Carbon Dioxide Solubility in Nonionic Deep Eutectic Solvents Containing Phenolic Alcohols

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Deep eutectic solvents (DES) are a new class of green solvents that have shown unique properties in several process applications. This study evaluates nonionic DES containing phenolic alcohols as solvents for carbon dioxide (CO_2) capture applications. Potential phenolic alcohols and the molar ratio between DES constituents were preselected for experimental investigations based on the conductor-like screening model for realistic solvation (COSMO-RS). CO_2 solubility was experimentally determined in two different DES, namely, L-menthol/thymol in 1:2 molar ratio and thymol/2,6-xylenol in 1:1 molar ratio, at various temperatures and pressures. CO_2 solubility in the studied systems was higher than that reported in the literature for ionic DES and ionic liquids. This study demonstrates that nonionic DES containing phenolic alcohols can be excellent, inexpensive, and simple solvents for CO_2 capture.

Keywords: CO_2 capture, COSMO-RS, ionic liquids, hydrophobic deep eutectic solvents, green solvents

INTRODUCTION

An increasing relevance has developed in removing carbon dioxide (CO_2) from gas mixtures, such as flue gas or biogas. Absorption in liquid solvents, in addition to membrane and absorption-based processes, is a major technology in this field. For many years, aqueous solutions of amines have been used for CO_2 absorption. However, they suffer from some drawbacks, such as high vapor pressure, which causes evaporation during solvent regeneration. Recently, ionic liquids (IL) have drawn attention for CO_2 capture application because of their negligible vapor pressure (Albo et al., 2010; Shiflett et al., 2010). Furthermore, the properties of IL can be tailored to the requirements of the specific application by combining different cations and anions (Jork et al., 2005). Although the hygroscopicity of IL can be overcome by using polymerized IL to prepare membranes for CO_2 capture applications (Kammakakam et al., 2020; Galiano et al., 2021), the issues of IL cost, instability, and purity remain (Sowmiah et al., 2009).

Nevertheless, owing to the aforementioned problems of IL, researchers have focused on an alternative solvent class that has some similarities to IL, while avoiding some of their drawbacks. Deep eutectic solvents (DES) are eutectic mixtures with a large depression in the eutectic temperature obtained by mixing a hydrogen bond acceptor and donor. DES are a new class of designer solvents, which can also be prepared by simple mixing of natural and nontoxic components, usually referred to as Natural DES (NADES) (Smith et al., 2014; van Osch et al., 2020). Similar to IL, physicochemical properties of DES can be tuned by selecting their constituents and additionally molar ratios of those. Moreover, DES are easier and less expensive to prepare compared to IL. Therefore, more attention is directed to their use in several process

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TABLE 1 | Prepared eutectic mixtures, their molar ratio, and water content.

Eutectic mixture	Mole ratio	Water content/ppm
L-menthol/thymol	1:2	144.2 ± 2.1
Thymol/2,6-xylenol	1:1	108.4 ± 6.7

applications, for example, in liquid–liquid chromatography (Roehrer et al., 2016; Bezold and Minceva, 2019; Cai and Qiu, 2019), extraction of bioactive compounds (Kalhor and Ghandi, 2019; Makoś et al., 2020; Perna et al., 2020; Rodríguez-Llorente et al., 2020; Fernández et al., 2022), and crystallization (Emami and Shayanfar, 2020; Hall et al., 2020; Hamilton et al., 2020; Potticary et al., 2020).

