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COSMO-RS Exploration of Highly CO₂-Selective Hydrogen-Bonded Binary Liquid Absorbents under Humid Conditions: Role of Trace Ionic Species

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ABSTRACT: It is critical to improve carbon capture efficiency while reducing costs to popularize carbon capture and storage. Considering the green chemistry and engineering objectives, this study theoretically explores the CO_2 absorption capacity of 1,533,528 hydrogen-bonded mixtures, i.e., deep eutectic solvents in a broad sense. Exhaustive statistical thermodynamic calculations well explain the experimental reports; it is confirmed that deep eutectic solvents containing ionic compounds have higher CO_2 selective absorption capacity than those composed of non-ionic species. Quantitative evaluation of hydrogen-bonding interaction also predicts that the capacity is higher when the ionic compounds work as hydrogen-bonding donors. This is because the trace ionic species weaken the hydrogen-bonding network in the mixtures to improve CO_2 physisorption.



1. INTRODUCTION

To achieve the targets set in the Paris Agreement, global CO_2 emissions must be reduced by 7.6% annually over the next decade.¹ This requires the effective use of carbon capture and storage (CCS) technologies. However, one of the barriers to the use of such systems is their absorption phase.² The cost of carbon capture is primarily influenced by the energy required for solvent regeneration, which is directly related to CO_2 -solvent interactions and the separation efficiency from CH_4 , CO, N_2 , H_2 , and other gases.^{2–5} Improving the efficiency lowers the carbon capture cost, facilitating the use of CCS technologies.

With this background, the development of efficient and sustainable CO2-absorbing liquids has received immense attention in chemical engineering and related fields;⁶⁻⁸ in this regard, room-temperature molten salts (ionic liquids; ILs) have been extensively studied.^{3,7-13} The physicochemical properties of ILs, such as viscosity, electrical conductivity, and CO_2 absorption capacity, can be tuned by combining various cations and anions.^{14,15} The problem with implementing IL absorbents in CCS technologies is their cost. Deep eutectic solvents (DESs) are a new category of solvents with characteristics similar to those of ILs. They are obtained as mixtures of hydrogen-bonding donors and acceptors (HBDs and HBAs),¹⁶⁻¹⁸ are suitable for reducing production costs, and impose fewer adverse environmental effects. Exploring the physicochemical properties of DESs corresponds with green chemistry and engineering objectives.¹⁹⁻²⁶ However, controlling physicochemical properties is less straightforward in DESs than in ILs, as it is impossible to predict the role of molecules (i.e., whether the molecule works as an HBA or HBD) in hydrogen-bonded mixtures solely from their chemical structures.

This study explores highly CO₂-selective hydrogen-bonded binary liquid absorbents by using the conductor-like screening model for realistic solvation (COSMO-RS) based on the ab initio statistical thermodynamics theory.^{27–29} The method has been widely used to evaluate thermodynamic properties of functional solutions, including DESs.^{9,10,22,30–32} Exhaustive COSMO-RS calculations are performed for 1,533,528 candidate mixtures composed of hydrogen-bonded species with various concentrations to screen their CO₂ absorption capacities.

2. THEORY

The COSMO-RS method evaluates intermolecular interactions in solutions based on the surface charge distribution of each molecule obtained from quantum chemical calculations.^{27–29} The total intermolecular interactions are described by the surface charge densities σ and σ' of the mutual contact area of all molecules in a solution, where $E_{\rm MF}$, $E_{\rm HB}$, and $E_{\rm vdW}$ are the misfit, hydrogen-bonding, and van der Waals interaction energies, respectively.

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$$E(\sigma, \sigma') = \frac{E_{\rm MF}(\sigma, \sigma') + E_{\rm HB}(\sigma, \sigma') + E_{\rm vdW}(\sigma, \sigma')}{a_{\rm eff}}$$
(1)

The misfit electrostatic interaction energy, i.e., residual nonsteric interaction energy, per unit area formed by contacting surface charge densities is represented using the effective contact area between the two surface segments $a_{\rm eff}$ and adjustable parameter α' .

$$E_{\rm MF}(\sigma, \sigma') = a_{\rm eff} \frac{\alpha'}{2} (\sigma + \sigma')^2$$
⁽²⁾

If σ equals $-\sigma'$, the misfit energy will vanish. When one molecule has strong positive surface charge densities and the other has strong negative ones, a hydrogen-bonding interaction is formed.

$$E_{\rm HB}(\sigma, \sigma') = a_{\rm eff} c_{\rm HB} \min\{0; \min(0; \sigma_{\rm don} + \sigma_{\rm HB}) \\ \max(0; \sigma_{\rm acc} - \sigma_{\rm HB})\}$$
(3)

Both $c_{\rm HB}$ and $\sigma_{\rm HB}$ are variable parameters. The van der Waals interaction energy is defined to depend only on the atom type that is involved in contact.

$$E_{\rm vdW}(\sigma, \sigma') = a_{\rm eff}(\tau_{\rm vdW} + \tau'_{\rm vdW}) \tag{4}$$

Here, $au_{\rm vdW}$ and $au'_{\rm vdW}$ are element-specific variable parameters.

