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Comprehensive analysis of thermodynamic models for CO_2 absorption into a blended N,N-diethylethanolamine-1,6-hexamethyl diamine (DEEA-HMDA) amine

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Abstract

In this work, CO_2 equilibrium solubility of 1M *N*,*N*-diethylethanolamine (DEEA):2M 1,6-hexamethyl diamine (HMDA), 1.5M DEEA:1.5M HMDA and 2M DEEA:1M HMDA was studied with a temperature range of 298–333 K and CO_2 partial pressure range of 8–100 kPa. Seven thermodynamic models including Empirical model, Kent and Eisenberg (KE) model, Hu–Chakma model, Austgen model, Helei Liu model, Liu et al. model, and Li–Shen model were developed by correlating reaction equilibrium constants with observed equilibrium solubility of CO_2 in mixed amine solvents. The evaluation of those models was conducted in terms of the average absolute relative deviation (AARD). The results indicated that Liu et al. model considering T, [Amine], P_{total} and [CO_2(aq)] can better represent this complex system with an AARD of 8.06%. Meanwhile, comprehensive comparison and analysis were also performed to identify the contribution of parameters to develop models, which could provide a guideline for the development of accurate thermodynamic models for representation of thermodynamic behaviors.

KEYWORDS

blended amine, CO_2 equilibrium solubility, DEEA-HMDA, thermodynamic models

1 | INTRODUCTION

Since the industrial revolution, human beings have become increasingly dependent on fossil fuels for their development. The emission of large amounts of CO_2 due to the consumption of fossil energy is the main cause that triggers the greenhouse effect, such as melting glaciers, rising sea levels, etc.[1] In the short term, fossil energy sources (oil, gas, and especially coal) would continue to dominate the global energy structure.[2] Carbon capture, utilization and storage (CCUS) technology is gradually coming into focus in response to climate change. Currently, researchers have discovered a variety of methods to capture CO_2, such as membrane separation, low-temperature distillation, solid material adsorption, chemical absorption, etc.[3] The amine-based chemical absorption has not only a high decarbonization capacity and high selectivity, but also has a low energy consumption, which is considered as a promising technology for achieving a goal of CO_2 reduction.

Monoethanolamine (MEA), methyl diethanolamine (MDEA), diethanolamine (DEA), Piperazine (PZ), and 2-amino-2-methyl-1-propanol (AMP) are the most widely used amine solvents. However, each amine has its disadvantages. Therefore, single-amine solvents still do not meet the need of improving CO_2 capture performance and reducing energy requirements in regeneration.[4–7] Therefore, combining the advantages of various amine types is needed to further enhance their performance.[8] For example, PZ was mixed with MEA,

Abbreviations: AMP, 2 amino-2-methyl-1-propanol; BAE, butyl ethanolamine; DEA, diethanolamine; DEAB, 4 diethylamino-2-butanol; DEEA, *N*,*N*-diethylethanolamine; DMAB, 4 (dimethylamino)-2-butanol; DPAB, 4 (dipropylamino)-2-butanol; EAE, *N*-ethylethanolamine; HEEAB, 4((2-hydroxyethyl)(ethyl)amino)-2-butanol; HEMAB, 4 ((2-hydroxyethyl)(methyl) amino)-2-butanol; HMDA, 1,6-hexamethyl diamine; MDEA, methyl diethanolamine; MEA, monoethanolamine; PZ, piperazine; 1DEA2P, 1-diethylamino-2-propanol; 1DMA2P, 1-dimethylamino-2-propyl alcohol; 3DMA1P, 3-dimethylamino-1-propanol.