CO$_2$ capture is one application that can benefit from DES. Existing studies have demonstrated the potential of DES for CO$_2$ capture (Krishnan et al., 2020; Song et al., 2020; Wazeer et al., 2021a; Wazeer et al., 2021b). However, most studies investigating CO$_2$ capture in DES proposed using ionic DES, which has the same drawbacks as those related to IL, especially in terms of hygroscopicity. Recently, hydrophobic DES based on natural and inexpensive nonionic constituents has attracted much attention (van Osch et al., 2019). Hydrophobic DES containing L-menthol possess outstanding properties, such as low viscosity and eutectic temperatures, especially when L-menthol is mixed with phenolic alcohols, such as thymol or carvacrol (Alhadid et al., 2020a; Alhadid et al., 2020b; Alhadid et al., 2021a; Alhadid et al., 2021b). Phenolic IL are good solvents for CO$_2$ capture applications (Vafaeezadeh et al., 2015). Therefore, hydrophobic DES containing phenolic alcohols are assumed to be promising candidates for CO$_2$ capture applications.

Nevertheless, the large pool of substances that can form DES can make selecting the DES constituents challenging. Furthermore, the ratio between the constituents can be tuned, which is an additional degree of freedom during the selection of DES constituents. Therefore, a predictive screening method could noticeably assist in preselecting DES constituents for CO$_2$ capture applications. The conductor-like screening model for realistic solvation (COSMO-RS) is a predictive thermodynamic model based on quantum mechanics and statistical thermodynamics (Klamt, 1995; Klamt et al., 1998; Eckert and Klamt, 2002). COSMO-RS successfully provides qualitative predictions for screening IL and ionic DES for gas capture applications (Völkl et al., 2012; Song et al., 2020; Liu et al., 2021; Qin et al., 2021).

This study investigates nonionic DES containing phenolic alcohols as potential solvents for CO$_2$ capture. COSMO-RS was used to screen a list of possible DES containing L-menthol and phenolic alcohols to preselect those with the highest CO$_2$ solubility. Further, CO$_2$ solubility was experimentally investigated for selected DES systems at various temperatures and pressures using an isochoric method.

MATERIALS AND METHODS

Eutectic Mixture Preparation
Pure components (L-menthol, purity ≥99%, Sigma Aldrich; thymol, purity ≥99%, Sigma Aldrich; 2,6-xylenol, purity 99%,

Acros Organics), was mixed under continuous stirring and gentle heating until a clear homogenous liquid was formed. The water content of the prepared eutectic mixtures was measured in triplicate using Karl Fischer Coulometer (Hanna Instrument, United States), and the results are shown in **Table 1**.

Carbon Dioxide Solubility Experiments
Before measurements, DES were degassed under vacuum for 48 h at a temperature of $T = 413.15$ K. After degassing, no mass loss was observed for the DES, indicating that there was no change in the stoichiometry between constituents and their negligible volatility under the experimental conditions. CO$_2$ from Westfalen AG, Germany, with a purity of 99.995% (quality 4.5), was used without further purification. The experiments were performed using a pressure-drop isochoric method at various temperatures and pressures. The apparatus and operational procedures of solubility measurements are described in detail in previous studies (Safarov et al., 2013; Safarov et al., 2014). For the current measurements, the installation was used without modification. The temperature in the measuring cell was held constant (at $T = 293.15$–323.15 K) with an uncertainty of $u(T) = 0.030$ K. A pressure transducer with an accuracy of 0.1% was used to measure the pressure of CO$_2$ filled in the gas reservoir. The temperature inside the gas reservoir was measured with an uncertainty of $u(T) = 0.015$ K. The initial amount of CO$_2$ in the gas reservoir was determined from its pressure and temperature using the Span and Wagner equation of state (Span and Wagner, 1996).

To determine the concentration of CO$_2$ in the solution, liquid and gas densities under experimental temperature and pressure were required. The density of DES was measured using a density meter (Density meter Easy D40, Mettler-Toledo GmbH, Germany), and the results are indicated in **Table 2**. The mass of CO$_2$ in the gas phase was calculated using its density and volume. The gas volume in the cell was found by deducting the liquid volume from the total cell volume. The increase in the liquid volume because of dissolved CO$_2$ was neglected (Safarov et al., 2013).