The chemical potential of solute s, μ_s (σ -potential), is expressed by the following equation using normalized distribution function $p_s(\sigma')$ (σ -profile), gas constant *R*, and temperature *T*.

$$\mu_{s}(\sigma) = -\frac{RT}{a_{\text{eff}}} \ln \left[\int p_{s}(\sigma') \exp\left\{ \frac{a_{\text{eff}}}{RT} (\mu_{s}(\sigma') - E(\sigma, \sigma')) \right\} \right] d\sigma' \right]$$
(5)

Then, the activity coefficient is defined by

$$\gamma_{\rm s} = \exp\!\left(\frac{\mu_{\rm s} - \mu_{\rm s}^0}{RT}\right) \tag{6}$$

where, μ_s^0 is the chemical potential in the standard state. Finally, using the infinite dilution activity coefficient γ_s^{∞} and saturated vapor pressure P_s^0 , the infinite dilution solubility (Henry's law constant: H_s) can be derived as follows.

$$H_{\rm s} = \gamma_{\rm s}^{\infty} P_{\rm s}^0 \tag{7}$$

In the COSMO-RS theory, the likelihood of hydrogenbonding interactions (hydrogen-bonding moments; $M_{\rm HBD/HBA}$) can be evaluated by integrating σ -profile $p_{\rm s}(\sigma)$.³³

$$M_{\text{HBD}/\text{HBA}} = \int p_{\text{s}}(\sigma) f(\sigma) d\sigma$$

with $f(\sigma) = \begin{cases} 0 & (-1.2 \le \sigma \le 1.2) \\ |\sigma \pm 1.2|(\sigma < -1.2, 1.2 < \sigma) \end{cases}$ (8)

The A to B molecular contact probabilities (P_{AB}) in the mixtures can be also evaluated using the following formula.

$$P_{AB} = \frac{x_{B} \sum_{i \in A} \sum_{j \in B} A_{i} A_{j} \gamma_{i} \gamma_{j} \exp\left(-\frac{E_{ij}}{kT}\right)}{A_{A,\text{total}} A_{\text{total}}}$$
(9)

where $\{A_i, A_{A,\text{total}}, A_{\text{total}}\}\$ are the surface areas of segment *i*, molecule A, and all the molecules in the mixture, respectively. γ_i and E_{ij} are the activity coefficients of segment *i* and interaction energy between the segments $\{i, j\}$, respectively. x_B is the mole fraction of molecule B.

3. COMPUTATIONAL METHODS

Binary mixtures comprising small 653 hydrogen-bonded species (MW < 200; listed in Table S1) were theoretically investigated thoroughly. 292 of the 653 molecules are solid, whereas the others are liquid under ambient conditions (20 °C). First, the stable conformations and surface charge densities of all species were calculated using quantum chemical calculations at the BP-D/TZVP level, which has been successfully applied to various functional liquids.^{22,30–32,34–38} Subsequently, $M_{\rm HBD/HBA}$ were calculated by eq 8. Here, the relative HBD/HBA nature strength (i.e., role of each molecule) in the hydrogen-bonded mixture was quantitatively evaluated by

$$\theta = \tan^{-1} \left(\frac{M_{\rm HBD}}{M_{\rm HBA}} \right) \tag{10}$$

where $\theta_A > \theta_B$ indicates that molecules A and B act as a relative HBD and HBA, respectively, in the mixture.

In this study, we considered 105,412 (= $_{292}C_1 \times _{361}C_1$) and 64,980 (= $_{361}C_2$) solid-liquid and liquid-liquid mixtures. Using the COSMO-RS method, Henry's law constants of the mixtures were evaluated for CO2, CH4, CO, N2, and H2 at 298.15 K. In the evaluation, the mole fractions x for the binary mixtures were varied from 0.0 to 1.0 in increments of 0.1. In other words, 1,533,528 (= $170,392 \times 9$) mixtures and the corresponding pure compounds were fully considered. The x values (i.e., which of the given two molecules is considered as the first or second components) were defined to satisfy H'_{00} < $H'_{1,0}$ using Henry's law constants of CO₂ absorption under a dry condition (H'_x) . Henry's law constants under humid conditions H_r (ternary mixtures with 2 wt % water) were also evaluated for practical applications.²⁴ TURBOMOLE7.0³⁹ and COSMOtherm (BP_TZVPD_FINE_21. ctd)⁴⁰ were used for quantum chemical and statistical thermodynamic calculations. Using the ratio of the Henry's law constants, the CO₂ selectivity relative to those of the other gases (CH_4 , CO, N_2 , and H₂) was evaluated.⁴¹

