Screening Deep Eutectic Solvents for CO₂ Capture With COSMO-RS

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In this work, 502 experimental data for CO₂ solubilities and 132 for Henry’s constants of CO₂ in DESs were comprehensively summarized from literatures and used for further verification and development of COSMO-RS. Large systematic deviations of 62.2, 59.6, 63.0, and 59.1% for the logarithmic CO₂ solubilities in the DESs (1:2, 1:3, 1:4, 1:5), respectively, were observed for the prediction with the original COSMO-RS, while the predicted Henry’s constants of CO₂ in the DESs (1:1.5, 1:2, 1:3, 1:4, 1:5) at temperatures ranging of 293.15–333.15 K are more accurate than the predicted CO₂ solubility with the original COSMO-RS. To improve the performance of COSMO-RS, 502 data points of CO₂ solubility in the DESs (1:2, 1:3, 1:4, 1:5) were used for correcting COSMO-RS with a temperature-pressure dependent parameter, and the CO₂ solubility in the DES (1:6) was predicted to further verify the performance of the corrected model. The results indicate that the corrected COSMO-RS can significantly improve the model performance with the ARDs decreasing down to 6.5, 4.8, 6.5, and 4.5% for the DESs (1:2, 1:3, 1:4, and 1:5), respectively, and the corrected COSMO-RS with the universal parameters can be used to predict the CO₂ solubility in DESs with different mole ratios, for example, for the DES (1:6), the corrected COSMO-RS significantly improves the prediction with an ARD of 10.3% that is much lower than 78.2% provided by the original COSMO-RS. Additionally, the result from COSMO-RS shows that the σ-profiles can reflect the strength of molecular interactions between an HBA (or HBD) and CO₂, determining the CO₂ solubility, and the dominant interactions for CO₂ capture in DESs are the H-bond and Van der Waals force, followed by the misfit based on the analysis of the predicted excess enthalpies.

Keywords: deep eutectic solvents, CO₂ capture, COSMO-RS, CO₂ solubility, Henry’s constant

INTRODUCTION

With the rapid development of industry, the demand for energy is growing. Fossil fuels currently account for the majority of energy supply (Rahmanifard and Plaksina, 2019). The use of fossil fuels poses a range of environmental problems. For example, the use of fossil fuels emits a large amount of carbon dioxide (CO₂) (Hanif et al., 2019; Hosseini et al., 2019). This, in turn, leads to the serious greenhouse-gas effect. It was reported that the global CO₂ emissions reached an all-time high of 33.143 billion tons in 2018 by the International Energy Agency (IEA) (Qu, 2018). This calls for CO₂ capture.
There are several technologies for CO₂ capture, for example, physical, or chemical solvent scrubbing (Abdeen et al., 2016) and pressure swing adsorption (Riboldi and Bolland, 2016). Because of the complexity of the gas components, most technologies still suffer from high energy demand, high cost, and serious secondary pollutions. Developing new capture technologies, including new solvents and novel processes, is the key point to CO₂ capture.

Recently, ionic liquids (ILs) have been proposed as potential candidates for CO₂ capture due to their unique properties. However, the conventional ILs are expensive mainly due to the complex synthesis process. The newly emerged DESs possess analogous properties to ILs and share many common properties with ILs, whereas DESs have additional merits of low cost, biodegradability, low toxicity, easy preparation, and no purification requirement (Sarmad et al., 2017a). The most fascinating property of DESs is the structural diversity, and it can be prepared by mixing a hydrogen bond donor (HBD) with a hydrogen bond acceptor (HBA) in appropriate mole ratios (Hayyan et al., 2013).

To develop DESs for CO₂ capture, the CO₂ absorption capacity (i.e., CO₂ solubility) in DESs is one of the important properties. It is reported that the CO₂ solubility in DESs depends on pressure, temperature, and the mole ratio of HBD to HBA, and it increases with increasing pressure and decreasing temperature (Sarmad et al., 2017a). Based on the studies of Kamps et al. (2003) and Aki et al. (2004), it was found that the CO₂ solubilities in DESs were comparable with the imidazolium-based ILs. Leron and Li measured the CO₂ solubilities in choline chloride (ChCl)-glycerol (GLY) 1:2 at 313.15 K and 0–6 MPa (Leron and Li, 2013). The result indicated that the measured CO₂ solubilities (0.1103–3.0718 mol/kg) in this DES are greater than those in the 1-ethyl-3-methylimidazolium-based ILs, such as 1-ethyl-3-methylimidazolium tetrafluoroborate, 1-ethyl-3-methylimidazolium hexafluorophosphate, and 1-ethyl-3-methylimidazolium ethylsulfate. Sarmad et al. reviewed the CO₂ solubilities in 45 DESs in wide ranges of mole ratio (HBA:HBD), temperature, and pressure (Sarmad et al., 2017a).

Based on this review, top three DESs with respect to CO₂ solubilities were acquired, i.e., 3.6929, 3.5592, and 3.1265 mol/kg for ChCl-GLY (1:2, 303.15 K, 5.863 MPa), ChCl-Urea (1:2, 303.15 K, 5.654 MPa), and ChCl-ethylene glycerol (EG) (1:2, 303.15 K, 0.5774 MPa), respectively.