Correlation of the Gas Solubility
Henry's law for a binary system (liquid + CO$_2$) for a non-ideal gas phase can be given as (Prausnitz and Shair, 1961)

$$y_{CO_2} \cdot \phi_{CO_2}(T, p) \cdot p = x_{CO_2} \cdot H_{CO_2} \tag{1}$$

TABLE 2 | Density of eutectic mixtures measured in this work[a].

T/K	ρ/kg m^{-3}	
	L-menthol/thymol (1:2)	Thymol/2,6-xylenol (1:1)
293.15	947.6	992.2
303.15	940.0	983.9
313.15	932.5	975.6
323.15	924.8	967.2

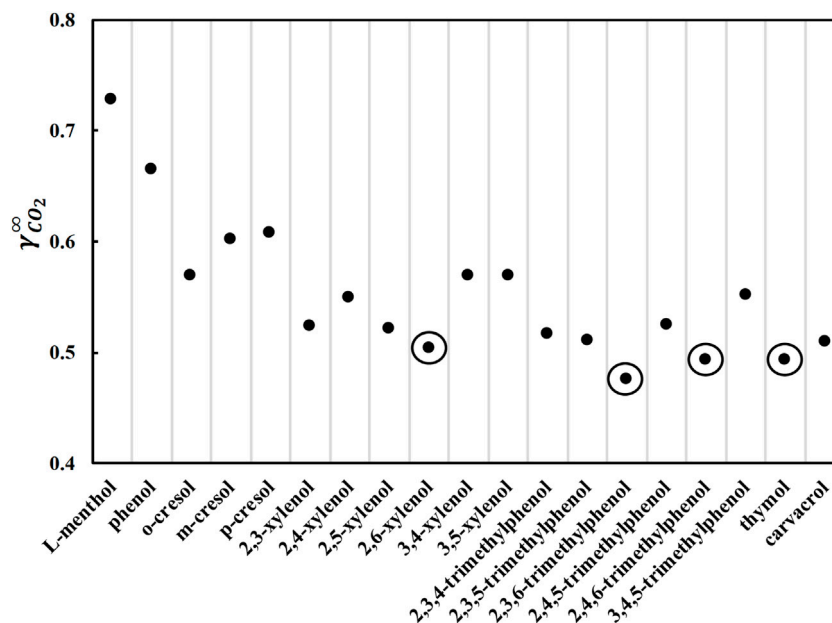[a]Standard uncertainty u(ρ) = 0.05 kg m^{-3}

FIGURE 1 | Activity coefficients at infinite dilution of carbon dioxide in pure L-menthol and various phenolic alcohols at 293.15 K calculated by COSMO-RS.

TABLE 3 | Experimental carbon dioxide (CO$_2$) solubility (both in weight percent w_{CO_2} and in mole fraction x_{CO_2}) in the L-menthol/thymol (MTH) eutectic system and calculated CO$_2$ fugacity coefficient (ϕ_{CO_2}) at various temperatures T and pressures p.[a]

T/K	p/MPa	w_{CO_2}, %	x_{CO_2} /Mole fraction	ϕ_{CO_2}[b]
323.11	4.1939	11.410	0.3082	0.8453
313.12	4.1543	12.090	0.3224	0.8295
303.18	4.0967	13.409	0.3488	0.8121
293.15	4.0201	15.769	0.3931	0.7931
323.15	3.5059	9.290	0.2616	0.8701
313.16	3.4703	10.173	0.2815	0.8570
303.13	3.4247	11.780	0.3159	0.8426
293.13	3.3691	13.335	0.3474	0.8265
323.14	2.5790	7.090	0.2088	0.9039
313.18	2.5541	7.615	0.2219	0.8942
303.13	2.5229	8.347	0.2395	0.8835
293.14	2.4860	9.297	0.2617	0.8716
323.02	1.6819	4.644	0.1442	0.9369
313.18	1.6662	5.027	0.1547	0.9305
302.98	1.6478	5.436	0.1659	0.9235
293.15	1.6281	5.937	0.1792	0.9155

