Fine-tuning the Basicity of Deep Eutectic Solvents by Substituting Guanidine for Urea in Reline

Tatsuya Umecky,* Akihiro Goto, Naoki Hayashi, and Kazuki Eguchi

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ABSTRACT: The physicochemical properties of deep eutectic solvents (DESs) depend on the combination of hydrogen bond acceptors and hydrogen bond donors used. The basicity of a DES significantly influences its performance in CO_2 chemical absorption, biomass and protein dissolution, and catalytic reactions. To the best of our knowledge, a strategy for fine-tuning the basicity of DESs has not yet been reported. Therefore, in this study, we substituted the base urea (Ur) in reline, which is a 1:2 mixture of choline chloride (ChCl) and Ur, with the superbase guanidine (Gu) to fine-tune its basicity. Binary (2Gu−ChCl) and ternary (Gu−Ur−ChCl) DESs were prepared, and their CO_2 absorption capacities were investigated at 313.2 K. The equimolar mixture Gu−Ur−ChCl absorbed CO_2 gas up to the molar ratio $[CO_2]/$ $[ChCl] \approx 1.0$. Therefore, the basicity of ChCl-based DES can be continuously varied by substituting more molecules of Ur with Gu. Our strategy of combining functional and non-functional molecules with similar structures to vary the basicity of DESs has potentially wide applications that utilize DESs in the future.
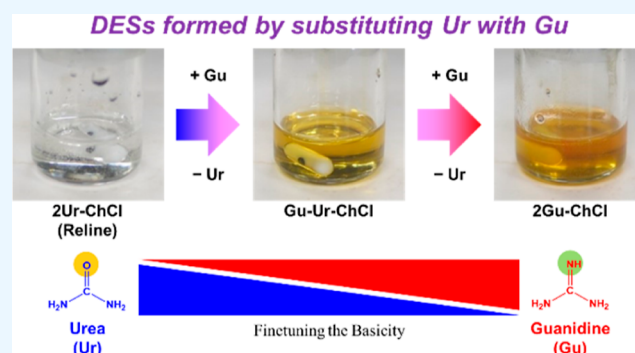
INTRODUCTION

Deep eutectic solvents (DESs) are prepared using hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs).[1−4] A typical example is the unconventional liquid 2Ur−ChCl formed by mixing the HBD solid urea (Ur, T_m = 406−407 K[5,6]) with the HBA solid choline chloride (ChCl, T_m = 575−578 K[5,6]). This DES with a molar ratio of $[Ur]/[ChCl]$ = 2 is called "reline". The molecular structures of ChCl and Ur are shown in Figure 1a,b, respectively. In general, DESs have low volatility and are similar to aprotic ionic liquids (APILs).
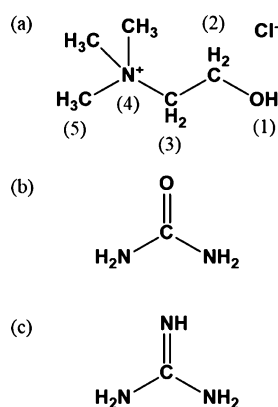
In addition, they are cheaper and easier to obtain than APILs. The physicochemical properties of DESs depend on the HBA and HBD used. Acidic DESs are utilized for acid-catalyzed reactions and biomass degradation.[7−9] The acidity of DESs is expressed by HBDs such as carboxylic and sulfonic acids and transition metal halides. Recently, an appropriate procedure for measuring the acidity of DESs has been suggested.[10] On the other hand, basic DESs are widely used in applications such as acid gas chemical absorption,[11−14] cellulose and protein dissolution,[15,16] and base-catalyzed reactions.[17,18] To prepare such basic DESs, the basic HBAs carbonate salts,[19] amino-functionalized aminium and iminium halides,[12,15] and hetero-cyclic compounds,[14,16] as well as the basic HBDs Ur and its derivatives[14,15,17,20] and amine compounds,[11,13,18,21] are used. Reline (2Ur−ChCl) has weak basicity owing to Ur.[20] The basic DES composed of monoethanolamine monohydrochloride (MEA·HCl) and ethylenediamine (EDA) in the molar ratio $[EDA]/[MEA·HCl]$ = 4 can absorb up to 39 wt % CO_2 gas.[13] Fine-tuning the basicity of DESs is important for their applications; however, basic compounds typically dissolve in

Figure 1. Molecular structures of (a) choline chloride (ChCl), (b) urea (Ur), and (c) guanidine (Gu).

conventional DESs.[22] To the best of our knowledge, a strategy for fine-tuning the basicity of DESs has not yet been reported.