Numerous possible DESs can be synthesized. It is nevertheless a challenge to identify and suggest the best DESs for capturing CO₂ based on the available experimental measurements only. A rapid and priori screening method to predict the CO₂ absorption capacity in DESs is needed. COSMO-RS (Conductor-like Screening Model for Real Solvents) is recommended for predicting some thermodynamic properties (Gonzalez-Miquel et al., 2011; Liu Y.-R., et al., 2016), such as activity coefficients, solubilities, and Henry's constants, and it can also be used for calculating the properties of mixtures at various temperatures and pressures, rendering it an effective tool to predict and develop task-specific DESs for a specific application. Previous work has demonstrated that Henry's constants can be used as one of the criteria to screen ILs for CO₂ capture (Manan et al., 2009; Palomar et al., 2011), and the Henry's constants of CO₂ in ILs have been successfully estimated with COSMO-RS (Gonzalez-Miquel et al., 2011). However, using COSMO-RS to predict the CO₂ solubility or the Henry's constant of CO₂ in DESs is still scarce. To the best of our knowledge, only Kamgar et al. (2017b) predicted CO₂ solubility in the DES of ChCl-Urea (1:2) with COSMO-RS, demonstrating a reliable prediction only at low pressures and high temperatures, where the gas could be assumed to be an ideal gas. No report is available to predict the Henry's constants of CO₂ in DESs and compare with the experimental results for verification.

The aim of this work was to predict CO₂ solubilities, the Henry's constants of CO₂, and the interactions for CO₂ capture in DESs with COSMO-RS. A comprehensive survey of the published experimental results of CO₂ solubility and Henry's
constant of CO₂ was firstly carried out. COSMO-RS was used to predict these two properties, and the predictions were compared with the experimental results. COSMO-RS was further developed with a correction based on the experimental CO₂ solubility to improve the model performance. The σ-profiles predicted by COSMO-RS were used to reflect the strength of molecular interactions between an HBA (or HBD) and CO₂, and the calculated excess enthalpy was applied to acquire the dominant interactions for CO₂ capture in DESs.

**COMPUTATIONAL DETAIL**

**COSMO-RS Computation Details**

COSMO-RS calculations were performed using the software COSMOtherm (version C3.0, release 14.01, applied with parameterization BP_TZVP_C30_1401, COSMologic, Leverkusen, Germany) (Larriba et al., 2017). Following the standard method, first, the quantum chemical Gaussian09 package was used to optimize the structure of the studied compounds at the B3LYP/6-31++G (d, p) level. Second, the COSMOfiles of the optimized structures were opened by Gaussian03, and the COSMO continuum solution models were obtained using the BVP86/TZVP/DGA1 level theory. Third, CO₂ solubility, the Henry’s constant of CO₂, σ-profiles, and excess enthalpy were determined with COSMO-RS (Liu Y.-R., et al., 2016). In computation, the temperature and pressure were set to be the same values as the experimental conditions.

In COSMO-RS, all DESs were implemented in COSMOtherm software following the electroneutral approach, where each DES was treated as three different compounds in a stoichiometric mixture (Larriba et al., 2017). For HBA, the mole fractions of the cation and anion were treated as equal, i.e., ncation = nanion = nHBA. The solubility and Henry’s constant of CO₂ were calculated based on the equations described by Klamt et al. (2001) and Loschen and Klamt (2014). The total and contribution of the excess enthalpy were calculated with the method reported by Casas et al. (2012).

In COSMO-RS, the solubility (X) (i.e., the mole fraction) of CO₂ in DESs was obtained with the following equation (Equation 1) (Li et al., 2014).

\[ X_{CO_2} = \frac{n_{CO_2}}{n_{CO_2} + n_{DES}} \] (1)

where \( n_{DES} \) is the mole quantity of absorbent, and it was obtained according to the mass weight and the mole mass of DESs.

To evaluate the model performance, the discrepancies between the results (i.e., CO₂ solubility X, Henry’s constant H) estimated with COSMO-RS and the corresponding experimental data points were quantified with the absolute relative error (ARD) as defined by Equation 2 (Kamgar et al., 2017a).

\[ \text{ARD\%} = \frac{100}{NP} \sum_{i=1}^{NP} \left| \frac{Y_{Exp} - Y_{COSMO-RS}}{Y_{Exp}} \right| \] (2)

where \( NP \) is the total number of data points. \( Y_{COSMO-RS} \) (i.e., \( \ln X_{CO_2} \) or \( H_{COSMO-RS} \)) is the result predicted with COSMO-RS (original or corrected) at a given temperature and pressure, and \( Y_{Exp.} \) is the corresponding experimental result (i.e., \( \ln X_{CO_2}^Exp. \) or \( H_{Exp.}^Exp. \)).

