COSMO-RS Analysis of CO₂ Solubility in N-Methyldiethanolamine, Sulfolane, and 1-Butyl-3-methyl-imidazolium Acetate Activated by 2-Methylpiperazine for Postcombustion Carbon Capture

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ABSTRACT: Novel aqueous (aq) blends of N-methyldiethanolamine (MDEA), sulfolane (TMSO₂), and 1-butyl-3-methyl-imidazolium acetate ([bmim][Ac]) with amine activator 2-methylpiperazine (2-MPZ) are analyzed through conductor-like screening model for real solvents (COSMO-RS) for possible application in the chemisorption of CO₂. The molecules associated are analyzed for their ground-state energy, σ potential, and σ surface. Thermodynamic and physicochemical properties have been assessed and paralleled with the experimental data. Vapor pressure of the blended systems and pure component density and viscosity have been compared successfully with the experimental data. Important binary interaction parameters for the aqueous blends over a wide temperature, pressure, and concentration range have been estimated for NRTL, WILSON, and UNIQUAC 4 models. The COSMO-RS theory is further applied in calculating the expected CO₂ solubility over a pressure range of 1.0–3.0 bar and temperature range of 303.15–323.15 K. Henry’s constant and free energy of solvation to realize the physical absorption through intermolecular interaction offered by the proposed solvents. Perceptive molecular learning from the behavior of chemical constituents involved indicated that the best suitable solvent is aq (MDEA + 2-MPZ).

1. INTRODUCTION

The quest to reduce CO₂ emissions via different routes has been a major concern over the past few decades. The process intensification of the existing CO₂ capture techniques and introduction of novel solvents for achieving the same through chemisorption or physisorption has been proposed by many researchers. An extensive lab-scale development of vapor–liquid equilibria, kinetic studies, thermophysical properties, calculation of binary interaction parameters, improvement in the existing modeling techniques, proposing new correlational analysis, optimizing the reaction or process parameters, defining the structural property relationships, heat of absorption, etc. are an integral part of the development of new solvents for CO₂ or other acid gas absorption applications. However, most of the experimental investigations at the pilot scale tend to be very expensive, and therefore, an efficient solvent screening through various analyses of the proposed solvents is the need of the hour to arrive at a conclusion of their possible applicability at the plant scale. Conclusively, researchers have shifted the research a step back at the quantum-molecular level to understand the basic phenomena of the novel solvents than to lab- or pilot-scale studies for achieving the anticipated CO₂ separation.

The conductor-like screening model for real solvents (COSMO-RS) is a method of quantum chemical calculations grouped with statistical thermodynamics. The same has been widely applied for accurate prediction of thermodynamic or essential behavioral properties such as Gibb’s free energy, activity coefficients, partition coefficients, etc. Calculating the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gaps to define the polarities or electronegativities associated with a specific molecule yields a useful insight for behavioral analysis of any molecule. This significantly reduces the amount of time, energy, and cost associated with the detailed study required for a set of selected solvents. The variations of the predictive capabilities of COSMO-RS can be deduced from a brief literature survey. COSMO-RS applications in the membrane separation processes through COSMOmic simulations have been widely studied in the recent past, indicating the efficiency of estimation of partition coefficients with fewer deviations from experimental studies in comparison to molecular dynamics simulation evaluations.

Received: October 30, 2020
Accepted: December 14, 2020
Published: December 30, 2020

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http://dx.doi.org/10.1021/acsomega.0c05298
ACS Omega 2021, 6, 747–761

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The self-assembly of the surfactants Triton X-114 and Triton X-100 in water solutions at different concentrations and temperatures has been reported,24 where the partition behavior of neutral solutes and micellar structures was studied. The research findings are of great value for extraction and purification through membrane processes using surfactants. The partition behavior of various amino acids at distinct ionization states was predicted successfully using COSMO-RS indicated25 for the extraction of biomolecules using surfactants. A detailed octanol/water partition coefficient prediction through the conceptual application of molecular dynamics and the subsequent input to COSMOmic results in efficient assemblies of complex multiphase fluids are also reported. However, the prediction accuracy depends highly on the i/p molecular structures acquired from molecular dynamics simulations.26 Similar studies can also be performed with respect to the CO2 capture process of adsorption through membranes.

Further with respect to CO2 absorption or adsorption, the important properties of understating are vapor pressure, excess enthalpy, excess Gibb’s energy, infinite dilution activity coefficient (IDAC), activity coefficients, chemical potentials, physicochemical properties such as density, viscosity, refractive index, toxicity, biodegradability, thermal stability, corrosion behavior, and CO2 solubility at a specified temperature and pressure, etc. Thorough knowledge of these properties plays a significant role in selecting a solvent. This is owing to the fact that each of these properties signifies the overall effectiveness of the CO2 capture process. For instance, if the selected solvent exhibits a high viscosity at the absorption temperature and pressure, the overall pumping costs from the regenerator and absorber columns are expected to be very high. On the other hand, if the chemical potentials of the selected solvents are negative in the selected range of temperature, the solvents will not react with CO2 chemically at all, leading to merely physisorption in the capture process.

Assessing the possibilities of COSMO-RS for the important parameters of prediction and analysis, the current study is proposed for CO2 capture through absorption. The nonlinearity exhibited in the absorption of CO2 in previously studied solvents17,28 suggests that using a quantum calculation method may yield an accurate estimation of various involved thermodynamic properties. The selection of proposed blends is based on an extensive literature survey. The analysis of amine activator 2-methylpiperazine (2-MPZ)3,4,29,30 for enhancement of CO2 capture is carried out in tertiary amine N-methyldiethanolamine (MDEA),31,32 physical solvent sulfolane (TMSO2),33,34 and imidazolium-based ionic liquid 1-butyl-3-methyl-imidazolium acetate ([bmim][Ac]).35,36 MDEA is reported to exhibit a high CO2 loading, although it has a low reaction rate. The latter is owing to the fact that MDEA acts only as a weak base to release free OH− that further interacts with CO2. Further, the reaction of MDEA with CO2 is less exothermic when compared to primary amines. MDEA additionally offers various advantages such as high thermal and chemical degradation opposition and low solution vapor pressure in comparison to monoethanolamine (MEA) and diethanolamine (DEA).37,38 TMSO2 is also considered for its qualities of high physical absorption capacity, high thermal stability, low heat of absorption, and lower corrosion characteristics.33,34 1-Butyl-3-methylimidazolium acetate, being a room-temperature ionic liquid, offers an insignificantly low vapor pressure and is recognized for its thermal stability and CO2 capture capacity.