In this study, we used guanidine (Gu, T_m = 323 K[6]) to fine-tune the basicity of ChCl-based DESs. The structure of Gu is shown in Figure 1c. Gu has a diamino group (NH$_2$−C(=X)−NH$_2$) similar to that in Ur. The basicity of Gu is higher than that of Ur owing to the presence of the imino group (=NH) in the former. Moreover, the melting temperature of Gu is lower than that of Ur. We prepared binary 2Gu−ChCl and ternary Gu−Ur−ChCl DESs and acquired their differential scanning calorimetry (DSC) thermograms and nuclear magnetic resonance (NMR) spectra. Their basicities and chemical solubilities in CO$_2$ were investigated.

EXPERIMENTAL SECTION

Synthesis of Gu. A free base Gu was prepared from guanidinium chloride (GuHCl, >99%, Sigma-Aldrich) according to a previously reported method.[23] Briefly, metal Na (99%, Sigma-Aldrich) was added to ethanol (anhydrous, >99.5%, Fujifilm Wako Pure Chemical) and refluxed at 353 K, while N$_2$ gas was passed through it to afford sodium ethoxide. An equimolar amount of GuHCl was slowly added to the prepared sodium ethoxide solution and then left overnight to separate into solid and liquid phases. The supernatant liquid was decanted to an eggplant flask, the ethanol solvent was removed using a rotary evaporator for ~4 h, and the residue was vacuum-dried for ~48 h to obtain solid Gu. Residual Na$^+$ and Cl$^-$ in solid Gu were not detected with fluorescence X-ray spectrometry (Shimadzu, EDX-800HS2). The moisture content of Gu determined by Karl Fisher titration was 0.35 wt %, which corresponds to a molar ratio of [H$_2$O]/[Gu] = 0.012.

Anal. Calcd for C$_1$H$_5$N$_3$: C, 20.33; H, 8.53; N, 71.14. Found: C: 19.85; H: 8.53; N: 70.70.

Preparation of DESs with Gu. Ur (99%, Fujifilm Wako Pure Chemical) was dried at room temperature for ≥24 h under reduced pressure before use. ChCl (≥98.0%, Tokyo Kasei) was recrystallized twice with ethanol and dried at 310 K for ≥4 h under reduced pressure. To prevent contact with moisture, the DES components were mixed at the desired molar ratio in a glove box saturated with N$_2$ gas. Homogeneous liquids were obtained by stirring the solid mixtures at 313.2 K for ≥1 h. Photographs of the prepared binary 2Gu−ChCl and ternary Gu−Ur−ChCl DESs as well as reline (2Ur−ChCl) are shown in Figure 2.

DSC Thermogram Measurement. The thermal behaviors of the DESs and their raw materials were examined using DSC (Seiko Instruments, DSC-220CU). A few milligrams of each sample were sealed in an aluminum pan. The DSC thermograms were acquired at a heating/cooling rate of 5 K min^{-1} in the temperature range of 223−373 K. The baselines of the thermograms were corrected using OriginPro 2023 software (OriginLab).