**DESs-Database and COSMOfiles**

A literature survey was conducted, and the DESs with CO₂ solubility and the Henry’s constant of CO₂ in DESs were summarized and used as databases for verifying and further developing COSMO-RS. According to the survey, for CO₂ solubility, the DESs with HBA:HBD at the mole ratios of 1:2, 1:3, 1:4, and 1:5 have more experimental results compared to those with other mole ratios, and they were selected for developing COSMO-RS model in this work, while the limited experimental results at the mole ratio of 1:6 were used for verification of the developed COSMO-RS. For Henry’s constants, the DESs (1:1.5, 1:2, 1:3, 1:4, 1:5) were chosen due to that sufficient experimental results are available for these DESs in literatures. The DESs databases together with the experimental measurement conditions are summarized in Tables 1, 2, respectively, and the detailed CO₂ solubilities and the Henry’s constants under different conditions are provided in Tables S1–S6.

To use COSMO-RS, the COSMOfiles for all the studied HBAs and HBDs are needed. In this work, those for the HBAs of ATPP⁺, AC⁺, BTEA⁺, BTMA⁺, and MTPP⁺, and for the HBDs of lactic acid (LA), ethylene glycol (EG), levulinic acid (LEV), furfuryl alcohol (FA), triethylene glycol (TEG), guaiacol (GC), decanoic acid (DecA), 1,4-butanediol (1,4-BUT), and 2,3-butanediol (2,3-BUT) were calculated based on the procedures described in the computation details. The optimized structures of HBAs and HBDs as well as the COSMOfiles from Gaussian are provided in Supplementary Information. The COSMOfiles for other HBAs and HBDs studied in this work as listed in Tables 1, 2 were directly taken from the COSMO-RS database.

**MODEL RESULTS AND DISCUSSION**

**CO₂ Solubility With COSMO-RS**

For conducting COSMO-RS prediction, 502 experimental data points of CO₂ solubilities in four types of DESs (1:2, 1:3, 1:4, 1:5) under different conditions summarized from the published work were used as the input to predict the CO₂ solubility. The model predictions were then compared with the experimental results. Together with the selected 502 experimental data points of CO₂ solubilities, the predicted results and the corresponding ARDs are listed in Tables S1–S4.