The solvents are chosen in such a manner as to provide molecular and thermodynamic insights into each category of solvents. The base solvents, i.e., MDEA, TMSO2, and [bmim][Ac], are proposed in the concentration range of 2.5–3.5 mol·kg⁻¹, whereas the concentration range of the activator is varied from 0.5 to 1.5 mol·kg⁻¹. The selected temperature range is 303.15–323.15 K in view of application in absorption phenomena. The variables studied in the respective range of solvents are based on the recommendations in the literature.30–39 Various important properties such as σ potential, σ profile, vapor pressure, pure component density and viscosity, infinite dilution activity coefficients, activity coefficients, Gibb’s free energy, chemical potential, CO2 solubility, Henry’s law coefficient, etc. have been analyzed through the COSMO-RS theory using

Table 1. Specifications of the Chemicals Used in the Present Study

| Chemical Name                      | Chemical Formula | Molecular weight | Source                  | Stated Mass fraction Purity | CAS no.       | Purification method          |
|-----------------------------------|------------------|------------------|-------------------------|-----------------------------|---------------|-----------------------------|
| 1-butyl-3-methyl-imidazolium acetate ([bmim][Ac]) | ![Chemical Structure](Image) | 198.26 | Sigma-Aldrich Co. | ≥0.95 | 284049-75-8 | Vacuum drying for 48 hrs |
| N-Methylidyethanolamine (MDEA) | ![Chemical Structure](Image) | 119.16 | Sigma-Aldrich Co. | ≥0.99 | 105-59-9 | None |
| 2-Methyl Piperazine (2-MPZ)        | ![Chemical Structure](Image) | 100.16 | Sigma-Aldrich Co. | 0.95 | 109-07-9 | None |
| Sulfolane (TMSO2)                  | ![Chemical Structure](Image) | 120.17 | Sigma-Aldrich Co. | 0.99 | 126-33-0 | None |
| Carbon dioxide (CO2)               | ![Chemical Structure](Image) | 44.01 | Linde India Ltd. | ≥0.99 | - | None |
Table 2. Detailed Description of the Mathematical Expressions for the Current Work

| sr. no. | property of the system | mathematical equation | description |
|---------|------------------------|-----------------------|-------------|
| 1       | profile of the whole system $p_i(\sigma)$ | $p_i(\sigma) = \sum_{s=1}^{n_s} x_s \times p_i(\sigma)$ | $x_s$ is the mole fraction of component “i” in the mixture $p_i(\sigma)$ is the $\sigma$ profile of any molecule $n_i(\sigma)$ is the number of distributed segments that has surface charge density $\sigma$ $A_i(\sigma)$ is the segment surface area that has charge density $\sigma$ $A_i$ is the area of the whole surface cavity rooted in the medium $\mu_i(\sigma)$ is the chemical potential of a surface segment $\sigma$ is the polarity of the surface under study |
| 2       | profile of molecule $X$ | $p_{\lambda X}(\sigma) = \frac{n_i(\sigma)}{n_i} = \frac{A_i(\sigma)}{A_i}$ | |
| 3       | a surface segment chemical potential with screening charge density | $\mu(\sigma) = -\frac{RT}{a_{\text{diff}}} \ln \left[ \int p_i(\sigma) \exp \left[ \frac{a_{\text{diff}}}{RT} (\mu(\sigma) - c(\sigma, \sigma')) \right] d\sigma \right]$ | |
| 4       | vapor pressure | $p_v = \exp \left[ \frac{(\mu_{\text{gas}} - \mu_i)}{RT} \right]$ | $p_v$ is the vapor pressure of the component under study $\mu_{\text{gas}}$ is the vapor pressure of the reference component if any considered $\mu_i$ is the chemical potential of the component in the gas phase $\mu_i$ is the chemical potential of the pure component in mixture $\sigma$ $R$ is the universal gas constant $T$ is the temperature at which the vapor pressure is to be estimated $\text{MW}_i$ is the molecular weight of the molecule $N_i$ is Avogadro’s number $V_i$ is the corrected molar liquid volume $\mu_{\text{gas}}$ is the pure component misfit interaction enthalpy $H_i^{\text{Hmix}}$ is the hydrogen-bonding enthalpy $\mu_{\text{cosmo}}$ is the COSMO volume $M_i$ is the second $\sigma$-moment $N_{\text{Ring}}$ is the number of ring atoms $A_i$ is the surface area associated with the molecule $A_i$ is the surface area $M_i$ is the second $\sigma$-moment of the compound $N_{\text{Ring}}$ is the number of ring atoms in the compound $\text{TS}$ is the pure component entropy at a specific temperature $c_{\text{qsp}}$, $G_{\text{mol}}$, $N_{\text{Ring}}$, $c_{\text{sw}}$, and $c_{\text{c}}$ are the generic parameters for the QSPR approach for liquid viscosity, with energy values in kcal mol$^{-1}$ and areas in Å$^2$ $\mu_i^{\text{PCC}}$ is the activity coefficient of component “i” at infinite dilution $\mu_i^{\text{PCC}}$ is the pseudo-chemical potential of “i” at infinite dilution $\mu_i^{\text{PCC}}$ is the chemical potential of “i” in its pure liquid state $\mu_i^{\text{PCC}}$ is the total vapor pressure of the mixture $x_i$ is the mole fraction of the compounds in the liquid phase $y_i$ is the mole fraction of compounds in the gas phase $e_i$ and $e_i'$ are the binary interaction parameters of the associated constituents $\alpha = \alpha_{i,j} = \alpha_{j,i}$ is the nonrandomness factor that signifies the molecule–molecule or molecule–electrolyte (if any) (default value of 0.3) $A_{i,j}$, $\phi_{i,j}$, $V_{i,j}$, $\theta_{i,j}$, $a_{i,j}$, and $a_{i,j}'$ are binary interaction parameters of the system under study |
| 5       | pure component density | $\rho_i = \frac{\text{MW}_i}{\text{MW}_i \times V_i}$ | |
| 6       | corrected molar liquid volume | | |
| 7       | pure component viscosity (based on a QSPR) | $\ln(\eta) = \left( c_{\text{qsp}} \times A_i \right) + \left( c_{\text{mol}} \times M_i^2 \right)$ | |
| 8       | activity coefficient at infinite dilution | $\ln \gamma_i^{\text{PCC}} = \frac{\mu_i^{\text{PCC}} - \mu_i^{\text{PCC}}}{RT}$ | $\gamma_i^{\text{PCC}}$ is the total vapor pressure of the mixture $\mu_i^{\text{PCC}}$ is the chemical potential of the pure component misfit interaction enthalpy $\mu_i^{\text{PCC}}$ is the hydrogen-bonding enthalpy $\mu_{\text{cosmo}}$ is the COSMO volume $M_i$ is the second $\sigma$-moment of the compound $N_{\text{Ring}}$ is the number of ring atoms in the compound $\text{TS}$ is the pure component entropy at a specific temperature $c_{\text{qsp}}$, $G_{\text{mol}}$, $N_{\text{Ring}}$, $c_{\text{sw}}$, and $c_{\text{c}}$ are the generic parameters for the QSPR approach for liquid viscosity, with energy values in kcal mol$^{-1}$ and areas in Å$^2$ $\mu_i^{\text{PCC}}$ is the activity coefficient of component “i” at infinite dilution $\mu_i^{\text{PCC}}$ is the pseudo-chemical potential of “i” at infinite dilution $\mu_i^{\text{PCC}}$ is the chemical potential of “i” in its pure liquid state $\mu_i^{\text{PCC}}$ is the total vapor pressure of the mixture $x_i$ is the mole fraction of the compounds in the liquid phase $y_i$ is the mole fraction of compounds in the gas phase $e_i$ and $e_i'$ are the binary interaction parameters of the associated constituents $\alpha = \alpha_{i,j} = \alpha_{j,i}$ is the nonrandomness factor that signifies the molecule–molecule or molecule–electrolyte (if any) (default value of 0.3) $A_{i,j}$, $\phi_{i,j}$, $V_{i,j}$, $\theta_{i,j}$, $a_{i,j}$, and $a_{i,j}'$ are binary interaction parameters of the system under study |
Table 2. continued