MDEA, and AMP to study their CO_2 absorption capacity.[9] It was found that the addition of PZ could greatly improve the absorption rate and capacity of CO_2. The absorption–desorption ability of CO_2 was studied by mixing MEA with tertiary amines.[10] It was found that mixing MEA with 1-diethylamino-2-propanol (1DMA2P) increased the absorption capacity, the absorption–desorption rate, and the recycling capacity of monoamines. Other researchers investigated the triamine blends, MEA-EAE-AMP and MEA-BAE-AMP that greatly improve CO_2 absorption capacity.[11] These amine mixtures can improve the CO_2 capture performance of monoamines to some extent, but they still have some problems, such as slow absorption, high energy consumption and high viscosity. To address the disadvantages of current amine solvent blends, new amine solvent blends are needed for combination.

A promising blended amine of *N*,*N*-diethylethanolamine-1,6-hexamethyl diamine (DEEA-HMDA) has attracted more attention as it provides excellent absorption–desorption and kinetic performance.[12–14] However, before the industrial application of DEEA-HMDA, it is necessary to determine the vapor–liquid balance data (VLE data) of the system, which is an important parameter to evaluate the CO_2 absorption performance and design the absorber. In order to correlate VLE data, some thermodynamic models are proposed for accurate prediction of VLE data. Therefore, the study and development of thermodynamic models for the DEEA-HMDA-CO_2-H_2O system are essential to describe the thermodynamic behaviors.

Kent and Eisenberg (KE) model including temperature parameter was used to correlate CO_2 solubility in sodium glycine aqueous solution and blended PZ-AMP, with AARD less than 10%.[15,16] Austgen model was used to predict the CO_2 equilibrium solubility of 3DMA1P and 1DMA2P with AARDs of 11.2% and 15%, respectively.[17,18] To enhance accuracy of model, Helei Liu model with parameters of T and free amine concentration ([Amine]) was used to predict CO_2 equilibrium solubility of seven tertiary amines with an AARD range from 1.7% to 24.8%.[19] Hu–Chakma model with the introduction of T, [Amine] and CO_2 physical solubility ([CO_2(aq)]) was used to predict the CO_2 equilibrium solubility of 3DMA1P, 1DMA2P, and DEAB, with all AARD less than 10%.[17,18,20] Li–Shen model contains parameters of T, [Amine], and α_{exp}. The model was used to predict the CO_2 equilibrium solubility of tertiary amine and AMP + PZ solution, where the minimum AARD value was 3.2% and the maximum AARD value was 66.4%.[19,21,22] In Liu et al. model, the parameters such as T, the system's total pressure (P_{total}), [CO_2(aq)] and [Amine] were considered. The CO_2 absorption solubility of nine tertiary amines was predicted with AARD all less than 10%.[17–19] Therefore, it could be that the prediction performance varied with the change of different thermodynamic models as well as different amine systems. Thus, it is essential to investigate the effect of parameters on prediction performance of models and develop proper thermodynamic models that can fully and completely describe a complex reaction system.

In this work, CO_2 equilibrium solubility of 1M DEEA:2M HMDA, 1.5M DEEA:1.5M HMDA, and 2M DEEA:1M HMDA with a temperature range of 298–333 K and CO_2 partial pressure of 8–100 kPa were fully investigated. In order to correlate observed results, several thermodynamic models including Empirical model, KE model, Austgen model, Li–Shen model, Hu–Chakma model, Helei Liu model, and Liu et al. model were employed and presented with the evaluation in terms of AARD. Meanwhile, the prediction results of different models were comprehensively analyzed to identify parameters that can better reflect the theoretical system and describe thermodynamic behaviors. This also could provide a guidance or framework for the establishment of a more accurate thermodynamic model and better description of thermodynamic behavior.

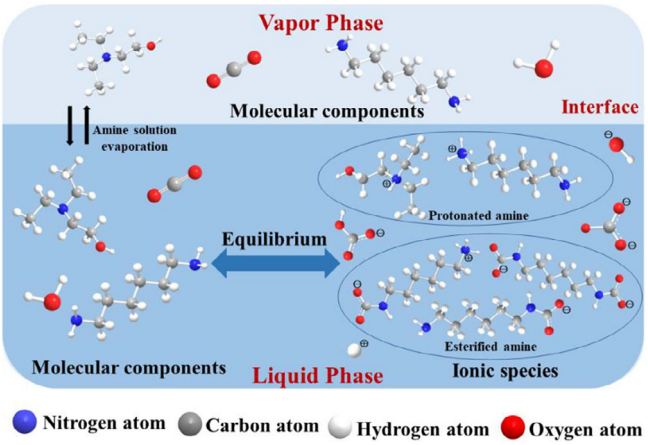

FIGURE 1 Schematic diagram of the CO_2 absorption process of *N*,*N*-diethylethanolamine-1,6-hexamethyl diamine (DEEA-HMDA) mixed amines.