Taking the results listed in Table S1 as examples, it can be observed that COSMO-RS is capable of predicting CO₂ solubilities in DESs, but qualitatively. For example, the experimental \( \ln X_{CO_2} \) of TMACl-LA (1:2) is \(-5.1743\) at 308 K, 194 kPa, and \(-5.2419\) at 318 K, 194 kPa. The increase of temperature from 308 to 318 K leads to a decrease of CO₂ solubility with a difference of \((\Delta \ln X_{CO_2} = -0.0676)\). The corresponding COSMO-RS predicted values of \( \ln X_{CO_2} \) are \(-2.9257\) and \(-3.1451\), respectively, indicating a temperature increase results in a decreased CO₂ solubility, however, the difference is \((\Delta \ln X_{CO_2} = -0.2194)\) that are much lower than the experimental observation. For different kinds of DESs, the predicted CO₂ solubility also provides the same trend with the
| DES         | HBA                        | HBD                        | Mole ratio (HBA:HBD) | Temperature range (K) | Press range (KPa) | Numbers of data | References        |
|-------------|----------------------------|----------------------------|----------------------|------------------------|-------------------|-----------------|------------------|
| ChCl-Phenol | Choline chloride           | Phenol                     | 1:2                  | 293.15–323.15          | 99–520.2          | 19              | Li et al., 2014  |
| BTEACl-AC   | Benzyltrimethylammonium chloride | Acetic acid               | 1:2                  | 298.15                 | 325–2054          | 6               | Sarmad et al., 2017b |
| BTMACl-AC   | Benzyltrimethylammonium chloride | Acetic acid               | 1:2                  | 298.15                 | 219–2037          | 7               |                  |
| BTMACl-GLY  | Benzyltrimethylammonium chloride | Glycerol                  | 1:2                  | 298.15                 | 394–2026          | 6               |                  |
| TBACl-AC    | Tetrabutylammonium chloride | Acetic acid               | 1:2                  | 298.15                 | 348–2002          | 6               |                  |
| TBABr-AC    | Tetrabutylammonium bromide | Acetic acid               | 1:2                  | 298.15                 | 388–2011          | 5               |                  |
| TEACl-AC    | Tetraethylammonium chloride | Acetic acid               | 1:2                  | 298.15                 | 281–2018          | 6               |                  |
| TEMACl-AC   | Triethylmethylammonium chloride | Acetic acid              | 1:2                  | 298.15                 | 198–1837          | 7               |                  |
| TEMACl-EG   | Triethylmethylammonium chloride | Ethylene glycol          | 1:2                  | 298.15                 | 138–1345          | 6               |                  |
| TEMACl-LA   | Triethylmethylammonium chloride | Lactic acid              | 1:2                  | 298.15                 | 143–1863          | 6               |                  |
| TEMACl-LEV  | Triethylmethylammonium chloride | Levulinic acid          | 1:2                  | 298.15                 | 136–1617          | 5               |                  |
| TEMACl-GLY  | Triethylmethylammonium chloride | Glycerol                  | 1:2                  | 298.15                 | 150–1648          | 5               |                  |
| TBACl-LA    | Tetrabutylammonium chloride | Lactic acid               | 1:2                  | 308, 318               | 93–1992, 93–1992 | 28              | Zubeir et al., 2014 |
| TEACl-LA    | Tetraethylammonium chloride | Lactic acid               | 1:2                  | 308, 318               | 97–1993, 94–1992 | 40              |                  |
| TMACl-LA    | Tetramethylammonium chloride | Lactic acid              | 1:2                  | 308, 318               | 98–1992, 95–1993 | 40              |                  |
| ChCl-DEG    | Choline chloride           | Diethylene glycol         | 1:3                  | 293.15–323.15          | 112.8–524         | 20              | Li et al., 2014  |
| ChCl-FA     | Choline chloride           | Furfuryl alcohol          | 1:3                  | 303.15–333.15          | 80.9–586.4        | 24              | Lu et al., 2015  |
| ChCl-LEV    | Choline chloride           | Levulinic acid           | 1:3                  | 303.15–333.15          | 69.8–579.8        | 24              |                  |
| ChCl-Phenol | Choline chloride           | Phenol                    | 1:3                  | 293.15–323.15          | 104.4–514.4       | 20              |                  |
| ChCl-TEG    | Choline chloride           | Triethylene glycol       | 1:3                  | 293.15–323.15          | 109.3–516         | 20              | Li et al., 2014  |
| TEACl-AC    | Tetraethylammonium chloride | Acetic acid              | 1:3                  | 298.15                 | 397–2016          | 6               | Sarmad et al., 2017b |
| TEACl-OCT   | Tetraethylammonium chloride | Octanoic acid            | 1:3                  | 298.15                 | 353–2018          | 6               |                  |
| MTPPBr-LEV  | Methyltriphenylphosphonium bromide | Levulinic acid       | 1:3                  | 298.15                 | 301–2068          | 7               |                  |
| ChCl-DEG    | Choline chloride           | Diethylene glycol         | 1:4                  | 293.15–323.15          | 110.4–526.9       | 20              | Li et al., 2014  |
| ChCl-FA     | Choline chloride           | Furfuryl alcohol          | 1:4                  | 303.15–333.15          | 65.2–585.4        | 24              | Lu et al., 2015  |
| ChCl-LEV    | Choline chloride           | Levulinic acid           | 1:4                  | 303.15–333.15          | 60–587.4          | 24              |                  |
| ChCl-Phenol | Choline chloride           | Phenol                    | 1:4                  | 293.15–323.15          | 108.2–529.1       | 20              | Li et al., 2014  |
| ChCl-TEG    | Choline chloride           | Triethylene glycol       | 1:4                  | 293.15–323.15          | 109.3–520.3       | 20              |                  |
| TMACl-AC    | Tetramethylammonium chloride | Acetic acid              | 1:4                  | 298.15                 | 294–1741          | 6               | Sarmad et al., 2017b |
| TPACl-EA    | Tetrapropylammonium chloride | Ethanolamine            | 1:4                  | 298.15                 | 481–2009          | 6               |                  |
| MTPPBr-AC   | Methyltriphenylphosphonium bromide | Acetic acid       | 1:4                  | 298.15                 | 173–2014          | 8               |                  |
| MTPPBr-1,2-PRO | Methyltriphenylphosphonium bromide | 1,2-Propanediol      | 1:4                  | 298.15                 | 220–2026          | 7               |                  |
| ChCl-LEV    | Choline chloride           | Levulinic acid           | 1:5                  | 303.15–333.15          | 71.5–581          | 24              | Lu et al., 2015  |
| ChCl-FA     | Choline chloride           | Furfuryl alcohol          | 1:5                  | 303.15–333.15          | 70.9–577.2        | 24              |                  |
| TPACl-AC    | Tetrapropylammonium chloride | Acetic acid              | 1:6                  | 298.15                 | 350–2030          | 6               | Sarmad et al., 2017b |
experiment results, for example, the experimental $\ln X_{\text{CO}_2}$ for TBACl-LA (1:2) is $-4.3513$ at 308 K, 194 kPa, which is greater than that of TMACl-LA (1:2) under the same condition. The prediction of COSMO-RS provides a value of $\ln X_{\text{CO}_2} = -2.2662$ for TBACl-LA (1:2) at 308 K, 194 kPa, which is also higher than that for TMACl-LA (1:2) (i.e., $\ln X_{\text{CO}_2} = -2.9257$). The results for other DESs listed in Tables S2–S4 show similar observations as those listed in Table S1. Hence, COSMO-RS can be used to screen DESs qualitatively, reducing the amount of unnecessary experimental measurements.

Further comparisons were performed based on $\ln X_{\text{CO}_2}$ between the experimental and COSMO-RS results. As shown in Figure 1, systematic deviations can be observed, i.e., all the COSMO-RS predictions are higher than the experimental results. With increasing pressure and decreasing temperature, the discrepancies become larger, which is consistent with the observation by Kamgar et al. (2017b). This indicates that using the COSMO-RS with the parameters obtained from the conventional compound systems to predict the thermodynamic properties of DESs will lead to large deviations, which was also pointed out by others (Han et al., 2018). One of the reasons can be attributed to the formation of nanoscopic structures in DESs (Cerajewski et al., 2018), which is completely different from the solvation properties of molecular solutes in the conventional solvents at the microscopic scale.