| sr. no. | property of the system | mathematical equation | description |
|---------|-------------------------|-----------------------|-------------|
| 12      | UNIQUAC 4 model         | ln(γi) = ln(γ∞i) + ln(λi) | “ln(γ∞i)” is the combinatorial contribution signifying the entropic size and shape transformations of the compounds |
|         |                         | ln(γ∞i) = ln \( \frac{\bar{\gamma}}{\bar{\gamma}_i} \) + \( \frac{\bar{\gamma}}{\bar{\gamma}_i} \ln \left( \frac{\bar{\gamma}}{\bar{\gamma}_i} \right) + \frac{\bar{\gamma}}{\bar{\gamma}_i} - \frac{\bar{\gamma}}{\bar{\gamma}_i} \sum_l \gamma_l \) | |
|         |                         | the parametric equations are as follows | |
|         |                         | \( \bar{\Phi} = \frac{\sum_l \gamma_l}{\sum_l \gamma_l} \) | “Φ” and “θ” are the normalized volume and surface area fraction of species “i” in the blended solvent |
|         |                         | \( \bar{\Theta} = \frac{\sum_l \gamma_l}{\sum_l \gamma_l} \) | |
|         |                         | \( l_i = \frac{2}{\gamma} (r - q) - (r - 1) \) | “x_i” is the mole fraction |
|         |                         | the enthalpy interactions among various constituents in the UNIQUAC 4 model are quantified by the residual contribution in the calculation of the activity coefficient; the mentioned term is described as | |
|         |                         | \( \ln(\gamma^0) = q_i \left[ 1 - \ln \left( \frac{\sum_j \Theta_j q_j}{\sum_j \Theta_j q_j} \right) - \sum_j \frac{\Theta_j q_j}{\sum_j \Theta_j q_j} \right] \) | “q_i” is the surface area for each individual species (x_i ≠ x_j) |
|         |                         | the enthalpy, being closely related to temperature, the residual contribution of binary interaction major parameters “e_i” is further taken as an inverse logarithm function of temperature and is given as | |
|         |                         | \( \ln(\gamma) = -\frac{\Delta H_k}{RT} = \frac{\gamma_i}{\bar{\gamma}_i} \) | “p_j” is the vapor pressure of the pure compound |
|         |                         | the compound-specific UNIQUAC volume and surface area parameters are presented as | |
|         |                         | \( r_i = \frac{3V_i^COSMO}{T} \) | “γ_j” is the activity coefficient |
|         |                         | \( q_i = \frac{3A_i^COSMO}{40} \) | “x_i” is the mole fraction |
| 13      | gas solubility          | \( p_j = p_j^0 \times x_i \times r_j \) | “p_j^0” is the partial pressure of compound “j” |
| 14      | Henry’s law coefficient | \( H_j = \exp \left( \frac{\mu_j^{\text{g}} - \mu_j^{\text{m}}}{R \times T} \right) = r_j^{\text{g}} \times p_j^0 \) | “μ_j^{\text{g}}” is the ideal gas-phase chemical potential |

COSMOtherm to evaluate the applicability of the proposed solvents.

2. COMPUTATIONAL METHODS AND THEORY

The molecules under study, i.e., N-methylidethanolamine (MDEA), sulfolane (TMSO), 1-butyl-3-methylimidazolium cation ([bmmim]), acetate anion ([Ac]), H2O, CO2, and 2-methylpiperazine (2-MPZ), were selected within COSMOtherm (COSMOlogic GmbH, Leverkusen, Germany). Single conformers with the least ground-state energy were selected for each of the molecular compounds obtained with BP-TZVPD-FINE-level COSMO calculations that incorporate a full geometry optimization by density functional theory (DFT) using the Becke and Perdew (BP) functional with the triple-ζ valence polarized (TZVP) basis set. The detailed specifications of the chemicals for the experimental work are presented in Table 1. The analysis of σ surface, σ potential, and vapor-liquid equilibrium and estimation of vapor pressure, pure component density and viscosity, infinite dilution activity coefficients, CO2 solubility, Henry’s law coefficient, and pK_a values are carried out over a wide range of temperatures using the respective modules within COSMOtherm. For pK_a calculations, the respective protonated structures of the molecules were developed using TURBOMOLE. All of the estimated values have been presented up to three significant digits after the decimal.

3. RESULTS AND DISCUSSION

The detailed mathematical relationships of various studied parameters with chemical potential are presented in Table 2. The conforming significance of the simulated properties has been considered alongside the analysis results.

3.1. σ Profile and σ Potential Analysis. The intermolecular interactions of the selected solvents among all of the constituents along with CO2 contribute largely toward CO2 solubility. This further hinges on the associated shape, size, polarity, and type of molecules. Chemical potential “μ” of any species in a solution is evaluated using screening charge density “σ” on the surface of molecules through the COSMO-RS theory within three major norms: (i) the liquid state is incompressible, (ii) all fragments of molecular surfaces can be in interaction
with one another, and (iii) individual pairwise interactions of molecular surface areas are permitted. This screening charge density also helps in understanding electrostatic interaction, hydrogen-bonding energy, dispersion, etc. The $\sigma$-profile of any molecule is obtained through the weighted sum of the profiles of all of its included components. $\sigma$ profiles also signify the spreading of screening charge density ($\sigma$) of molecules. This distribution is carried out in three categories: (a) nonpolar region ($-0.0084 \ e\cdot\AA^{-2} < \sigma < 0.0084 \ e\cdot\AA^{-2}$), hydrogen-bond donor (HBD) region ($\sigma < -0.0084 \ e\cdot\AA^{-2}$), and hydrogen-bond acceptor (HBA) region ($\sigma > 0.0084 \ e\cdot\AA^{-2}$).

The $\sigma$ surfaces of H$_2$O, [bmim] cation, [Ac] acetate anion, CO$_2$, 2-MPZ, MDEA, and TMSO$_2$ are shown in Figure 1 along with the energy associated with each molecule. The zones in the figure can be explained as follows. Red: hydrogen-bond acceptor; blue: hydrogen-bond donor; and green: nonpolar section of the molecule. Single conformers with the least ground-state energy associated with the molecule were considered for the current work.

The $\sigma$ profile and the corresponding $\sigma$ potential for the molecules functional to majorly chemical potential are shown in Figure 2. These properties define the attraction of selected solvents with the desired solute, thereby determining the extent of possible separation.

The negative polarities of any molecule are indicated by positive screening charge density in a $\sigma$-scale and vice versa. The least $\sigma$ surface was obtained for H$_2$O in the extensive range of $-0.02 \ e\cdot\AA^{-2}$, and $+0.02 \ e\cdot\AA^{-2}$ specifies the positive and negative polarities of the associated atoms in the H$_2$O molecule. Successively, it can also be seen from Figure 2a that key portions of $\sigma$ charge densities of the [bmim] cation, TMSO$_2$, MDEA, and 2-MPZ are negative and those for CO$_2$ and the [Ac] anion are positive in nature. Further, the peak intensities of MDEA and 2-MPZ are very competitive with each other, indicating the possible high CO$_2$ solubility offered by both. Also, if the peaks of TMSO$_2$ are analyzed, it can be perceived to have a positive and negative $\sigma$ charge density with two sharp peaks. The higher peak is, however, present on the negative side. It can thus be concluded that as CO$_2$ and selected solvents present different charge densities, the selected solvents could provide good CO$_2$ absorption. This conclusion is in agreement with the fact that the negative surface pieces of
[bmim], 2-MPZ, TMSO₂, and MDEA can react essentially with the positive surface pieces of CO₂. Although the [bmim] cation is seen to provide the highest negative surface, on combining it with the associated [Ac] cations’ positive surface, it results in overall less polarity available in comparison to MDEA and 2-MPZ.