NMR Spectra Measurement. The prepared DESs (~1 cm^3) were transferred into outer NMR tubes (Shigemi, PS-001-7) with an outer diameter of 5 mm, whereas the reference standards were transferred into inner NMR tubes (Shigemi, PN-001) with an outer diameter of 3 mm. The following reference standards were used: 0.75 wt % sodium 3-(trimethylsilyl)propionic-2,2,3,3-d_4 in D$_2$O (99.9 atom %-D, Sigma-Aldrich) for ^{1}H and ^{13}C NMR, neat CD$_3$NO$_2$ (99 atom %-D, Sigma-Aldrich) for ^{15}N NMR, and 0.10 mol dm^{-3} NaCl (Fujifilm Wako Pure Chemical, Guaranteed Reagent) in D$_2$O
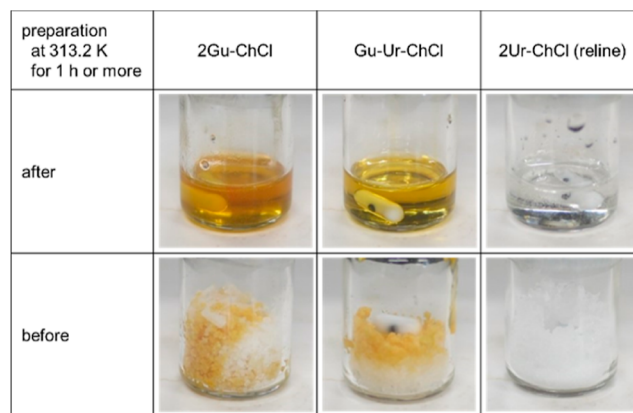

Figure 2. Photographs of the prepared binary 2Gu−ChCl and ternary Gu−Ur−ChCl DESs as well as reline (2Ur−ChCl).

(99.9 atom %-D, Sigma-Aldrich) for ^{35}Cl NMR. The double tubes were placed in an NMR spectrometer (Agilent, NMR 400 MHz system) for ≥30 min, and the ^{1}H, ^{13}C, ^{15}N, and ^{35}Cl NMR spectra were recorded at 313.2 K. The chemical shift data were corrected using the volumetric magnetic susceptibilities of the DESs determined by the external double-reference method.[24] Hexamethyldisiloxane (>99.5%, NMR grade, Sigma-Aldrich) was used as the external double-reference standard.

CO$_2$ Chemical Solubility Measurement. The DESs (2.0 cm^3) were transferred into test tubes using a micropipette (Gilson, Pipetman P-1000). The test tube was purged with N$_2$ gas for ≥30 min at a flow rate of 10 cm^3 min^{-1}. CO$_2$ absorption in DESs was conducted using high-purity CO$_2$ gas (>99.995%, Taiyo Nippon Sanso) at 313.2 ± 0.5 K and a flow rate of 10 cm^3 min^{-1}. The equilibrium mass (m_{abs}) of CO$_2$ absorbed in the DESs was determined by subtracting the mass (m_{gas}) owing to the replacement of N$_2$ with CO$_2$ in the gas phase in the test tube from the apparent increased mass (m_{app}): $m_{abs} = m_{app} − m_{gas}$.

RESULTS AND DISCUSSION

Figure 3 shows the DSC thermograms of 2Gu−ChCl, Gu−Ur−ChCl, reline, and their raw materials. Figure S1 shows the DSC thermograms of mixtures at different ([Gu]+[Ur])/[ChCl] ratios. Latent heat transfer of pure Ur in the measured temperature range is not likely because of its high melting temperature.[5,6] For pure ChCl, we observed a thermal change
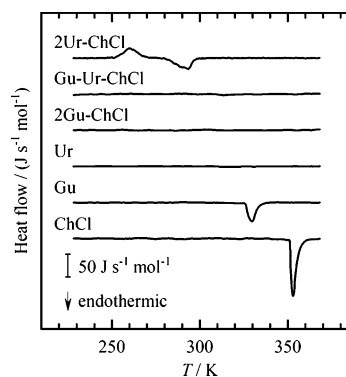

Figure 3. DSC thermograms of 2Gu−ChCl, Gu−Ur−ChCl, and reline and their raw materials.

at 351 K, which is consistent with previous reports of a solid−solid transition at 351−352 K.[25,26] The DSC thermogram of pure Gu shows an endothermic peak and a solid−liquid transition beginning at 325 K. Reline exhibited a transition from the supercooled state to a liquid state with increasing temperature, attributed to consecutive crystallization and melting, which is consistent with a previous report.[27] However, no latent heat transfer was observed for 2Gu−ChCl and Gu−Ur−ChCl in the temperature range of 223−373 K, suggesting that these DESs were maintained in the fluid state. This indicates that the substitution of Gu for Ur in reline lowered the melting temperatures of the resultant DESs. All Gu-containing mixtures exhibit high fluidity, and as shown in Figure S1, no thermal change is observed in the measured temperature range. Therefore, Gu is considered to be an excellent HBD candidate for DES formation.