[a]Standard uncertainties u are: u(T) = 0.030 K, u(p) = 0.1%, u(w) = 0.01 wt%, and u(x) = 0.0001 mol fraction.
[b]Calculated using the Span and Wagner equation of state (Span and Wagner, 1996) implemented in ThermoFluids (Springer, V. 1.0).

where y_{CO_2} and x_{CO_2} are the mole fraction of CO$_2$ in the gas and liquid phases, respectively; ϕ_{CO_2} is the fugacity coefficient of CO$_2$ in the gas phase, and H_{CO_2} is Henry's constant. Due to the negligible vapor pressure of the studied eutectic mixtures at studied temperatures (Xin et al., 2021) (see also **Supplementary Table S1** in **Supplementary Material** for calculations), the gas phase can be assumed as pure CO$_2$, i.e., $y_{CO_2} = 1$ (see also **Supplementary Table S1** in
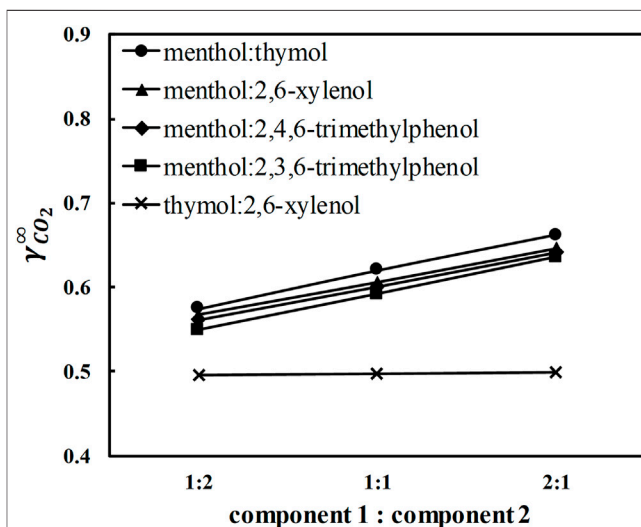

FIGURE 2 | Activity coefficients at infinite dilution of carbon dioxide in selected eutectic mixtures at 293.15 K calculated by COSMO-RS.

Supplementary Material for calculations). Henry's constant can be defined using the following equation.

$$H_{CO_2} = \lim_{p \to 0}\left[\frac{\phi_{CO_2}(T, p) \cdot p}{x_{CO_2}}\right] \quad (2)$$

COSMO-RS Calculations

The solubility of CO$_2$ in eutectic mixtures was screened a priori by evaluating CO$_2$ activity coefficients at infinite dilution. The

TABLE 4 | Experimental carbon dioxide (CO₂) solubility (both in weight percent w_{CO_2} and in mole fraction x_{CO_2}) in the thymol/2,6-xylenol (T26X) eutectic system and CO₂ calculated fugacity coefficient (ϕ_{CO_2}) at various temperatures T and pressures p.[a]

T/K	p/MPa	w_{CO_2}, %	x_{CO_2} /Mole fraction	ϕ_{CO_2}[b]
322.90	4.0853	11.549	0.2878	0.8492
313.13	4.0441	12.563	0.3078	0.8339
303.17	3.9840	14.856	0.3506	0.8172
293.22	3.9057	17.093	0.3895	0.7990
323.14	3.3380	9.512	0.2455	0.8762
313.15	3.3029	10.417	0.2646	0.8638
303.13	3.2563	11.456	0.2859	0.8502
293.14	3.1988	13.073	0.3176	0.8352
323.13	2.6988	7.477	0.2000	0.8995
313.15	2.6696	8.022	0.2125	0.8895
303.16	2.6344	9.205	0.2388	0.8784
293.15	2.5932	10.284	0.2619	0.8661
323.14	1.6670	4.462	0.1263	0.9375
313.15	1.6500	4.909	0.1377	0.9313
303.16	1.6300	5.398	0.1501	0.9243
293.15	1.6070	6.057	0.1663	0.9166