**Henry's Constant With COSMO-RS**

The Henry's constants of CO$_2$ in DESs (1:1.5, 1:2, 1:3, 1:4, 1:5) with 132 data points were predicted with COSMO-RS and compared with the experimental results (Figure 2). The specific values of the experimental and predicted Henry's constants are listed in Table S6, and the ARDs are summarized in Table 3. From Table S6, it can be found that the predicted Henry's constants are in agreement with

### Table 2: DESs database studied in this work for Henry's constants of CO$_2$.

| DES       | HBA           | HBD           | Mole ratio (HBA:HBD) | Temperature range (K) | Points | References          |
|-----------|---------------|---------------|----------------------|-----------------------|--------|---------------------|
| ChCl-Urea | Choline chloride | Urea         | 1:1.5                | 313.15–333.15         | 3      | Li et al., 2008     |
| ChCl-Urea | Choline chloride | Urea         | 1:2                  | 313.15–333.15         | 3      |                    |
| ChCl-Urea | Choline chloride | Urea         | 1:2                  | 308.2–328.2           | 3      | Xie et al., 2013    |
| ChCl-Phenol | Choline chloride | Phenol     | 1:2                  | 293.15–323.15         | 4      | Li et al., 2014     |
| TMACl-LA  | Tetramethylammonium chloride | Lactic acid | 1:2                  | 308–318               | 2      | Zubeir et al., 2014 |
| TEACl-LA  | Tetraethylammonium chloride | Lactic acid | 1:2                  | 308–318               | 2      |                    |
| TBACl-LA  | Tetraethylammonium chloride | Lactic acid | 1:2                  | 308–318               | 2      |                    |
| TBACl-DecA | Tetrabutylammonium chloride | Decanoic acid | 1:2                  | 298.15–323.15         | 3      | Zubeir et al., 2018 |
| N$_8881$Br-DecA | Methyltrioctylammonium bromide | Decanoic acid | 1:2                  | 298.15–306.15         | 2      |                    |
| ChCl-EG   | Choline chloride | Ethylene glycol | 1:2                  | 303.15                | 1      | Haider et al., 2018 |
| TBABr-EG  | Tetrabutyl ammonium bromide | Ethylene glycol | 1:2, 1:3, 1:4        | 303.15               | 1, 1, 1|                    |
| TBAbr-DEG | Tetrabutyl ammonium bromide | Diethylene glycol | 1:2, 1:3, 1:4    | 303.15               | 1, 1, 1|                    |
| ChCl-1,2 PRO | Choline chloride | 1,2-propanediol | 1:3, 1:4             | 293.15–323.15         | 4, 4   | Chen et al., 2014   |
| ChCl-2,3 BUT | Choline chloride | 2,3-butanediol | 1:3, 1:4             | 293.15–323.15         | 4, 4   |                    |
| ChCl-1,4 BUT | Choline chloride | 1,4-butanediol | 1:3, 1:4             | 293.15–323.15         | 4, 4   |                    |
| ChCl-DEG  | Choline chloride | Diethylene glycol | 1:3, 1:4             | 293.15–323.15         | 4, 4   | Li et al., 2014     |
| ChCl-FA   | Choline chloride | Furfuryl alcohol | 1:3, 1:4             | 293.15–323.15         | 4, 4   | Lu et al., 2015     |
| ChCl-LEV  | Choline chloride | Levulinic acid | 1:3, 1:4             | 293.15–323.15         | 4, 4   |                    |
| ChCl-Phenol | Choline chloride | Phenol     | 1:3, 1:4             | 293.15–323.15         | 4, 4   | Li et al., 2014     |
| ChCl-TEG  | Choline chloride | Triethylene glycol | 1:3, 1:4             | 293.15–323.15         | 4, 4   |                    |
| ChCl-GC   | Choline chloride | Guaiacol     | 1:3, 1:4, 1:5        | 293.15–323.15         | 4, 4, 4| Liu X. B. et al., 2017 |
| ACCL-GC   | Acetylcocaine chloride | Guaiacol | 1:3, 1:4, 1:5        | 293.15–323.15         | 4, 4, 4|                    |
| ATPPbr-DEG | Allytriphenyl phosphonium bromide | Diethylene glycol | 1:4                  | 303.15               | 1      | Ghaedi et al., 2017 |
| ATPPbr-TEG | Allytriphenyl phosphonium bromide | Triethylene glycol | 1:4                  | 303.15               | 1      |                    |
| ChCl-FA   | Choline chloride | Furfuryl alcohol | 1:5                  | 303.15–333.15         | 4      | Lu et al., 2015     |
| ChCl-LEV  | Choline chloride | Levulinic acid | 1:5                  | 303.15–333.15         | 4      |                    |
FIGURE 1 | Experimental ln $X_{CO_2}$ vs. the ln $X_{CO_2}$ predicted with the original COSMO-RS. (A) HBA:HBD 1:2; (B) HBA:HBD 1:3; (C) HBA:HBD 1:4; (D) HBA:HBD 1:5.