$$S_{\rm CO2/gas} = \frac{H_{\rm gas}}{H_{\rm CO2}} \tag{11}$$

For mixtures predicted to have improved CO_2 absorption properties even under humid conditions, the geometries and electronic structures related to hydrogen-bonding properties were investigated. Fingerprints (MACCS keys)^{42,43} based on SMILES^{44,45} were used for the geometry-based investigation. Using the MACCS keys, the presence of 166 substructures was evaluated based on binary bits. The structural similarity of the target molecules was verified numerically by comparing the keys. For the electronic-structure-based investigation, the excess contact probabilities (ΔP_{AB}) were used. ΔP_{AB} is the difference between the real contact probabilities (P_{AB}) and ideal ones, i.e., mole fraction of B (x_B). In this analysis, the CO₂ mole fraction was set as 0.1.

$$\Delta P_{\rm AB} = P_{\rm AB} - x_{\rm B} \tag{12}$$



Figure 1. Screening scheme applied. (a) Narrowing process of the hydrogen-bonded mixtures. The possibilities for higher CO₂ capacity upon mixing under dry conditions were considered (17,681/135,433: lower triangle). (b) CO₂/CH₄ selectivity versus the inverse Henry's law constant of CO₂ under dry conditions for the 17,681 mixtures. (c) CO₂/CH₄ selectivity versus the inverse Henry's law constant of CO₂ under humid conditions (with 2 wt % of water) for the 438 mixtures. Light-red and blue plots are for the cases where $\theta_{ion} < \theta_{mol}$ and $\theta_{ion} > \theta_{mol}$ in mixtures containing ionic species (\blacktriangle : choline acetate, +: betaine hydrochloride, $\textcircled{\bullet}$: choline chloride). The gray plots are for mixtures not containing ions.



Figure 2. Average bits and difference heatmap of the critical 60 MACCS keys (see Table S3) for the organic molecules composing the Class I and II mixtures (light-red and blue, respectively). The color shades of the difference heatmap give the relative importance of molecular information for each Class of mixtures.

4. RESULTS AND DISCUSSION

4.1. Screening of Hydrogen-Bonded Mixtures. The screening process applied in this study is summarized in Figure 1. First, the candidates were narrowed by hydrogen-bonding stabilization $[E_{HB}(\sigma,\sigma') < 0]$ upon mixing (135,433/1,533,528: Figure 1a). They were further refined with the improvements in CO₂ absorption capacity (17,681/135,433: lower triangle of Figure 1a). Considering the CO₂/CH₄ selectivity, it was clarified that mixtures including ionic species (choline acetate,

betaine hydrochloride, and choline chloride; ChCl) would be more effective than those composed of non-ionic species (Figure 1b). These data are consistent with the experimental results.^{19–21} Practically, a small amount of water is often added to reduce the viscosity of DESs; however, the effect of water addition on CO₂ absorption capacity is not clear.^{24,46,47} Among the narrowed 17,681 mixtures, 438 were predicted to maintain satisfactory CO₂ absorption capacities even under humid conditions (Figure 1c). Further analyzing the role of ionic species, it was found that more effective absorbents would be obtained when ionic species act as an HBD (blue in Figure 1c). The selectivity from CO, N_2 , and H_2 was also evaluated (Figure S1).

4.2. Chemical Structure Analysis. Hereafter, a set of 48 ChCl-based mixtures was analyzed, which was predicted to have improved CO_2 absorption capacities. The mixtures where ChCl acts as an HBA/HBD are listed in Table S2 as Class I/II, respectively.