[a]*Standard uncertainties u are: u(T) = 0.030 K, u(p) = 0.1%, u(w) = 0.01 wt%, and u(x) = 0.0001 mol fraction.*
[b]*Calculated using the Span and Wagner equation of state (Span and Wagner, 1996) implemented in ThermoFluids (Springer, V. 1.0).*

activity coefficients of CO₂ at infinite dilution in different pure constituents and eutectic mixtures were calculated using the COSMO-RS model (BIOVIA COSMOtherm X19, Dassault Systèmes) and BP_TZVP_19. ctd parameters. Molecular conformations of components were obtained using BIOVIA COSMOconf 17 (Dassault Systèmes). The geometry optimization and screening charge density were determined by density functional theory calculations using BP86 functional and def-TZVP basis set by Turbomole version 6.6 (TURBOMOLE GmbH).

RESULTS AND DISCUSSION

Screening With COSMO-RS

To enable the usage of a DES in CO₂ capture applications, the DES should 1) be liquid in the appropriate temperature range, i.e., approximately room temperature; and 2) be a good solvent for CO₂. A number of nonionic DES containing phenolic alcohols can satisfy these two criteria. The phenolic alcohols considered in this study are phenol, methylphenols (cresols), dimethylphenols (xylenols), trimethylphenols, and two natural phenolic terpenes, thymol (2-isopropyl-5-methylphenol) and carvacrol (5-isopropyl-2-methylphenol). Phenolic alcohols with higher molecular weights or dihydroxy benzenes were not considered because they are not expected to form liquid DES at room temperature because of their high melting temperature and enthalpy (Alhadid et al., 2019). When phenolic alcohols are mixed with L-menthol, a significant negative deviation from the ideal behavior is expected (Alhadid et al., 2020b; Alhadid et al., 2021a). The negative deviation from the ideal behavior results in the formation of DES with a sufficiently low melting temperature. Thus, it is desirable to have L-menthol as a DES
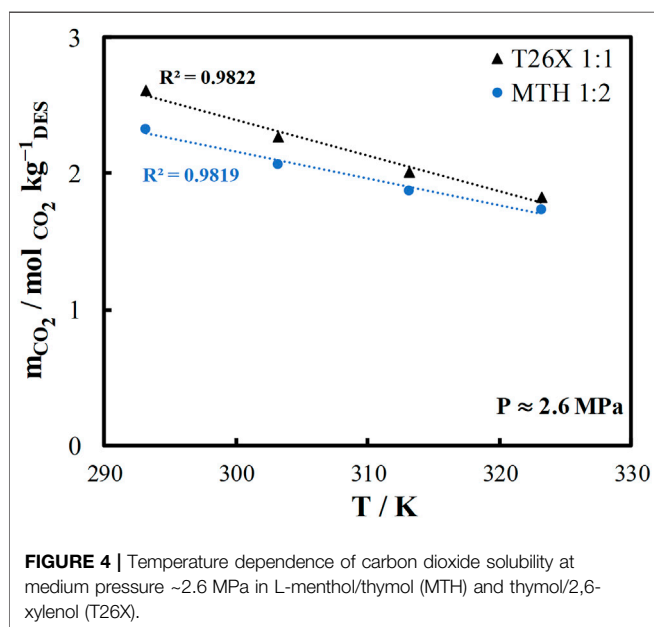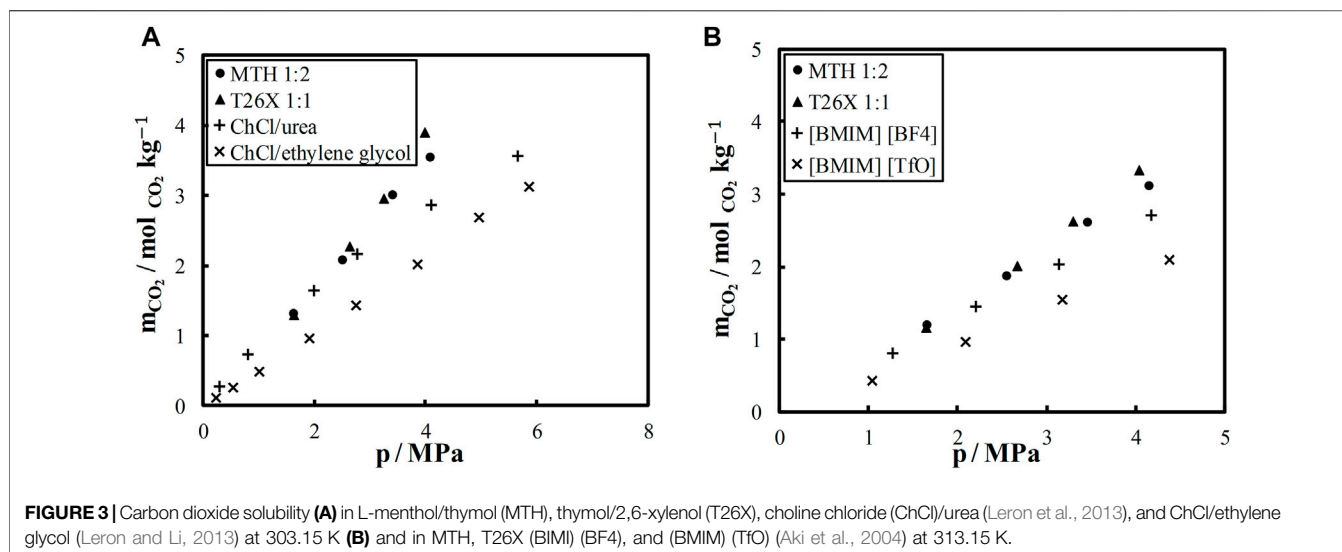
TABLE 5 | Calculated carbon dioxide Henry's constant (H_{CO_2}) in the studied systems.