FIGURE 2 | Experimental vs. predicted Henry's constants with the original COSMO-RS.

**TABLE 3 | ARDs for the Henry's constants determined experimentally with respect to those predicted with the original COSMO-RS.**

| HBA:HBD | 1:1.5 | 1:2 | 1:3 | 1:4 | 1:5 |
|---------|-------|-----|-----|-----|-----|
| ARD     | 13.7% | 29.9% | 28.6% | 34.4% | 36.3% |

because the Henry's constant is inversely proportional to the CO$_2$ solubility (Liu X. Y., et al., 2016). A 13.7–36.3% deviation can be observed as listed in **Table 3**, indicating that the predicated Henry's constants are more accurate than the predicted CO$_2$ solubility with the original COSMO-RS (**Table 4**).

**COSMO-RS Correction for CO$_2$ Solubility**

Although, from one side, it is unfortunate to observe a large deviation between the experimental CO$_2$ solubility and the COSMO-RS prediction, from the other side, it illustrates that it is possible to develop a systematic correction of COSMO-RS for improving the model performance of CO$_2$ solubility in DESs. Liu et al. reported a corrected COSMO-RS for predicting the activity coefficient of CO$_2$ in ILs and acquired a good agreement between the experimental and predicted results after correction (Liu et al., 2018). Following this idea, in this work, a temperature-pressure-dependent correction was firstly proposed as summarized in Equations 3–6 (**Table 4**) for the DESs with the
TABLE 4 | Corrected COSMO-RS for predicting \( \ln X_{CO_2} \) in the DESs of four mole ratios.

| Mole ratio | Correction, T in K, P in KPa \( \ln X_{CO_2}^{corr.} = \ln X_{CO_2}^{COSMO-RS} - A \times T + BP + C \) | ARDs compared to experimental \( \ln X_{CO_2} \) |
|------------|-----------------------------------------------------------------|-----------------------------------------------|
| 1:2        | \( \ln X_{CO_2}^{corr.} = -1.1980 \times 10^3 + 3.4453 \times 10^{-4} P + 1.4186 \) | 62.2% 6.5% (3) |
| 1:3        | \( \ln X_{CO_2}^{corr.} = -9.4659 \times 10^2 + 5.4618 \times 10^{-4} P + 0.2488 \) | 59.6% 4.8% (4) |
| 1:4        | \( \ln X_{CO_2}^{corr.} = -8.6186 \times 10^2 + 6.4121 \times 10^{-4} P - 0.1682 \) | 63.0% 6.5% (5) |
| 1:5        | \( \ln X_{CO_2}^{corr.} = -2.2721 \times 10^2 + 5.1644 \times 10^{-4} P - 2.0832 \) | 59.1% 4.5% (6) |

FIGURE 3 | Experimental \( \ln X_{CO_2} \) vs. the \( \ln X_{CO_2} \) calculated with the corrected COSMO-RS models using Equations 3–6 (square symbol) and Equation 10 (circular symbol). (A) HBA:HBD 1:2; (B) HBA:HBD 1:3; (C) HBA:HBD 1:4; (D) HBA:HBD 1:5.

same mole ratio. As displayed in Table 4, the corrected COSMO-RS includes three parameters, i.e., \( A (K^{-1}) \), \( B (KPa^{-1}) \), and \( C \), and these parameters were adjusted based on the experimental \( CO_2 \) solubility at different temperatures and pressures for each group of DESs, i.e., the DESs with the same mole ratio. The predicted results with the corrected COSMO-RS are given in Tables S1–S4. The performance of the corrected COSMO-RS is further illustrated in Figure 3, and the deviations in ARDs between the experimental and modeling results are reported in Table 4. It can be found that, with the corrected COSMO-RS, i.e., the COSMO-RS with a temperature-pressure-dependent parameter, the predicted logarithmic \( CO_2 \) solubilities (square symbol in Figure 3) are in agreement with the experimental results, with much smaller ARDs of 6.5, 4.8, 6.5, and 4.5% for these four groups of DESs compared to the ARDs with the original COSMO-RS. According to the results listed in Tables S1–S4, the ARD decreases with increasing temperature, which agrees with the observation by Kamgar et al. (2017b). As shown in Table 4, the adjustable parameters \( A (K) \), \( B (KPa^{-1}) \), and \( C \) in four corrected Equations 3–6 are almost linearized with the mole ratios. To further improve the model prediction capacity, the adjustable parameters \( A \), \( B \), and \( C \) were set to be mole-ratio-dependent which can be described as follows:

\[
A = k_1 \times w + k_2 \tag{7}
\]

\[
B = k_3 \times w + k_4 \tag{8}
\]

\[
C = k_5 \times w + k_6 \tag{9}
\]

where \( w \) is the mole ratio, being 2, 3, 4, 5, etc.