The intermolecular interaction of a solvent toward the molecular surface that it comes in contact with polar or nonpolar behavior can be qualitatively discussed in terms of the σ potential. The positive σ potential of CO₂ over the studied charge density of −0.03 to +0.03 eÅ⁻² indicates its capability as a H-bond acceptor (Figure 2b). The σ potential behavior of CO₂ is almost symmetrical and concave in nature over the entire charge density. On the contrary, the parameter is asymmetrical for [bmim], [Ac], 2-MPZ, MDEA, and TMSO₂, leaning more to the negative side of charge density. Additionally, only the [bmim] cation is associated with a positive σ potential in the negative surface charge density region. The molecules signifying a −ve σ potential act as H-bond donors, whereas the +ve σ potential suggests that CO₂ is a H-bond acceptor. However, understanding the [bmim] cation alone does not provide any technical application since, in the present study, it is associated with the [Ac] anion. Combining the chemical potentials of both the [bmim] cation and the [Ac] anion leads to the overall negative charge density, proposing it to be a H-bond donor. The formation or loss of a H bond is usually at the S, N, or O atoms of any molecules. At a molecular level, the possible interaction of CO₂ with any chosen solvent depends highly on the H-bond acceptor or donor capacity. The interaction strength of CO₂ can hence be determined with the order as MDEA > 2-MPZ > [bmim][Ac] > TMSO₂ > H₂O. At a lab or plant scale, the same concept is understood by the reaction mechanism of zwitterions, proton exchange reactions, and formation or dissolution of bicarbonates, unstable/stable dicarbamates, and dicarbamates.

3.2. Vapor Pressure Analysis. The potential applications of any solvent in diverse fields of chemical engineering depend on many important characteristics such as thermal and mechanical stability, low degradation and toxicity levels, the extent of biodegradation offered, recyclability, vapor pressures, etc. Among these many essential features, vapor pressure is considered to be very important for the CO₂ capture process. This is due to the fact that any solvent exhibiting high vapor pressure will lead to huge losses during regeneration. Also, if the vapor pressure is too high, the solubility of CO₂ or other acid solute gases decreases at high temperatures. The latter is because, at high temperatures, the diffusivity is expected to increase considerably. On the other hand, if the vapor pressure is too low, e.g., in the case of pure ionic liquids, the diffusion is also too less at low temperatures. Hence, an optimum vapor pressure is desired combining it with the associated [Ac] cations’ positive surface, it results in overall less polarity available in comparison to MDEA and 2-MPZ.

The intermolecular interaction of a solvent toward the molecular surface that it comes in contact with polar or nonpolar behavior can be qualitatively discussed in terms of the σ potential. The positive σ potential of CO₂ over the studied charge density of −0.03 to +0.03 eÅ⁻² indicates its capability as a H-bond acceptor (Figure 2b). The σ potential behavior of CO₂ is almost symmetrical and concave in nature over the entire charge density. On the contrary, the parameter is asymmetrical for [bmim], [Ac], 2-MPZ, MDEA, and TMSO₂, leaning more to the negative side of charge density. Additionally, only the [bmim] cation is associated with a positive σ potential in the negative surface charge density region. The molecules signifying a −ve σ potential act as H-bond donors, whereas the +ve σ potential suggests that CO₂ is a H-bond acceptor. However, understanding the [bmim] cation alone does not provide any technical application since, in the present study, it is associated with the [Ac] anion. Combining the chemical potentials of both the [bmim] cation and the [Ac] anion leads to the overall negative charge density, proposing it to be a H-bond donor. The formation or loss of a H bond is usually at the S, N, or O atoms of any molecules. At a molecular level, the possible interaction of CO₂ with any chosen solvent depends highly on the H-bond acceptor or donor capacity. The interaction strength of CO₂ can hence be determined with the order as MDEA > 2-MPZ > [bmim][Ac] > TMSO₂ > H₂O. At a lab or plant scale, the same concept is understood by the reaction mechanism of zwitterions, proton exchange reactions, and formation or dissolution of bicarbonates, unstable/stable dicarbamates, and dicarbamates.

### Table 3. Comparison of Experimental and COSMO Predicted Vapor Pressure of Aq (MDEA + 2-MPZ), Aq (TMSO₂ + 2-MPZ), and Aq ([bmim][Ac] + 2-MPZ) Systems

| System          | T (K)  | 303.15 Experimental | 303.15 Predicted | 303.15 %AAD | 313.15 Experimental | 313.15 Predicted | 313.15 %AAD | 323.15 Experimental | 323.15 Predicted | 323.15 %AAD | 333.15 Experimental | 333.15 Predicted | 333.15 %AAD | 343.15 Experimental | 343.15 Predicted | 343.15 %AAD |
|-----------------|--------|---------------------|------------------|------------|---------------------|------------------|------------|---------------------|------------------|------------|---------------------|------------------|------------|---------------------|------------------|------------|
| Aq (MDEA + 2-MPZ) | (3.509 + 0.509) | 48.9 | 38.412 | 62.1 | 68.191 | 109.6 | 115.879 | 16.255 |
| Aq (MDEA + 2-MPZ) | (3.017 + 0.008) | 47.6 | 38.628 | 61.4 | 68.545 | 98.6 | 116.437 |
| Aq (MDEA + 2-MPZ) | (2.502 + 1.509) | 33.1 | 38.856 | 60.7 | 68.917 | 90.3 | 117.023 |
| Aq (TMSO₂ + 2-MPZ) | (3.501 + 0.509) | 56.5 | 38.624 | 65.5 | 68.393 | 111.7 | 115.958 | 15.777 |
| Aq (TMSO₂ + 2-MPZ) | (3.012 + 0.008) | 55.2 | 38.709 | 65.5 | 68.552 | 102.0 | 116.243 |
| Aq (TMSO₂ + 2-MPZ) | (2.500 + 1.509) | 53.8 | 38.829 | 62.1 | 68.767 | 101.4 | 116.614 |
| Aq ([bmim][Ac] + 2-MPZ) | (3.507 + 0.509) | 45.5 | 37.839 | 60.7 | 67.039 | 100.7 | 113.719 | 13.407 |
| Aq ([bmim][Ac] + 2-MPZ) | (3.002 + 1.008) | 44.1 | 38.074 | 60.7 | 67.454 | 101.4 | 114.423 |
| Aq ([bmim][Ac] + 2-MPZ) | (2.510 + 1.509) | 44.1 | 38.306 | 58.6 | 67.863 | 101.4 | 115.116 |
to achieve both absorption and regeneration cost-effectively. Considering that the initial screening of solvents for any application requires major experimental investigations, the cost-effectiveness can be reduced, provided that the proficient prediction methods for such properties are available. In the same line, many researchers have proposed vapor pressure estimation through traditional or modified thermodynamic equations such as PR-EoS, UNIFAC, UNIFAC-Lei, etc.\(^46\)−\(^50\) The efficacy of any such model depends on the number of assumptions made during calculations, in addition to the number of thermodynamic parameters calculated. For the current work, quantum calculations through COSMO-RS are carried out including the combinatorial and residual parametric contributions of the molecules under study. The vapor pressures are estimated using the boiling points of individual pure constituents of the systems under study as the reference point.