T/K	H_{CO_2} /MPa	
	L-menthol/thymol (1:2)	Thymol/2,6-xylenol (1:1)
293.15	8.52 ± 0.13	9.45 ± 0.32
303.15	8.98 ± 0.13	10.45 ± 0.23
313.15	9.61 ± 0.25	11.46 ± 0.15
323.15	10.51 ± 0.30	12.52 ± 0.17

constituent. First, the activity coefficients of CO₂ at infinite dilution were calculated using COSMO-RS in pure constituents at 293.15 K because the physicochemical properties of pure constituents influence the physicochemical properties of DES (Alhadid et al., 2021b), and the results are shown in **Figure 1**. As COSMO-RS is based on quantum mechanical calculations, the calculated activity coefficients implicitly include the atomistic rationalization and quantify the intermolecular interactions between CO₂ and the constituents in the liquid phase. The low CO₂ activity coefficient values indicate strong intermolecular interactions between CO₂ and the constituents and, accordingly, high CO₂ solubility. The calculated CO₂ activity coefficients in all phenolic alcohols are lower than in L-menthol (cyclohexyl alcohol) (**Figure 1**), proving that CO₂ solubility is relatively high in phenolic alcohols.

Figure 1 shows that the limiting activity coefficients decrease with the addition of methyl groups to phenolic alcohols. The general order of the CO₂ activity coefficients in phenolic alcohols is phenol > methylphenol (cresol) > dimethylphenol (xylenol) > trimethylphenols. Furthermore, compared to thymol and carvacrol, substituting a methyl group with an isopropyl group, i.e., 2,5-xylenol, decreases CO₂ limiting activity coefficients. By comparing different isomers, the limiting activity coefficients are lower in isomers with methyl groups at position 2, i.e., close to the hydroxyl group. Furthermore, the lowest values of CO₂ activity coefficients are observed in dimethyl and trimethyl isomers with a methyl group on the two and six positions, respectively. The CO₂ activity coefficient in thymol is lower than that in carvacrol, as the isopropyl group is nearer to the hydroxyl group in thymol than to carvacrol. Therefore, the structure of the phenolic alcohol influences CO₂ solubility. The four marked phenolic alcohols with the lowest limiting activity coefficient values in CO₂ were considered potential DES constituents for further screening.