Figures S2−S5 show the ^1H, ^{13}C, ^{15}N, and ^{35}Cl NMR spectra of DESs, respectively, measured using the external reference method.[24] The corrected ^1H, ^{13}C, and ^{15}N NMR chemical shifts (δ_{cor}) as a function of the [Gu]/([Gu]+[Ur]) molar ratio are shown in Figures S6−S8, respectively. The corrected ^{35}Cl NMR chemical shifts, shown in Figure 4, are
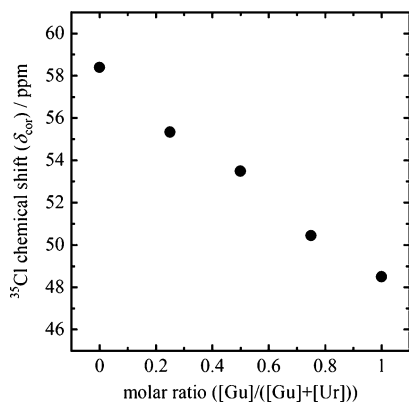

Figure 4. Corrected ^{35}Cl NMR chemical shifts in the prepared DESs as a function of the [Gu]/([Gu]+[Ur]) molar ratio.

larger than that of the external reference (0.10 mol dm^{-3} NaCl in D_2O). This suggests that the hydrogen-bonding of Cl$^-$ ions with Gu, Ur, and the hydroxy groups of ChCl in the DESs is weaker than that with D_2O molecules. The upfield shift of the ^{35}Cl peak suggests an increase in the electron density of Cl$^-$ owing to the substitution of Gu for Ur, which weakens the hydrogen-bonding of Cl$^-$ with the other moieties in the DESs. The Cl$^-$ ion in reline interacts with the amino groups of Ur and the hydroxy group of the (2-hydroxyethyl)-trimethylammonium (Ch$^+$) cation.[28,29] Therefore, as the Ur molecules are replaced by Gu molecules, the hydrogen-bonding of Gu with Ur and Ch$^+$ in the DES strengthens, thereby weakening the hydrogen-bonding of Cl$^-$ with the other moieties in the DES. This complex hydrogen-bonding also explains the lowered melting temperatures of the Gu-substituted binary and ternary DESs.

To evaluate the basicity of the prepared DESs, the CO$_2$ absorption capacity of the prepared DESs was measured at 313.2 K. Figure 5a shows the m_{app} of the DES solutions as a function of their exposure time (t) to CO$_2$. A comparison of five Gu-containing DESs with reline revealed that Gu plays a significant role in the chemical absorption of CO$_2$. Figure 5b shows the relationship between the molar ratios of [CO$_2$]/
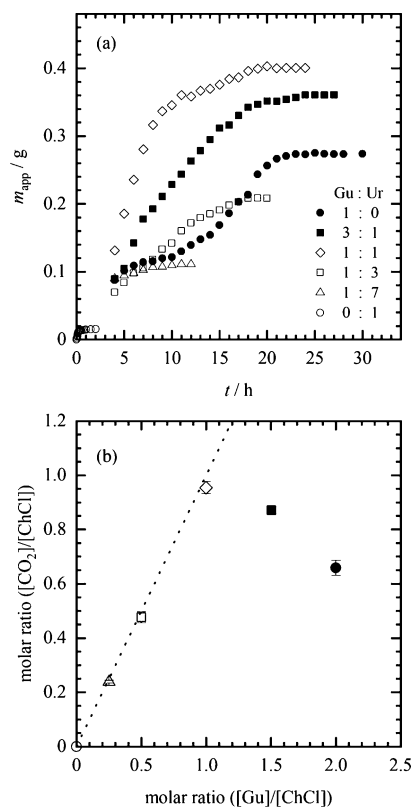

Figure 5. Relationship between (a) apparent increased mass (m_{app}) of the DES solutions and exposure time (t) to CO$_2$ and (b) molar ratios of [CO$_2$]/[ChCl] and [Gu]/[ChCl]. The molar ratio ([Gu]+[Ur])/[ChCl] was maintained constant at 2. The dotted line in (b) represents the stoichiometric ratio [CO$_2$]/[Gu] = 1.