### Table 4. COSMO Predicted Antoine Equation Coefficients in Aq (MDEA + 2-MPZ), Aq (TMSO\(_2\) + 2-MPZ), and Aq ([bmim][Ac] + 2-MPZ) Systems\(^a\)

| system                               | concentration (mol kg\(^{-1}\)) | A      | B               | C               |
|--------------------------------------|---------------------------------|--------|-----------------|-----------------|
| aq (MDEA + 2-MPZ)                    | (3.509 + 0.509)                 | 18.101 | 3495.889        | −61.252         |
|                                      | (3.017 + 1.008)                 | 18.106 | 3498.779        | −61.057         |
|                                      | (2.502 + 1.509)                 | 18.112 | 3501.691        | −60.853         |
| aq (TMSO\(_2\) + 2-MPZ)              | (3.501 + 0.509)                 | 18.072 | 3495.181        | −60.728         |
|                                      | (3.012 + 1.008)                 | 18.086 | 3500.407        | −60.568         |
|                                      | (2.500 + 1.509)                 | 18.099 | 3504.717        | −60.426         |
| aq ([bmim][Ac] + 2-MPZ)              | (3.507 + 0.509)                 | 18.065 | 3498.714        | −60.718         |
|                                      | (3.002 + 1.008)                 | 18.083 | 3504.428        | −60.511         |
|                                      | (2.510 + 1.509)                 | 18.097 | 3508.562        | −60.358         |

\(^a\)ln(P) = A − \frac{B}{(T + C)} (P is in millibar and T is in kelvin).

### Table 5. Comparison of Experimental and COSMO Predicted Density (\(\rho\), kg m\(^{-3}\)) of Pure MDEA, TMSO\(_2\), 2-MPZ, and [bmim][Ac]

| system | data | MDEA | 2-MPZ | TMSO\(_2\) | [bmim][Ac] |
|--------|------|------|-------|------------|------------|
| T (K)  |      | \(\rho_{\text{exp}}\) | \(\rho_{\text{pred}}\) | \(\rho_{\text{pred}}\) | \(\rho_{\text{pred}}\) | \(\rho_{\text{exp}}\) | \(\rho_{\text{pred}}\) | \(\rho_{\text{pred}}\) | \(\rho_{\text{pred}}\) |
| 298.15 | 1036.8 | 984.816 | 875.5 | 995.703 | 1013.3 | 1346.294 | 1052.1 | 1067.123 |
| 303.15 | 1032.9 | 979.811 | 872.7 | 990.128 | 1008.1 | 1340.947 | 1049.1 | 1063.032 |
| 308.15 | 1029.2 | 974.833 | 869.8 | 986.363 | 1004.3 | 1335.579 | 1045.9 | 1058.923 |
| 313.15 | 1025.4 | 969.882 | 866.9 | 981.711 | 1000.4 | 1330.191 | 1043.0 | 1054.796 |
| 318.15 | 1020.9 | 964.957 | 863.9 | 977.069 | 996.0 | 1324.783 | 1040.0 | 1050.652 |
| 323.15 | 1017.7 | 960.059 | 860.9 | 972.441 | 992.8 | 1319.356 | 1037.0 | 1046.493 |
| 328.15 | 1012.9 | 955.187 | 857.8 | 967.824 | 988.4 | 1313.911 | 1034.1 | 1042.318 |
| 333.15 | 1009.1 | 950.341 | 854.7 | 963.220 | 985.1 | 1308.450 | 1031.1 | 1038.129 |
| % AAD  | 5.439 | 13.189 | 32.936 | 1.067 |

### Table 6. Comparison of Experimental and COSMO Predicted Viscosity (\(\eta\), mPa s) of Pure MDEA, 2-MPZ, and TMSO\(_2\)

| system | data | MDEA | 2-MPZ | TMSO\(_2\) | [bmim][Ac] |
|--------|------|------|-------|------------|------------|
| T (K)  |      | \(\eta_{\text{exp}}\) | \(\eta_{\text{pred}}\) | \(\eta_{\text{pred,aspen}}\) | \(\eta_{\text{pred,COSMO}}\) | \(\eta_{\text{exp}}\) | \(\eta_{\text{pred}}\) | \(\eta_{\text{pred}}\) |
| 298.15 | 77.75 | 3.839 | 0.47 | 4.462 | 10.28 | 2.917 |
| 303.15 | 56.26 | 3.459 | 0.46 | 4.005 | 10.22 | 2.648 |
| 308.15 | 46.47 | 3.127 | 0.45 | 3.607 | 9.06 | 2.411 |
| 313.15 | 34.66 | 2.836 | 0.43 | 3.259 | 7.84 | 2.202 |
| 318.15 | 28.67 | 2.580 | 0.42 | 2.954 | 6.58 | 2.016 |
| 323.15 | 23.29 | 2.354 | 0.41 | 2.686 | 6.18 | 1.851 |
| 328.15 | 17.42 | 2.154 | 0.40 | 2.449 | 5.19 | 1.705 |
| 333.15 | 14.55 | 1.976 | 0.39 | 2.239 | 4.88 | 1.573 |
| % \(10^{-2} \times AAD\) | 0.911 | 6.405 | 0.707 |

### Table 7. COSMO Predicted Activity Coefficients of MDEA, TMSO\(_2\), and 2-MPZ at Infinite Dilution in Water

| system | data | T (K) | MDEA | TMSO\(_2\) | 2-MPZ |
|--------|------|-------|------|------------|-------|
|        |      | 298.15 | 303.15 | 308.15 | 313.15 | 318.15 | 323.15 | 328.15 | 333.15 |
| \(\gamma^\infty\) |      |       |       |       |       |       |       |       |       |
| MDEA   | 0.671 | 0.823 | 0.997 | 1.193 | 1.411 | 1.650 | 1.909 | 2.186 |
| TMSO\(_2\) | 4.255 | 4.493 | 4.719 | 4.931 | 5.126 | 5.304 | 5.462 | 5.601 |
| 2-MPZ  | 0.246 | 0.305 | 0.375 | 0.455 | 0.549 | 0.655 | 0.774 | 0.908 |
correlated and experimental values of the parameters under study is obtained through calculation of deviation using the following equation

\[
\% \text{ AAD} = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{Y_{\text{exp}} - Y_{\text{mod}}}{Y_{\text{exp}}} \right|
\]  

(1)

where \(N\), \(Y_{\text{exp}}\), and \(Y_{\text{mod}}\) indicate the number of data points, experimental value, and modeled or COSMOtherm estimated value of any variable, respectively.

The vapor pressures of aqueous (aq) (MDEA + 2-MPZ), aq (TMSO2 + 2-MPZ), and aq ([bmim][Ac] + 2-MPZ) have been measured using the validated experimental methodology of our previous work. The measurements have been carried out at 303.15, 313.15, and 323.15 K and a total solvent concentration of 4.0 mol kg\(^{-1}\). The activator 2-MPZ concentration is among the experimental and predicted values of vapor pressures for aq (MDEA + 2-MPZ), aq (TMSO2 + 2-MPZ), and aq ([bmim][Ac] + 2-MPZ) are 16.255, 15.777, and 13.407%, respectively. The deviations obtained through the COSMO-RS theory is quite less when compared to the analytical expressions used for similar estimations. Nonetheless, the obtained deviations can be attributed to the uncertainties associated with the experimental procedure inclusive of variations in temperature, pressure, and compositions, which have been retained constant throughout the experimentation. Also, while performing quantum calculations, such macroscopic deviations are not considered.