To obtain \( k_1 \)-\( k_6 \), in this work, the experimental results of \( CO_2 \) solubilities in the DESs with four mole-ratios of 1:2, 1:3, 1:4, and 1:5 were used, and, in total, 502 experimental data points were included in fitting with a linear least square method. The
fitted parameters of $k_1$-$k_6$ together with the corresponding ARDs are listed in Table 5, and the fitted CO$_2$ solubilities are given in Tables S1–S4.

To illustrate the fitting performance with this set of universal parameters ($k_1$-$k_6$), the CO$_2$ solubilities obtained with the corrected COSMO-RS (circular symbol) were compared with the experimental results as well as those with the corrected COSMO-RS but using the individual parameters at each mole-ratio. As shown in Figure 4, the predicted $\ln X_{\text{CO}_2}^{corr}$ with the corrected COSMO-RS using the universal parameters (i.e., Equation 10) agrees with the experimental data, and only a slight deviation can be observed between these two corrected COSMO-RS models, i.e., with Equation 10 and Equations 3–6, respectively. Additionally, from Table 5, it can be found that the ARDs with Equation 10 are 6.8, 5.2, 6.6, and 4.7% for the DESs at mole ratios of 1:2, 1:3, 1:4, and 1:5, respectively, which are almost the same as the ARDs calculated individually with Equations 3–6 (Table 4). All these indicate that it is reasonable to use the mole-ratio-dependent parameters.

$$\ln X_{\text{CO}_2}^{corr} = \ln X_{\text{CO}_2}^{\text{COSMO-RS}} + \left( k_1 \times w + k_2 \right) \times \frac{1}{T} + \left( k_3 \times w + k_4 \right) \times P + \left( k_5 \times w + k_6 \right)$$  

(10)

**Further Verification of the Corrected COSMO-RS**

COSMO-RS with the universal parameters $k_1$–$k_6$ can be used to predict CO$_2$ solubilities in the DESs with any mole ratios according to Equation 10. In order to further investigate the model prediction capacity, it was used to predict CO$_2$ solubilities in the DESs at the mole ratio of 1:6. This type of DES was excluded in parameter fitting for correcting COSMO-RS due to the limited number of available experimental data points. The comparison of the prediction with the experimental data as well as those predicted with the original COSMO-RS is displayed in Table S5 and Figure 4. From Figure 4, it can be seen that the ARD between $\ln X_{\text{CO}_2}^{\text{COSMO-RS}}$ and $\ln X_{\text{CO}_2}^{\text{Exp}}$ is 78.2%, while it is only 10.3% between $\ln X_{\text{CO}_2}^{\text{corr}}$ and $\ln X_{\text{CO}_2}^{\text{Exp}}$, indicating that the corrected COSMO-RS is applicable for different kinds of DESs.

In summary, COSMO-RS is a predictive model, but the performance is not always satisfactory for the DESs with CO$_2$. The model performance of CO$_2$ solubility in DESs can be improved significantly with the corrected COSMO-RS.

**Further Investigation With COSMO-RS and Discussion**

**σ-Profiling Prediction**

The molecular interactions between two compounds can be linked to their σ-profiles, the wider the complementary of their σ-profiles (i.e., in the same region, the σ-profile for one compound increases, while that for the other compound decreases), the stronger the molecular interactions between these two compounds. In this work, in order to study the effects of HBAs and HBDs on the interactions with CO$_2$, the HBAs of TMACl, TBACl, TBABr, and BTMACl as well as the HBDs of AC, GLY, and LA were selected to predict the σ-profiles. The predicted results are listed in Table S7 and illustrated in Figure 5. Following the previous work, the σ-profiles can be divided into three regions: H-bond donor region ($\sigma < -0.0082$ e/Å$^2$), non-polar region ($-0.0082 < \sigma < +0.0082$ e/Å$^2$), and H-bond acceptor region ($\sigma > +0.0082$ e/Å$^2$) (Liu Y. R. et al., 2017). In the H-bond acceptor region, the σ-profiles of HBAs for TMACl and TBACl are almost the same. However, the σ-profile of TBACl has a wider region complemented with CO$_2$ than that for TBACl in both H-bond donor and non-polar regions, indicating that TBACl has a strong interaction with CO$_2$ compared to TMACl. Meanwhile, the location of the σ-profile peak in the H-bond acceptor region also reflects the interaction strength with CO$_2$. TBACl and TBABr have the same σ-profile curves in the H-bond acceptor region while in the H-bond donor region, the peak of TBACl (0.019 e/Å$^2$) is located to the right of TBABr (0.017 e/Å$^2$), evidencing that TBACl has a stronger interaction with CO$_2$ than TBABr. The σ-profile prediction shows that both the alkyl chain length of cations and the different types of anions of HBAs can affect the CO$_2$ solubility, agreeing with the experimental results of X$_{\text{CO}_2}$(TBACl-LA 1:2) > X$_{\text{CO}_2}$(TMACl-LA 1:2) (Zubeir et al., 2014) and X$_{\text{CO}_2}$(TBACl-AC 1:2) > X$_{\text{CO}_2}$(TBABr-AC 1:2) (Sarmad et al., 2017b) at the same temperature and pressure. Additionally, as shown in Figure 5, it can be seen that AC is more complementary with CO$_2$ than GLY, and the σ-profile curve of AC is lower than that of GLY. This implies that AC as the HDB in DES has a strong interaction with CO$_2$ with respect to GLY, being consistent with the experimental results of X$_{\text{CO}_2}$(BTMACl-AC 1:2) > X$_{\text{CO}_2}$(BTMACl-GLY 1:2) at the same temperature and pressure (Sarmad et al., 2017b). Therefore, the σ-profile can be used to reflect the interaction strength of a DES with CO$_2$. 