[ChCl] and [Gu]/[ChCl] when CO$_2$ reaches dissolution equilibrium in the DESs; the dotted line represents the stoichiometric ratio [CO$_2$]/[Gu] = 1. The error bars in Figure 5b represent the deviation determined from three absorption experiments. The errors of [CO$_2$]/[Gu] are less than ±0.03. Table 1 summarizes the [CO$_2$]/[Gu] molar ratios, densities

Table 1. Experimental Densities (ρ), Gu Concentrations (C_{Gu}), and [CO$_2$]/[Gu] Molar Ratios of the Prepared DESs

Gu/Ur[a]	ρ/g cm^{-3}[b]	C_{Gu}/mol dm^{-3}	[CO$_2$]/[Gu]
1:0	1.1644 (0.0005)	9.03	0.33
3:1	1.1757 (0.0001)	6.83	0.58
1:1	1.1961 (0.0001)	4.62	0.95
1:3	1.2136 (0.0001)	2.34	0.95
1:7	1.2204 (0.0003)	1.18	0.95
0:1	1.2216 (0.0002)	0	

[a]The molar ratio ([Gu]+[Ur])/[ChCl] was maintained constant at 2. [b]The values of ρ were determined from three replicate measurements with a densimeter (DSA5000, Anton-Paar).

(ρ), and Gu concentrations (C_{Gu}) in the DESs before CO$_2$ absorption. The amount of CO$_2$ absorbed depended on C_{Gu}. Increasing C_{Gu} in ternary Gu−Ur−ChCl DES up to 4.62 mol dm^{-3} increases the amount of CO$_2$ absorbed while maintaining the molar ratio [CO$_2$]/[Gu] at ∼1; however, a further increase in C_{Gu} lowered the amount of CO$_2$ absorbed. The molar ratios of CO$_2$ absorbed to the superbase of 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) and 1,5-diazabicyclo[4.3.0]non-5-ene in reline have been reported to be more than ∼1.[22] The

maximum mass ratio of CO_2 to the prepared DESs was 16 wt % for Gu−Ur−ChCl. These values are less than those previously reported for the DESs. For example, a CO_2 mass ratio of 39 wt % has been achieved for 4EDA-MEA·HCl, which, to the best of our knowledge, is the highest chemical solubility of CO_2 among pure DESs.[13] One of the possible causes of the lower mass ratio of CO_2 to DESs is the lower C_{Gu}. The estimated ρ of 4EDA-MEA·HCl is ~1 g cm^{-3},[30] which implies that the EDA molarity is more than 12 mol dm^{-3}.

Figure 6 shows the ^{13}C NMR spectra of Gu−Ur−ChCl DES at [Gu]/[Ur] = 1 before and after CO_2 absorption. Figure S10
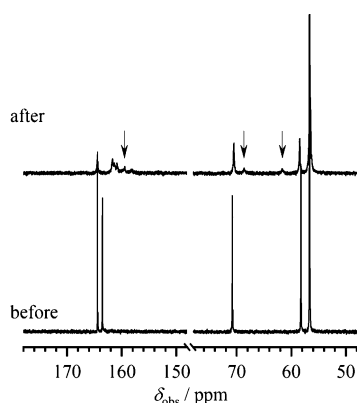

Figure 6. ^{13}C NMR spectra of the Gu−Ur−ChCl DES before and after CO_2 absorption.