### 3.3. Estimation of Pure Component Density and Viscosity

The experimental analysis of pure component density and viscosity has been reported by many researchers for different purposes in carbon capture systems, mainly for estimation of kinetic parameters and pumping costs, concise designing of absorption–stripper columns, understanding the nonideal behavior through analysis of viscosity deviation or excess molar properties, etc. In the present work, pure component density and viscosity are estimated through the quantitative structure–property relationship (QSPR) approach, which consists of many inherent properties of the involved molecules (Table 2). The pure component density and viscosity measurements have been carried out using a density and sound velocity meter (DSA 5000 M, Anton Paar, Austria) and an Anton Paar AMVn rolling ball viscometer with the standard uncertainties of 0.5 kg mol\(^{-1}\) and 0.07 mPa s. The adopted detailed methodology can be referred to from our previous work.

A comparison of the experimental and COSMO estimated density and viscosity of the involved chemical species is presented in Tables 5 and 6. For the case of 2-MPZ, since it is in crystalline form, the experimental measurement was difficult and hence viscosity was estimated using Aspen plus and

| System | Temperature (K) | Estimated Parameters |
|--------|-----------------|----------------------|
| **Table 8. COSMO Predicted NRTL Parameters for the Activity Coefficients in (H\(_2\)O (1) + MDEA (2) + 2-MPZ (3)), (H\(_2\)O (1) + TMSO2 (2) + 2-MPZ (3)), and (H\(_2\)O (1) + [bmim][Ac] (2) + 2-MPZ (3)) Systems** |
| **system** | **T (K)** | **aq (MDEA + 2-MPZ)** | **aq (TMSO2 + 2-MPZ)** | **aq ([bmim][Ac] + 2-MPZ)** |
|-----------|------------|----------------------|----------------------|----------------------|
| **λ\(_{12}\)** | 303.15 | 313.15 | 323.15 | 303.15 | 313.15 | 323.15 | 303.15 | 313.15 | 323.15 |
| **λ\(_{13}\)** | 0.233 | 0.221 | 0.224 | 0.210 | 0.232 | 0.258 | 11.673 | 10.800 | 10.011 |
| **λ\(_{23}\)** | 4.132 | 3.878 | 3.658 | 4.199 | 3.944 | 3.719 | 4.251 | 3.838 |
| **λ\(_{21}\)** | 1.817 | 1.731 | 1.641 | 0.518 | 0.525 | 0.528 | 5.144 | 4.904 | 4.675 |
| **λ\(_{31}\)** | 0.865 | 0.918 | 0.964 | 0.223 | 0.250 | 0.276 | 0.376 | 0.381 | 0.384 |
| **λ\(_{32}\)** | 1.209 | 1.103 | 0.994 | 1.259 | 1.126 | 0.994 | 1.247 | 1.173 | 1.098 |
| **λ\(_{32}\)** | 0.315 | 0.327 | 0.347 | 0.275 | 0.319 | 0.361 | 0.087 | 0.099 | 0.112 |
| **RMSD** | 0.329 | 0.309 | 0.291 | 0.394 | 0.378 | 0.355 | 0.749 | 0.687 | 0.630 |

| **Table 9. COSMO Predicted WILSON Parameters for the Activity Coefficients in (H\(_2\)O (1) + MDEA (2) + 2-MPZ (3)), (H\(_2\)O (1) + TMSO2 (2) + 2-MPZ (3)), and (H\(_2\)O (1) + [bmim][Ac] (2) + 2-MPZ (3)) Systems** |
| **system** | **T (K)** | **aq (MDEA + 2-MPZ)** | **aq (TMSO2 + 2-MPZ)** | **aq ([bmim][Ac] + 2-MPZ)** |
|-----------|------------|----------------------|----------------------|----------------------|
| **τ\(_{12}\)** | 303.15 | 313.15 | 323.15 | 303.15 | 313.15 | 323.15 | 303.15 | 313.15 | 323.15 |
| **τ\(_{13}\)** | 0.223 | 0.221 | 0.224 | 0.210 | 0.232 | 0.258 | 11.673 | 10.800 | 10.011 |
| **τ\(_{23}\)** | 4.132 | 3.878 | 3.658 | 4.199 | 3.944 | 3.719 | 4.251 | 3.838 |
| **τ\(_{21}\)** | 1.817 | 1.731 | 1.641 | 0.518 | 0.525 | 0.528 | 5.144 | 4.904 | 4.675 |
| **τ\(_{31}\)** | 0.865 | 0.918 | 0.964 | 0.223 | 0.250 | 0.276 | 0.376 | 0.381 | 0.384 |
| **τ\(_{32}\)** | 1.209 | 1.103 | 0.994 | 1.259 | 1.126 | 0.994 | 1.247 | 1.173 | 1.098 |
| **τ\(_{32}\)** | 0.315 | 0.327 | 0.347 | 0.275 | 0.319 | 0.361 | 0.087 | 0.099 | 0.112 |
| **RMSD** | 0.329 | 0.309 | 0.291 | 0.394 | 0.378 | 0.355 | 0.749 | 0.687 | 0.630 |

https://dx.doi.org/10.1021/acsomega.0c05298
ACS Omega 2021, 6, 747–761
The estimation of IDACs of aqueous, non-aqueous, organic, or ionic liquid systems, through COSMO- 
RS, is reported in the literature to be very efficient owing to the 
reason the same being evaluated in the absence of mean-
field approximation. The nonpolarity or active polarity of a 
compound is decided by the higher or lower value of IDACs in 
the system (Table 2). Table 7 presents the COSMO predicted 
infinitesimal activity coefficients of MDEA, 2-MPZ, and 
TMSO2 in H2O as a function of temperature in the range of 
298.15−333.15 K. With an increase in the temperature, IDACs of 
MDEA, TMSO2, and 2-MPZ in water were found to increase. 
Although the IDACs values for MDEA and 2-MPZ are very low 
in comparison to the TMSO2 values, for the currently studied 
solvent. The chemical potential is also considered a sum total 
of energy such as internal, density, temperature, enthalpy, etc., of any mole-
ule. This indicates the dependency of acid−gas separations at 
a molecular level on the thermodynamic properties such as 
chemical potential, enthalpy, Gibbs’ free energy, etc.

Henceforth, the vapor−liquid equilibrium of the ternary 
mixtures of aq (MDEA + 2-MPZ), aq (TMSO2 + 2-MPZ), and 

aq ([bmm][Ac] + 2-MPZ) related to the nonlinear behavior of the various constituents involved is determined using the COSMO-RS theory. The VLE estimated through COSMO is based on the vapor pressure and activity coefficients of individual pure constituents in the mixture (Table 2). The VLE is additionally modeled using NRTL, WILSON, and UNIQUAC 4 models. The obtained VLE data is presented in the form of activity coefficients, excess Gibbs free energy, excess enthalpy, chemical potential, and individual partial pressures associated with each system at 303.15, 313.15, and 323.15 K. The total pressures of the aq (MDEA + 2-MPZ), aq (TMSO2 + 2-MPZ), and aq ([bmm][Ac] + 2-MPZ) systems are taken to be 0−124 mbar. The difference between the COSMO and NRTL/WILSON/UNIQUAC 4 model predicted activity coefficients is calculated in terms of the root-mean-square deviation (RMSD) using the following equation

\[ \text{RMSD} = \sqrt{\frac{\sum_{i=1}^{n} (\gamma_{\text{COSMO}} - \gamma_i)^2}{n}} \]  

where \( \gamma_{\text{COSMO}} \) is the COSMO predicted property and \( \gamma_i \) is the NRTL, WILSON, or UNIQUAC predicted property value.