Further, potential DES containing L-menthol with 2,6-xylenol, thymol, 2,3,6-trimethylphenol, and 2,4,6-trimethylphenol were screened using COSMO-RS. The calculated activity coefficients of CO₂ at infinite dilution in five different DES and ratios between the constituents at 293.15 K are shown in **Figure 2**. CO₂ activity coefficients in L-menthol-based DES at any molar ratio are in the order L-menthol:thymol (MTH) > L-menthol:2,6-xylenol (M26X) > L-menthol:2,4,6-trimethylphenol (M246) > L-menthol:2,3,6-trimethylphenol (M236) (**Figure 2**), which is consistent with the order of CO₂ activity coefficients in the pure phenolic alcohols present in the DES (see **Figure 1**).

FIGURE 3 | Carbon dioxide solubility **(A)** in L-menthol/thymol (MTH), thymol/2,6-xylenol (T26X), choline chloride (ChCl)/urea (Leron et al., 2013), and ChCl/ethylene glycol (Leron and Li, 2013) at 303.15 K **(B)** and in MTH, T26X (BIMI) (BF4), and (BMIM) (TfO) (Aki et al., 2004) at 313.15 K.

FIGURE 4 | Temperature dependence of carbon dioxide solubility at medium pressure ~2.6 MPa in L-menthol/thymol (MTH) and thymol/2,6-xylenol (T26X).

Moreover, increasing the molar ratio of the phenolic alcohol to L-menthol decreases CO_2 activity coefficients. Therefore, it is logical to select L-menthol-based DES containing trimethylphenols in a 1:2 ratio between the constituents as potential solvents for CO_2 capture. However, melting properties of pure constituents influence the melting temperature of the DES (Alhadid et al., 2019). M236 and M246 in 1:2 ratio are solid at room temperature, which is attributed to the high melting temperature of 2,3,6- and 2,4,6-trimethylphenols (T_m = 331.2 and 342.15 K, respectively) (Verevkin, 1999). MTH and M26X in 1:2 ratio are liquid at room temperature (Alhadid et al., 2021a), which indicates that both can be considered for further experimental investigation. CO_2 activity coefficients in MTH and M26X at 1:2 ratio are of

similar values (**Figure 2**). However, MTH is considered a better option because of the low toxicity of thymol compared to 2,6-xylenol. Therefore, MTH was chosen for measurements.

Next, eutectic mixtures containing two phenolic alcohols were considered. These eutectic mixtures are expected to show ideal solution behavior with no significant decrease in the melting temperature of the mixture relative to pure constituents (Alhadid et al., 2019). For such mixtures, the melting temperature of the DES at any ratio between constituents can be obtained from the solid–liquid phase diagram based on the pure constituent melting properties. A brief explanation of solid–liquid equilibrium calculations is given in the **Supplementary Material**. Based on the ideal solution model calculations, thymol: 2,6-xylenol (T26X) eutectic system should form a liquid mixture at room temperature. The calculated eutectic composition and temperature for T26X are $x_{e,thymol}$ = 0.46, and T_e = 292.8 K, respectively (see **Supplementary Material** for details about the calculations). Altering the ratio between constituents in T26X does not influence CO_2 activity coefficients (**Figure 2**), in contrast to what is observed in L-menthol-based DES. Thus, the molar ratio close to the eutectic ratio of the T26X system (~1:1 ratio) was selected to ensure that the mixture is liquid at room temperature. Eventually, the two DES, MTH in 1:2 ratio, and T26X in 1:1 ratio were selected for the solubility measurements.

