type I phase behavior, characterized by a singular immiscibility zone. The observation in Figure 8 reveals that all of the systems exhibit positive tie-line slopes, which signifies that the HDES-rich phase has a higher quantity of phenol compared to the water-rich phase at equilibrium. This suggests that a smaller quantity of solvent is required to achieve a significant level of extraction. In addition, it can be observed that the slopes of the data increase as the concentration of phenol (the solute) increases. This implies that when the solute concentration decreases, there is an increase in the concentration of solvent (HDES) needed to extract the solute from the solution. Figure 8 demonstrates a positive correlation between the length of the tie-lines and the degree of immiscibility.

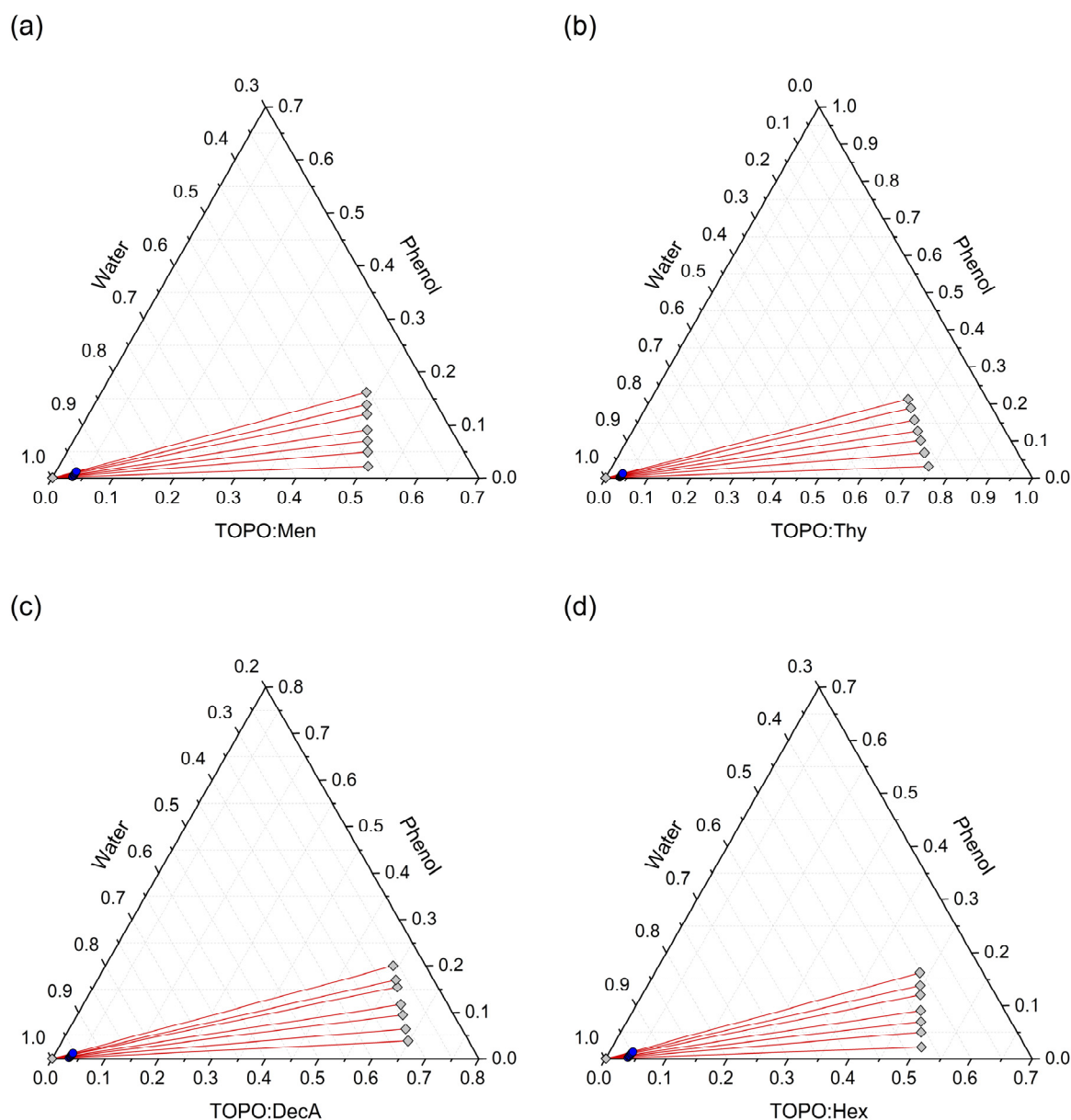


Figure 8. Ternary liquid–liquid equilibrium diagram in mole fraction for (a) water (1) + phenol (2) + TOPO:Men (3); (b) water (1) + phenol (2) + TOPO:Thy (3); (c) water (1) + phenol (2) + TOPO:DecA (3); and (d) water (1) + phenol (2) + TOPO:Hex (3). Blue dots indicate the feed composition.

4. Conclusions

As a conclusion, the most important findings of this work could be summarized by the following points:

- After a thorough evaluation of the phenol removal performance of 73 HDESs based on COSMO-RS computational screening, the most promising HDESs for phenol removal were identified as being TOPO:Men, TOPO:Hex, TOPO:DecA, and TOPO:Thy (all at 1:1 molar ratio). These candidates have been selected for further experimental validation.
- According to the experimental LLE results, the TOPO and menthol combination exhibited the maximum extraction efficiency (96%) at 7% phenol content and demonstrated the best phenol removal capability of the chosen HDESs.
- The physicochemical characteristics of the chosen HDESs, such as density, viscosity, FTIR, ^1H NMR, and TGA, also revealed that they have a high thermal sta-

bility and a low degree of water solubility, making them appropriate for phenol extraction applications.

- The results of this investigation point out HDESs as a potentially effective replacement for traditional solvents for the elimination of phenolic contaminants from aqueous effluents.
- Finally, this study shows that hydrophobic deep eutectic solvents have the ability to remove phenolic contaminants from aqueous effluents in a sustainable and efficient manner.

Future studies should investigate the use of HDESs to remove a wider range of pollutants from aqueous effluents as well as other phenolic pollutants to expand the field. This includes investigating the efficiency and selectivity of HDESs for different target pollutants. In addition, further development of techniques for regeneration and reuse of HDESs after phenol extraction would improve the sustainability and economic feasibility of the process. It is important to conduct a comprehensive investigation of the stability and performance of HDESs during multiple extraction cycles.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w15244289/s1>, Figure S1: GC calibration curve of naphthalene/phenol. Figure S2: Viscosity of HDESs at different temperatures. Figure S3: Density of HDESs at different temperatures. Figure S4: GC calibration curve of naphthalene/phenol. Figure S5: Viscosity of HDESs at different temperatures. Figure S6: Density of HDESs at different temperatures. Figure S7: FTIR analysis of TOPO:Thy HDES and its individual components. Figure S8: FTIR analysis of TOPO:DecA HDES and its individual components. Figure S9: FTIR analysis of TOPO:Hex HDES and its individual components. Figure S10: ^1H NMR spectra of TOPO:Hex HDES. The peak around 7.25 is the peak of chloroform. Figure S11: ^1H NMR spectra of TOPO:Thy HDES. The peak around 7.25 is the peak of chloroform. Figure S12: ^1H NMR spectra of TOPO:DecA HDES. The peak around 7.25 is the peak of chloroform; Table S1: Comparison of phenolic compound extraction efficiencies using VOCs, ILs, and HDESs as extractants. Table S2: Chemical structures of different chemicals investigated in this study. Table S3: COSMO-RS screening results. Refs. [48–53] are cited in supplementary materials.

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