The activity coefficients and binary interaction parameters for NRTL, WILSON, and UNIQUAC 4 models of the systems under study were estimated and are presented in Tables 8, 9, and 10, respectively. The majority of the binary interaction parameters of the studied systems are found to be different because the systems are asymmetric, i.e., \( \tau_{ij} \neq \tau_{ji} \).

The obtained results are presented graphically for aq (MDEA + 2-MPZ), aq (TMSO2 + 2-MPZ), and aq ([bmm][Ac] + 2-MPZ) in Figures 4, 5, and 6, respectively. The mole fraction of water is 0.7 for the presented data. The activity coefficients of 2-MPZ are found to be very less when compared to MDEA and H2O (Figure 4a). The temperature dependency of the parameter is observed not to be high. Also, as a function of the MDEA concentration, the activity coefficients of 2-MPZ were found to show an inverse relationship. However, for both MDEA and H2O, it does not change much. Insignificant deviations of \( H^E \) (excess enthalpy) and \( G^E \) (excess Gibbs free energy) with respect to the temperature change from 303.15 to 323.15 K are observed (Figure 4b). Nevertheless, both the properties were found to have negative values that increase as a function of the MDEA concentration. The
−ve $G^\circ$ indicates the spontaneous mixing because of the thermodynamic driving forces between the involved components and $−ve H^\circ$ indicates an exothermic reaction/mixing in both the systems that are proven by the values of heat of absorption.$^{66,67}$ The chemical potential, on the other hand, is observed to be more temperature-dependent. The values of $\mu_{H_2O}$ remain almost unchanged. Decreasing the concentration of 2-MPZ results in high chemical potential of MDEA and vice versa (Figure 4c).

Similarly, with respect to the TMSO$_2$ concentration, the activity coefficients of TMSO$_2$ and H$_2$O are observed to decrease and increase slightly simultaneously as a function of TMSO$_2$ (Figure 5a). The behavior of 2-MPZ is similar to that found for the aq (MDEA + 2-MPZ) system. The behavior of all three systems with respect to chemical potential is found to be very similar (Figures 5c and 6c). The activity coefficients for [bmm][Ac] are very less when compared to 2-MPZ and H$_2$O at any given concentration (Figure 6a). This is also expected due to the lesser chemisorption but greater physisorption behavior conferred by the ionic liquid to the acid gas. Also, though the $H^\circ$ and $G^\circ$ values obtained in the aq ([bmm][Ac] + 2-MPZ) system are negative but are a function of [bmm][Ac], the values are found to further decrease unlike those for the other two systems (Figure 6b).

### 3.6. CO$_2$ Solubility in Aq (MDEA + 2-MPZ), Aq (TMSO$_2$ + 2-MPZ), and Aq ([bmim][Ac] + 2-MPZ)

The experimental measurement at the lab scale or estimation of CO$_2$ solubility in suitable solvents has been a key research area for application.$^{29,34}$ Considering the lower partial pressures of CO$_2$ in the flue gas stream, the CO$_2$ solubility has been predicted using the activity coefficients estimated through COSMO-RS over the temperature and pressure range of 303.15−323.15 K and 1.0−3.0 bar for aq (MDEA + 2-MPZ), aq (TMSO$_2$ + 2-MPZ), and aq ([bmim][Ac] + 2-MPZ) systems at varying compositions. The solubilities are presented in terms of the mole fraction of CO$_2$ in the liquid phase ($x_{CO_2}$). An inverse relationship between the CO$_2$ solubility and temperature for all of the studied solvent blends was observed (Figure 7). Further, although increasing the CO$_2$ pressure as well as the activator 2-MPZ concentration in all solvents resulted in an increase in CO$_2$ solubility (Table 1), however, in the case of the aq (MDEA + 2-MPZ) system, CO$_2$ solubility is observed to be almost similar over the chosen compositional range. This may be attributed to the fact that MDEA is a tertiary amine when compared with TMSO$_2$ and [bmim][Ac], which have higher CO$_2$ solubility. Hence, with the increasing concentration of 2-MPZ in the aqueous blends of (MDEA + 2-MPZ), the concentration of MDEA is also simultaneously decreased. Hence, the CO$_2$ solubility at high MDEA concentration can be understood to be compensated by a decrease in the 2-MPZ concentration. Decisively, the highest CO$_2$ solubility is observed for the aq (MDEA + 2-MPZ) concentration at 303.15 K. However, it should be also considered that there may be a deviation when the same solvents are studied experimentally for CO$_2$ absorption. This discrepancy may be attributed to variables affecting the process, nonideality associated with gas and liquid phases, vapor pressures, temperature, maintenance of the partial pressure in the system, etc.

### 3.7. Estimation of Henry’s Constant in CO$_2$ and N$_2$O and Free Energy of Solvation

Henry’s constant signifies the physical solubility conferred by any solvent selectively to a gas that can either be measured experimentally or through the mathematical expressions available in the literature.$^{68} H_{CO_2}$ or $H_{N_2O}$ is a contributive property through misfit in the intermolecular interactions, hydrogen bonding, and van der Waals forces of attraction. The estimation of Henry’s law coefficient involves the estimation of solvation free energies, which are
further related to the chemical potential associated with the gas and solvent at a specified temperature and pressure (Table 2). The calculated results are reported in Figure 8 and Table 12 for all of the systems under study. A low value of Henry’s law coefficient indicates a higher CO₂ solubility. It can thus be inferred from the obtained results that increasing the concentration of 2-MPZ from ≈0.5 to ≈1.5 mol·kg⁻¹, for all base solvents of TMSO₂ and [bmim][Ac], yields an increase of physical solubility, whereas the maximum physical solubility in the case of aq (MDEA + 2-MPZ) is obtained at a 1.008 mol·kg⁻¹ concentration of 2-MPZ. Increasing the 2-MPZ concentration further in the aq (MDEA + 2-MPZ) system results in a decrease in physical solubility that may be owing to the fact that the number of amino groups in the overall blend has increased, which majorly contributes to chemical solubility. Further, the solubilities are found to be much higher at low temperatures for all systems. Henry’s law coefficients for CO₂ and N₂O are obtained in the order: aq (MDEA + 2-MPZ) > aq (TMSO₂ + 2-MPZ) > aq ([bmim][Ac] + 2-MPZ) systems.

3.8. Estimation of the Dissociation Constant (pKₐ) of MDEA and 2-MPZ. Proton exchange is considered to be one of the major reactions that occur during the interaction between CO₂ and amines.²⁶⁹ This proton exchange reaction rate constant is often described using the dissociation constant (pKₐ) of the reaction. The −ve log of pKₐ of conjugate acid reveals the extent of basicity offered by the chosen solvent. The above property can be either measured experimentally using the acid–base titration method or can also be predicted using quantum methods. The dissociation constants of 2-MPZ and MDEA have been calculated using COSMO. Initially, single conformers with ground-state energy were selected. The selected geometry was then edited to create a cationic structure of the same. Further, this cationic structure was optimized to calculate the energy using Turbomole software. The generated cationic structures along with the optimized energy are presented in Figure 9. Based on the free-energy change in any molecule and corresponding cationic structure, the pKₐ values were estimated in water, acetonitrile, and tetrahydrofuran solvents. The predicted pKₐ values of MDEA and 2-MPZ are given in Table 13 at 25 °C. Simulated results show that the pKₐ values of 2-MPZ are relatively higher compared with MDEA in all solvents, demonstrating it to have the possibility of enhanced CO₂ solubility.