Experimental Solubility

CO_2 solubility in the two DES was measured based on the pressure-drop isochoric method at four different pressures (~4, 3, 2, and 1 MPa) and four different temperatures (293.15, 303.15, 313.15, and 323.15 K). The CO_2 solubility in weight percentage (w_{CO_2}) and mole fraction (x_{CO_2}), as well as its fugacity coefficient (ϕ_{CO_2}) calculated using Span and Wagner equation of state for the MTH and T26X system are shown in **Tables 3**, **4**, respectively. The values of Henry's constant at different temperatures calculated using **Eq. 2** are shown in **Table 5**. As one would expect, the solubility of CO_2 in the two studied systems decreases as temperature increases.

Further, the CO_2 solubility in the studied DES was compared with that in some ionic DES and IL reported in the literature. The comparison was made in terms of molality, i.e., moles of CO_2 absorbed per mass of solvent. The results are shown in **Figure 3**. CO_2 solubility at 303.15 K in two ionic DES, namely, choline chloride (ChCl)/urea and ChCl/ethylene glycol in 1:2 molar ratio, is compared with the two DES from this study in **Figure 3A**. As seen, CO_2 solubility is significantly higher in nonionic DES than in ionic DES, especially at high pressures (**Figure 3A**). The CO_2 solubility in MTH and T26X is also higher than in the two IL (BMIM) (BF4) and (BMIM) (TfO), as shown in **Figure 3B**. In addition to good CO_2 solubility, nonionic DES are more stable, less hygroscopic, and less expensive than IL and ionic DES.

The solvent capacity to absorb CO_2 is not the only selection criterion to consider when selecting a solvent for CO_2 capture applications. The temperature dependence of CO_2 solubility is critical as well because CO_2 should be absorbed with high solubility and desorbed from the solvent at a higher temperature for solvent regeneration. Thus, a strong temperature dependence is required for CO_2 solubility to reduce the energy demand for desorption. The temperature dependence of CO_2 solubility in the two DES being studied is shown in **Figure 4**. The T26X system shows a slightly higher CO_2 solubility than the MTH system. Furthermore, the T26X system has a stronger temperature dependence. Therefore, the T26X system can be identified as a very promising candidate for CO_2 capture applications.

CONCLUSION

This study examines the use of nonionic DES for CO_2 capture applications. DES were designed to contain phenolic alcohols for improving CO_2 solubility and L-menthol to decrease the melting temperature of the DES. COSMO-RS was used to preselect the DES constituents from a pool of possible phenolic alcohols and to tune the molar ratio between the constituents. It was found that the structure of phenolic alcohols can influence CO_2 solubility. Furthermore, increasing the phenolic alcohol molar content in the DES can enhance the CO_2 solubility. However, the selection of the constituents and their molar ratio was restricted by the melting temperature of the DES. The COSMO-RS screening results identified two potential DES: MTH in 1:2 molar ratio and T26X in 1:1 molar ratio.

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In the two preselected DES, the CO_2 solubility was studied experimentally using a pressure-drop isochoric method at various temperatures and pressures. The high experimentally determined CO_2 solubility in the two DES validated the COSMO-RS preselection, demonstrating the model's advantage as a screening tool. CO_2 solubility in the DES proposed in this study is significantly higher than in ionic DES and IL proposed in the literature. Furthermore, the temperature dependence of CO_2 solubility in DES proves their suitability for CO_2 capture applications. The high solubility of CO_2 at lower temperatures and its high decrease at higher temperatures make the two DES promising candidates for CO_2 capture. This study shows that simple and widely available organic substances can be used to form novel solvents with unique properties.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/**Supplementary Material**, further inquiries can be directed to the corresponding authors.

AUTHOR CONTRIBUTIONS

Conceptualization: AA; Investigation: AA and JS; Formal Analysis: AA, JS, and LM; Writing–Original Draft: AA and JS; Writing–Review and Editing: LM, KM, and MM; Supervision: KM and MM.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fchem.2022.864663/full#supplementary-material

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