![Figure 4](image-url)
TABLE 5 | Adjustable parameters of Equation 10 and the corresponding ARDs.

| Adjustable parameters | ARDs compared to experimental ln X_{CO2} |
|-----------------------|---------------------------------------|
| k_1/(K)              | 1:2         | 1:3         | 1:4         | 1:5         |
| 48.5344              | 1.2%        | 2.1%        | 0.6%        | 1.6%        |
| k_2/(K)              | 9.4696 x 10^{-5} | 2.1975 x 10^{-4} | -0.3249     | 1.3184     |
| k_3/(KPa^{-1})       | 6.8%        | 5.2%        | 6.6%        | 4.7%        |
| k_4/(KPa^{-1})       | 2.1975 x 10^{-4} | 1.3184     |             |             |
| k_5                   |             |             |             |             |
| k_6                   |             |             |             |             |

Excess Enthalpy Prediction

The total excess enthalpy of six kinds of DESs at infinitely dilute CO_{2} concentrations predicted by COSMO-RS was illustrated in Figure 6. These DESs can be divided into three types: (1) TMACI-LA 1:2 and TBACI-LA 1:2 have the same HBD and molar ratio but different HBA; (2) ChCl-DEG 1:3 and ChCl-TEG 1:3 have the same HBA and molar ratio but different HBD; (3) ChCl-FA 1:3 and ChCl-FA 1:5 have the same HBA and HBD but different molar ratios. The higher the absolute values of excess enthalpy, the stronger the interaction between DES and CO_{2}, i.e., the higher the capacity for CO_{2} capture. As shown in Figure 6, the absolute excess enthalpy of TBACI-LA 1:2+CO_{2} is higher than that for TMACI-LA 1:2+CO_{2}, indicating that TBACI-LA 1:2 has a higher capacity for CO_{2} capture. The comparison of ChCl-DEG 1:3+CO_{2} and ChCl-TEG 1:3+CO_{2} shows that ChCl-TEG 1:3+CO_{2} has a higher absolute excess enthalpy compared to ChCl-DEG 1:3+CO_{2} system, being in agreement with the experimental results obtained by Sarmad et al. (2017b) and Ghaedi et al. (2017), i.e., increasing the alkyl chain length in HBA and HBD results in an increased CO_{2} solubility. Moreover, by increasing the molar ratio of HBD in DES, the absolute excess enthalpy of ChCl-FA 1:5+CO_{2} is increased compared to ChCl-FA 1:3+CO_{2} system, which agrees with the experimental results (Lu et al., 2015). Therefore, predicting excess enthalpy may be an efficient option for designing the potential DES for CO_{2} capture.

CONCLUSION

This work established a database containing 502 experimental data points for CO_{2} solubility and 132 for the Henry's constant of CO_{2} in DESs. This database was used for further verification and development of COSMO-RS.

The logarithmic CO_{2} solubility predicted with the original COSMO-RS shows ARDs of 62.2, 59.6, 63.0, and 59.1% for the DESs with the HBD/HBA at 1:2, 1:3, 1:4, and 1:5, respectively. The Henry's constants of CO_{2} in the DESs (1:1.5, 1:2, 1:3, 1:4, 1:5) predicted with the original COSMO-RS with ARDs of 13.7–36.3% are more accurate compared to the predicted CO_{2} solubilities. To improve the performance, COSMO-RS was corrected based on 502 data points of CO_{2} solubility.
in the DESs (1:2, 1:3, 1:4, 1:5). It shows that the adjustable parameters in the corrected COSMO-RS can be universal, the corrected COSMO-RS with the universal parameters can be used to reliably predict the CO$_2$ solubility in DESs, and the ARDs for the logarithmic CO$_2$ solubility in the DESs (1:2, 1:3, 1:4, 1:5) are of 6.8, 5.2, 6.6 and 4.7%, respectively. The corrected COSMO-RS with the universal parameters was further used to predict CO$_2$ solubility in the DESs (1:6), showing that a much lower ARD (10.3%) compared to that with the original COSMO-RS (ARD, 78.2%). Additional, the σ-profiles can reflect the strength of molecular interactions between an HBA (or HBD) and CO$_2$, and the dominant interactions for CO$_2$ capture in DESs are the H-bond and Van der Waals force, followed by the misfit, according to the results of excess enthalpies.

This work provides a reliable tool for DESs screening and the corrected COSMO-RS can be used to quantitatively predict CO$_2$ solubilities in DESs.

DATA AVAILABILITY STATEMENT

All datasets generated for this study are included in the article/Supplementary Material.

AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct and intellectual contribution to the work, and approved it for publication.

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SUPPLEMENTARY MATERIAL

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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