2 | THEORETICAL SECTION

2.1 | Reaction mechanism

Chemical reactions involved in the CO_2 absorption into DEEA-HMDA solution were described as follows:

$$DEEAH^+ \overset{K_1}{\leftrightarrow} DEEA + H^+ \quad (1)$$

$$HMDAH^+ \overset{K_2}{\leftrightarrow} HMDA + H^+ \quad (2)$$

$$HMDA + CO_2 \overset{K_3}{\leftrightarrow} HMDACOO^- + H^+ \quad (3)$$

$$HMDACOO^-H^+ \overset{K_4}{\leftrightarrow} HMDACOO^- + H^+ \quad (4)$$

$$HMDACOO^- + CO_2 \overset{K_5}{\leftrightarrow} HMDA(COO^-)_2 + H^+ \quad (5)$$

$$CO_2 + H_2O \overset{K_6}{\leftrightarrow} HCO_3^- + H^+ \quad (6)$$

$$HCO_3^- \overset{K_7}{\leftrightarrow} CO_3^{2-} + H^+ \quad (7)$$

$$H_2O \overset{K_8}{\leftrightarrow} OH^- + H^+ \quad (8)$$

In this system, the presence of two amino groups of HMDA made this reaction system product more components, which made it more complex as indicated in Figure 1.

The various substances result from CO_2 absorption all follow laws of mass balance, charge balance, which were expressed as follows:

Mass balance of DEEA:

$$[\mathrm{DEEA}]_t = \left[\mathrm{DEEAH}^+\right] + [\mathrm{DEEA}] \tag{9}$$

HMDA mass balance:

$$[\mathrm{HMDA}]_t = \left[\mathrm{HMDAH}^+\right] + [\mathrm{HMDACOO}^-] + \left[\mathrm{HMDACOO}^-\mathrm{H}^+\right] + [\mathrm{HMDA}] + \left[\mathrm{HMDA}(\mathrm{COO}^-)_2\right] \tag{10}$$

Carbon mass balance:

$$([\mathrm{DEEA}]_t + [\mathrm{HMDA}]_t)\cdot\alpha_{CO_2} = \left[\mathrm{HCO}_3^-\right] + \left[\mathrm{CO}_3^{2-}\right] + [\mathrm{CO}_2] + [\mathrm{HMDACOO}^-] + \left[\mathrm{HMDACOO}^-\mathrm{H}^+\right] + \left[\mathrm{HMDA}(\mathrm{COO}^-)_2\right] \tag{11}$$

Charge balance:

$$\left[\mathrm{H}^+\right] + \left[\mathrm{DEEAH}^+\right] + \left[\mathrm{HMDAH}^+\right] = \left[\mathrm{HCO}_3^-\right] + 2\cdot\left[\mathrm{CO}_3^{2-}\right] + [\mathrm{OH}^-] + [\mathrm{HMDACOO}^-] + 2\cdot\left[\mathrm{HMDA}(\mathrm{COO}^-)_2\right] \tag{12}$$

where, $[\mathrm{DEEA}]_t$ and $[\mathrm{HMDA}]_t$ are the initial concentrations of DEEA and HMDA, respectively; α_{CO_2} is the loading of CO_2 in mixed amine solution; $[CO_2]$ is the physical solubility of CO_2 and can be calculated from Henry's law equation as follow:

$$P_{CO_2} = \mathrm{He}\cdot[\mathrm{CO}_2] \tag{13}$$

where P_{CO_2} is the partial pressure of CO_2, He represents Henry's law constant, which can be calculated as Equation (14)[21]:

$$\mathrm{He} = \exp\left(22.2819 - \frac{1.38306\times10^4}{T} + \frac{6.9135\times10^6}{T^2} - \frac{1.559\times10^9}{T^3} + \frac{1.2004\times10^{11}}{T^4}\right) \tag{14}$$