First, geometric differences between organic molecules (non-ChCl components of Class I and II mixtures) were investigated by MACCS keys. The average bits (values from 0 to 1) of the critical 60 keys and class differences are represented as heatmaps (Figure 2 and Table S3). From the heatmap, a mixture design guideline for higher CO_2 absorption was obtained (Table 1). Four Class II HBA molecules

Table 1. Important Chemical Structures in the MACCS Keys' Difference Analysis (Figure 2)

key	description		
85	CN(C)C	N attached to $\geq 3 \text{ C}$	
100	ACH2N	N attached to a CH ₂	
111	NACH2A	N separated from a CH ₂ by two bonds	
122	AN(A)A	N attached to ≥3 A	
148	AQ(A)A	non-C attached to ≥3 A	
158	C-N	N in C–N single bonds	
161	Ν	nitrogen atoms	

[(diisopropylamino)ethanol, 3-(dimethylamino)-1-propanol, 1-piperidineethanol, and *N*,*N*-dimethylaminoethanol] are tertiary amines with the OH group linked by $-(CH_2)_n - (n \ge 2)$, whereas 44 Class I HBD molecules did not have this structure. It was clarified that the CO₂ selective absorption capacities were properly controlled by the formation of intramolecular hydrogen-bonding interactions in organic molecules.

Further details for Class I also showed that CO_2 absorption capacities worsen when the HBD is a diol or amino alcohol. This is because the presence of OH/NH₂ groups strengthens the intermolecular hydrogen-bonding interactions $E_{\rm HB}(\sigma,\sigma')$ in the systems (Table S2). It can be considered that hydrogenbonding overstabilization is a factor in reducing the physisorption space.

4.3. Intermolecular Interaction Analysis. Next, the CO_2 -solvent interaction energies in water-containing mixtures were evaluated by eq 1. Figure 3a clearly shows that the more the interaction energy is stabilized, the easier the CO_2 absorption process is. Figure 3b also illustrates that the excess contact probabilities of CO_2 to ChCl were negatively proportional to the inverse Henry's law constant of CO_2 , whereas those to organic molecules were positively proportional. It can be concluded that CO_2 prefers to form van der Waals interactions with organic molecules in the systems. For CO_2 physisorption, the quadrupole of CO_2 needs to fit well with the voids in the mixture. These results were physicochemically consistent.

Finally, the σ -potentials for two classes of mixtures under humid conditions were investigated (Figure 4). Here, the smaller absolute values of σ , at which the σ -potential becomes negative in the HBD/HBA region, mean that the corresponding capacities within the mixture are more prominent; the symmetrical M-shaped potentials show the existence of strong



Figure 3. Correlation for the inverse Henry's law constants under humid conditions with (a) CO_2 -solvent interaction energies and (b) excess contact probability of CO_2 to ChCl (filled squares) and organic molecules (open squares). Light-red and blue plots are for the Class I and II mixtures, respectively.



Figure 4. σ -Potentials for ChCl-based 48 mixtures under humid conditions (light-red: Class I and blue: Class II).

(well-balanced) hydrogen-bonding networks in the systems. From Figure 4, it can be confirmed that all 48 mixtures have hydrogen-bonding networks. However, the strength in the Class II mixtures is weaker than that in Class I. As mentioned above, the intramolecular hydrogen-bonding interaction is formed in organic molecules belonging to Class II mixtures. It can be considered that the intramolecular interactions affect the hydrogen-bonding network in the solutions, resulting in electronic state differences between the two classes of solvents.

Generally, the physisorption of CO_2 requires both enthalpic and entropic gains because of the strengthened CO_2 -solvent interaction and increased free volume in the absorbent.⁴⁸ This study suggests that Class II obtained both gains; when ChCl acted as a relative HBD, the intermolecular hydrogen-bonding interaction weakened, and the CO_2 -solvent van der Waals interaction was stabilized. It could be concluded that the two classes of mixtures have different gas absorption mechanisms.

5. CONCLUSIONS

This study comprehensively evaluated the physicochemical properties of 1,533,528 hydrogen-bonded solvents using the COSMO-RS method. The calculation results explained

previous experimental reports, i.e., DESs containing trace ions have higher CO_2 -selective absorption capacities than those composed of non-ionic species. To examine the role of each molecule, we proposed to determine the relative HBD/HBA nature strength based on quantum chemical calculations. Surprisingly, it was predicted that ionic-based mixtures exhibit higher CO_2 absorption capacity and selectivity when ions act as HBDs than as HBAs. In the former case, hydrogen-bonding interactions within organic molecules weaken intermolecular interactions. It was considered that the mixtures with HBD ions obtain both enthalpic and entropic gains. Further investigation of the solution dynamics using quantumchemistry-based molecular dynamics is currently underway.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c08250.

Chemical space; CO₂ selectivity from CO, N₂, and H₂; 48 ChCl-based mixtures screened by COSMO-RS; and description of MACCS keys (PDF)

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Author Contributions

N.K. and H.M. conceived the project. N.K. generated the molecular library. S.W. performed thermodynamic calculations with guidance from H.M. The manuscript was written through contributions from all authors. All authors have approved the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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