shows the ^{13}C NMR spectra of the Gu−Ur−ChCl DES with [Gu]/[Ur] = 1/7, Gu, and DBU in (2-hydroxyethyl)-trimethylammonium bis(trifluoromethylsulfonyl)amide (ChTf$_2$N) APIL, and DBU in 1-butanol (1BuOH) before and after CO_2 absorption. DBU and alcohol react with CO_2 to form a pair of a protonated DBU cation and a carbonate anion, which is termed a "switchable solvent".[31] In the spectrum of DBU-1BuOH after CO_2 absorption, the δ_{obs} ^{13}C peak at 161 ppm is attributed to the carbonate group ($-OCO_2^-$) formed from CO_2 and alcohol. Similar carbonate products form in the ChTf$_2$N APIL solutions containing DBU or Gu. In the spectrum of the ChTf$_2$N solution after CO_2 absorption, the δ_{obs} at 159 ppm is attributed to the carbonate group of 2-(trimethylammonio)ethyl carbonate (N(CH$_3$)$_3$−CH$_2$−CH$_2$−OCO$_2^-$, Ch$^+$CO$_2^-$) formed from CO_2 and Ch$^+$. The upfield δ_{obs} peaks at 61 and 68 ppm, indicated by the arrows in Figure S10, are attributed to the ethylene group ($-CH_2CH_2-$) of Ch$^+$CO$_2^-$. The three δ_{obs} peaks at 61, 68, and 159 ppm in the spectrum of Gu−Ur−ChCl DES (Figure 6) are attributed to Ch$^+$CO$_2^-$ formed from the reaction of CO_2 with Gu and Ch$^+$ as follows: Gu + Ch$^+$ + CO$_2$ → GuH$^+$ + Ch$^+$CO$_2^-$. This reaction is confirmed by δ_{obs} = 161 ppm observed in the spectra of Gu−Ur−ChCl DESs and Gu-ChTf$_2$N solution (Figures 6 and S10, respectively). However, the products for the Gu−Ur−ChCl DES and Gu−ChTf$_2$N APIL solutions are different; GuH$^+$ and Ch$^+$CO$_2^-$ are the products for the Gu−ChTf$_2$N APIL solution, whereas GuH$^+$, Ch$^+$CO$_2^-$, and an unknown compound with a peak at δ_{obs} = 162 ppm are the products for the Gu−Ur−ChCl DES. This indicates that reaction mechanisms other than carbonate formation occurred in the Gu−Ur−ChCl DES. In addition, the CO_2 absorption mechanism is different in the Gu−Ur−ChCl DES and Gu−ChTf$_2$N APIL solutions owing to the presence of Ur and Cl$^-$

in the former and Tf$_2$N$^-$ in the latter. These reaction mechanisms are yet to be determined.

CONCLUSIONS

In this study, we fine-tuned the basicity of binary and ternary Gu-containing DESs. The DESs were prepared from Gu, Ur, and ChCl using a simple, previously reported method. The Gu-containing DESs exhibited lower melting temperatures than that of reline. In addition, these prepared DESs were liquids at 223−373 K and can chemically absorb CO_2 gas. The amount of CO_2 absorbed increased with increasing C_{Gu} up to 4.62 mol dm^{-3}, following which it decreased. The DES comprising an equimolar mixture of Gu and Ur (Gu−Ur−ChCl) demonstrated the optimal mixing ratio in CO_2 absorption. This suggests that the basicity of DESs can be fine-tuned by substituting a non-functional molecule with an analogous functional molecule. We believe that this strategy can be applied to the preparation of DESs in which not only basicity but also other physicochemical properties, for example, eutectic temperature and viscosity, can be fine-tuned.

ASSOCIATED CONTENT

⬡ **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c00706.

> DSC thermograms of mixtures with different ([Gu]+[Ur])/[ChCl] ratios; ^{1}H, ^{13}C, ^{15}N, and ^{35}Cl NMR spectra of DESs with different molar ratios; ^{1}H, ^{13}C, and ^{15}N NMR chemical shifts (δ_{cor}) as a function of molar ratios; relationship between the apparent increased mass (m_{app}) of the Gu-Ur-ChCl solutions and exposure time (t) to humidified CO_2; and ^{13}C NMR spectra of the DBU-1BuOH, DBU-ChTf$_2$N, Gu-ChTf$_2$N, and Gu-Ur-ChCl solutions before and after CO_2 absorption (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Smith, E. L.; Abbott, A. P.; Ryder, K. S. Deep Eutectic Solvents (DESs) and Their Applications. *Chem. Rev.* **2014**, *114*, 11060−11082.