### Table 11. COSMO Predicted CO₂ Solubility (100 × x) from 1.0 to 3.0 Bar Pressure in the Temperature Range of 303.15–323.15 K

| (MDEA + 2-MPZ) (mol·kg⁻¹) | (TMSO₂ + 2-MPZ) (mol·kg⁻¹) | ([bmim][Ac] + 2-MPZ) (mol·kg⁻¹) |
|-----------------------------|-----------------------------|----------------------------------|
| 3.509 + 0.509               | 3.501 + 0.509               | 3.507 + 0.509                    |
| 1.0 0.069 0.058 0.049       | 0.054 0.045 0.039           | 0.054 0.045 0.039                |
| 1.5 0.103 0.086 0.074       | 0.081 0.068 0.058           | 0.081 0.068 0.058                |
| 2.0 0.137 0.115 0.099       | 0.108 0.091 0.078           | 0.108 0.091 0.078                |
| 2.5 0.171 0.144 0.123       | 0.135 0.113 0.097           | 0.135 0.113 0.097                |
| 3.0 0.205 0.172 0.148       | 0.162 0.136 0.116           | 0.162 0.136 0.116                |
| (3.017 + 1.008) 1.0 0.069 0.058 0.049 | (3.012 + 1.008) 0.056 0.047 0.040 | (3.002 + 1.008) 0.056 0.047 0.040 |
| 1.5 0.103 0.087 0.074       | 0.084 0.071 0.061           | 0.084 0.070 0.060                |
| 2.0 0.137 0.115 0.099       | 0.112 0.094 0.081           | 0.111 0.094 0.080                |
| 2.5 0.171 0.144 0.123       | 0.141 0.118 0.101           | 0.139 0.117 0.100                |
| 3.0 0.205 0.173 0.148       | 0.169 0.142 0.121           | 0.167 0.140 0.120                |
| (2.502 + 1.509) 1.0 0.069 0.058 0.049 | (2.500 + 1.509) 0.058 0.049 0.042 | (2.510 + 1.509) 0.058 0.049 0.042 |
| 1.5 0.103 0.086 0.074       | 0.088 0.074 0.063           | 0.087 0.073 0.063                |
| 2.0 0.137 0.115 0.099       | 0.117 0.098 0.084           | 0.116 0.097 0.083                |
| 2.5 0.171 0.144 0.123       | 0.146 0.122 0.105           | 0.144 0.121 0.104                |
| 3.0 0.205 0.173 0.148       | 0.175 0.147 0.126           | 0.173 0.146 0.125                |

“x is the mole fraction of CO₂ in the loaded solvent.

Figure 8. COSMO predicted Henry’s constant of CO₂ and N₂O in (a) aq (MDEA + 2-MPZ), (b) aq (TMSO₂ + 2-MPZ), and (c) aq ([bmim][Ac] + 2-MPZ) systems as a function of composition and temperature.
Table 12. COSMO Predicted Henry’s Constant (H, bar) and Gibbs’ Free Energy of Solvation (∆G, kcal·mol⁻¹) in the Temperature Range of 303.15–323.15 K

| aq (MDEA + 2-MPZ) (mol·kg⁻¹) | T (K) | aq (TMSO₂ + 2-MPZ) (mol·kg⁻¹) | T (K) | aq ([bmm][Ac] + 2-MPZ) (mol·kg⁻¹) | T (K) |
|-----------------------------|------|-----------------------------|------|--------------------------------|------|
| CO₂ H 303.15 1.067 8.683 | 303.15 | 1396.815 | 313.15 | 1572.858 | 323.15 | 1741.921 | 3.057 + 0.509 | 1400.345 | 1575.528 | 1744.370 |
| ∆G 4.363 4.368 | 1.067 | 0.509 | 4.364 | 4.368 | 4.793 |
| N₂O H 2-MPZ | 303.15 | 1100.644 | 1238.922 | 313.15 | 1371.935 | 323.15 | 1371.935 |
| ∆G 4.219 | 4.363 | 4.368 | 4.379 |
| CO₂ H 2-MPZ | 303.15 | 1097.466 | 1235.339 | 313.15 | 1368.044 | 323.15 | 1368.044 |
| ∆G 4.217 | 4.333 | 4.546 |
| CO₂ H 2-MPZ | 303.15 | 1099.129 | 1237.204 | 313.15 | 1370.175 | 323.15 | 1370.175 |
| ∆G 4.218 | 4.431 | 4.540 |
| N₂O H 2-MPZ | 303.15 | 918.970 | 1050.473 | 313.15 | 1179.077 | 323.15 | 1179.077 |
| ∆G 4.110 | 4.329 | 4.542 |
| CO₂ H 2-MPZ | 303.15 | 1054.550 | 1208.024 | 313.15 | 1358.521 | 323.15 | 1358.521 |
| ∆G 4.193 | 4.416 | 4.633 |

1 bar of gas per 1 mol of solvent is taken as the reference state for the H and ∆G calculation.

4. CONCLUSIONS

A comprehensive thermodynamic analysis through the COSMO-RS theory has been carried out for the proposed enhanced CO₂ solubility by 2-methylpiperazine in aqueous solvents of N-methyldiethanolamine, sulfolane, and 1-butyl-2-methylimidazolium acetate. The appositeness of chosen solvents, i.e., MDEA, TMSO₂, and [bmm][Ac], and their blends with 2-MPZ is determined using σ potential and σ surface analyses. The results indicate the suitability of 2-MPZ for a variety of solvents under study. Conclusively, the aqueous blend of MDEA and 2-MPZ is preferred over other solvents. Vapor pressures of the solvents, pure component density, and viscosity are also simulated and compared with experimental data, indicating a featured calculation through the involved method. The minimum deviations for estimation of vapor pressure and density for [bmm][Ac] with % AAD are 13.407 and 1.067, respectively. Additionally, activity coefficients of thermodynamic models, viz., NRTL, WILSON, and UNIQUAC 4 model parameter sets, are assessed for aq (MDEA + 2-MPZ), aq (TMSO₂ + 2-MPZ), and aq ([bmm][Ac] + 2-MPZ) systems. The nonideal behavior of the systems is indicated by the simulated values of infinite dilution activity coefficients, activity coefficient, excess enthalpy, excess Gibbs’ free energy, and chemical potential. CO₂ solubility in all of the solvents is predicted at 303.15–323.15 K and 1.0–3.0 bar pressure. Moreover, COSMO anticipated pKₐ values of MDEA and 2-MPZ indicate a higher pKₐ value for 2-MPZ than MDEA. This further confirms the expected higher CO₂ solubility in 2-MPZ when compared with MDEA.

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank Pandit Deendayal Petroleum University, Gandhinagar, India, for providing the necessary computational and experimentation facilities.

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Figure 9. Turbomole optimized generated (a) N-methyldiethanol-amine cation and (b) 2-methylpiperazine cation.

### Table 13. pKₐ Values of MDEA and 2-MPZ at 298.15 K in Various Solvents

| solvent | pKₐ | acetonitrile | tetrahydrofuran |
|---------|-----|-------------|-----------------|
| MDEA    | 3.758 | 12.176      | 8.836           |
| 2-MPZ   | 5.885 | 14.333      | 10.387          |

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