(2) Hansen, B. B.; Spittle, S.; Chen, B.; Poe, D.; Zhang, Y.; Klein, J. M.; Horton, A.; Adhikari, L.; Zelovich, T.; Doherty, B. W.; Gurkan, B.; Maginn, E. J.; Ragauskas, A.; Dadmun, M.; Zawodzinski, T. A.; Baker, G. A.; Tuckerman, M. E.; Savinell, R. F.; Sangoro, J. R. Deep Eutectic Solvents: A Review of Fundamentals and Applications. *Chem. Rev.* **2021**, *121*, 1232−1285.

(3) Yu, D.; Xue, Z.; Mu, T. Eutectics: Formation, Properties, and Applications. *Chem. Soc. Rev.* **2021**, *50*, 8596−8638.

(4) Ramón, D. J., Guillena, G., Eds. In *Deep Eutectic Solvents, Synthesis, Properties, and Applications*; Wiley-VCH: Weinheim, Germany, 2020.

(5) Abbott, A. P.; Capper, G.; Davies, D. L.; Rasheed, R. K.; Tambyrajah, V. Novel Solvent Properties of Choline Chloride/Urea Mixtures. *Chem. Commun.* **2003**, 70−71.

(6) *CRC Handbook of Chemistry and Physics*, 86th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 2005.

(7) Qin, H.; Hu, X.; Wang, J.; Cheng, H.; Chen, L.; Qi, Z. Overview of Acidic Deep Eutectic Solvents on Synthesis, Properties and Applications. *Green Energy Environ* **2020**, *5*, 8−21.

(8) Delbecq, F.; Khodadadi, M. R.; Rodriguez Padron, D.; Varma, R.; Len, C. Isosorbide: Recent Advances in Catalytic Production. *Mol. Catal.* **2020**, *482*, 110648.

(9) Chen, Z.; Wang, Y.; Cheng, H.; Zhou, H. Hemicellulose Degradation: An Overlooked Issue in Acidic Deep Eutectic Solvents Pretreatment of Lignocellulosic Biomass. *Ind. Crop. Prod.* **2022**, *187*, 115335.

(10) Zhou, F.; Shi, R.; Wang, Y.; Xue, Z.; Zhang, B.; Mu, T. Acidity Scales of Deep Eutectic Solvents based on IR and NMR. *Phys. Chem. Chem. Phys.* **2022**, *24*, 16973−16978.

(11) Trivedi, T. J.; Lee, J. H.; Lee, H. J.; Jeong, Y. K.; Choi, J. W. Deep Eutectic Solvents as Attractive Media for CO_2 Capture. *Green Chem.* **2016**, *18*, 2834−2842.

(12) Zhang, K.; Hou, Y.; Wang, Y.; Wang, K.; Ren, S.; Wu, W. Efficient and Reversible Absorption of CO_2 by Functional Deep Eutectic Solvents. *Energy Fuels* **2018**, *32*, 7727−7733.

(13) Shukla, S. K.; Mikkola, J.-P. Intermolecular Interactions upon Carbon Dioxide Capture in Deep-Eutectic Solvents. *Phys. Chem. Chem. Phys.* **2018**, *20*, 24591−24601.

(14) Jiang, B.; Ma, J.; Yang, N.; Huang, Z.; Zhang, N.; Tantai, X.; Sun, Y.; Zhang, L. Superbase/Acylamido-Based Deep Eutectic Solvents for Multiple-Site Efficient CO_2 Absorption. *Energy Fuels* **2019**, *33*, 7569−7577.

(15) Parnica, J.; Antalik, M. Urea and Guanidine Salts as Novel Components for Deep Eutectic Solvents. *J. Mol. Liq.* **2014**, *197*, 23−26.

(16) Fu, H.; Wang, X.; Sang, H.; Hou, Y.; Chen, X.; Feng, X. Dissolution Behavior of Microcrystalline Cellulose in DBU-based Deep Eutectic Solvents: Insights from Spectroscopic Investigation and Quantum Chemical Calculations. *J. Mol. Liq.* **2020**, *299*, 112140.

(17) Zhu, A.; Jiang, T.; Han, B.; Zhang, J.; Xie, Y.; Ma, X. Supported Choline Chloride/Urea as a Heterogeneous Catalyst for Chemical Fixation of Carbon Dioxide to Cyclic Carbonates. *Green Chem.* **2007**, *38*, 169−172.

(18) Yang, X.; Zou, Q.; Zhao, T.; Chen, P.; Liu, Z.; Liu, F.; Lin, Q. Deep Eutectic Solvents as Efficient Catalysts for Fixation of CO_2 to Cyclic Carbonates at Ambient Temperature and Pressure through Synergetic Catalysis. *ACS Sustainable Chem. Eng.* **2021**, *9*, 10437−10443.

(19) Naser, J.; Mjalli, F.; Jibril, B.; Al-Hatmi, S.; Gano, Z. Potassium Carbonate as a Salt for Deep Eutectic Solvents. *Int. J. Chem. Eng. Appl.* **2013**, *4*, 114−118.

(20) Mjalli, F. S.; Ahmed, O. U. Characteristics and Intermolecular Interaction of Eutectic Binary Mixtures: Reline and Glyceline. *Korean J. Chem. Eng.* **2016**, *33*, 337−343.

(21) Bahadori, L.; Chakrabarti, M. H.; Mjalli, F. S.; AlNashef, I. M.; Manan, N. S. A.; Hashim, M. A. Physicochemical Properties of Ammonium-based Deep Eutectic Solvents and Their Electrochemical Evaluation using Organometallic Reference Redox Systems. *Electrochim. Acta* **2013**, *113*, 205−211.

(22) Pandey, B. A.; Pandey, A.; Pandey, S. Superbase-Added Choline Chloride-Based Deep Eutectic Solvents for CO_2 Capture and Sequestration. *ChemistrySelect* **2017**, *2*, 11422−11430.

(23) Yamada, T.; Liu, X.; Englert, U.; Yamane, H.; Dronskowski, R. Solid-State Structure of Free Base Guanidine Achieved at Last. *Chem.—Eur. J.* **2009**, *15*, 5651−5655.

(24) Mizuno, K.; Tamiya, Y.; Mekata, M. External Double Reference Method to Study Concentration and Temperature Dependences of Chemical Shifts Determined on a Unified Scale. *Pure Appl. Chem.* **2004**, *76*, 105−114.

(25) Petrouleas, V.; Lemmon, R. M. Calorimetric Studies of Choline Chloride, Bromide, and Iodide. *J. Chem. Phys.* **1978**, *69*, 1315−1316.

(26) Lobo Ferreira, A. I. M. C.; Vilas-Boas, S. M.; Silva, R. M. A.; Martins, M. A. R.; Abranches, D. O.; Soares-Santos, P. C. R.; Almeida Paz, F. A.; Ferreira, O.; Pinho, S. P.; Santos, L. M. N. B. F.; Coutinho, J. A. P. Extensive Characterization of Choline Chloride and Its Solid-Liquid Equilibrium with Water. *Phys. Chem. Chem. Phys.* **2022**, *24*, 14886−14897.

(27) Azmi, S.; Koudahi, M. F.; Frackowiak, E. Reline Deep Eutectic Solvent as a Green Electrolyte for Electrochemical Energy Storage Applications. *Energy Environ. Sci.* **2022**, *15*, 1156−1171.

(28) Hammond, O. S.; Bowron, D. T.; Edler, K. J. Liquid Structure of the Choline Chloride-Urea Deep Eutectic Solvent (Reline) from Neutron Diffraction and Atomistic Modelling. *Green Chem.* **2016**, *18*, 2736−2744.

(29) Ashworth, C. R.; Matthews, R. P.; Welton, T.; Hunt, P. A. Doubly Ionic Hydrogen Bond Interactions Within the Choline Chloride-Urea Deep Eutectic Solvent. *Phys. Chem. Chem. Phys.* **2016**, *18*, 18145−18160.

(30) Pishro, K. A.; Murshid, G.; Mjalli, F. S.; Naser, J. Investigation of CO_2 Solubility in Monoethanolamine Hydrochloride Based Deep Eutectic Solvents and Physical Properties Measurements. *Chin. J. Chem. Eng.* **2020**, *28*, 2848−2856.

(31) Jessop, P. G.; Heldebrant, D. J.; Li, X.; Eckert, C. A.; Liotta, C. L. Reversible Nonpolar-to-polar Solvent. *Nature* **2005**, *436*, 1102.