2.2 | Thermodynamic models development

In this work, the thermodynamic model of the blended DEEA-HMDA was developed with the introduction of the expressions of K_i, which could be adjusted by the introduction of more parameters into K_i expressions from a basic mode of KE model as shown in Table 1. And then, all K_i expressions were used to build the models based on the observed results of CO_2 solubility and reaction mechanism.

All reaction equilibrium equations, mass balance equations, and experimental CO_2 equilibrium solubility were solved by using the software. As a result, the calculated values of CO_2 equilibrium solubility could be generated. The specific process was as follows:

According to Equations (1)–(8), reaction equilibrium constants of K_1–K_8 can be expressed as follows:

$$K_1 = \frac{[\mathrm{DEEA}]\cdot\left[\mathrm{H}^+\right]}{\left[\mathrm{DEEAH}^+\right]} \tag{15}$$

$$K_2 = \frac{[\mathrm{HMDA}]\cdot\left[\mathrm{H}^+\right]}{\left[\mathrm{HMDAH}^+\right]} \tag{16}$$

$$K_3 = \frac{[\mathrm{HMDACOO}^-]\cdot\left[\mathrm{H}^+\right]}{[\mathrm{HMDA}]\cdot[\mathrm{CO}_2]} \tag{17}$$

$$K_4 = \frac{[\mathrm{HMDACOO}^-]\cdot\left[\mathrm{H}^+\right]}{\left[\mathrm{HMDACOO}^-\mathrm{H}^+\right]} \tag{18}$$

$$K_5 = \frac{\left[\mathrm{HMDA}(\mathrm{COO}^-)_2\right]\cdot\left[\mathrm{H}^+\right]}{[\mathrm{HMDACOO}^-]\cdot[\mathrm{CO}_2]} \tag{19}$$

$$K_6 = \frac{\left[\mathrm{HCO}_3^-\right]\cdot\left[\mathrm{H}^+\right]}{[\mathrm{CO}_2]} \tag{20}$$

$$K_7 = \frac{\left[\mathrm{CO}_3^{2-}\right]\cdot\left[\mathrm{H}^+\right]}{\left[\mathrm{HCO}_3^-\right]} \tag{21}$$

$$K_8 = \left[\mathrm{H}^+\right]\cdot[\mathrm{OH}^-] \tag{22}$$

Empirical formulas of reaction equilibrium constants K_2, K_4, K_6, K_7, and K_8 can be obtained from the literature,[21,23] which are expressed as follows:

$$K_2 = \exp\left(-1.6664 - \frac{7001.6}{T}\right) \tag{23}$$

$$K_4 = \exp\left(-1.847 - \frac{7986}{T}\right) \tag{24}$$

$$K_6 = \exp\left(-241.818 + \frac{29.8253\times10^4}{T} - \frac{1.48528\times10^8}{T^2} + \frac{0.332647\times10^{11}}{T^3} - \frac{0.282393\times10^{13}}{T^4}\right) \tag{25}$$

$$K_7 = \exp\left(-294.74 + \frac{36.4385\times10^4}{T} - \frac{1.84157\times10^8}{T^2} + \frac{0.415792\times10^{11}}{T^3} - \frac{0.354291\times10^{13}}{T^4}\right) \tag{26}$$

$$K_8 = \exp\left(39.5554 - \frac{9.879\times10^4}{T} + \frac{0.568827\times10^8}{T^2} - \frac{0.146451\times10^{11}}{T^3} + \frac{0.136145\times10^{13}}{T^4}\right) \quad (27)$$

Values of K_1, K_3, and K_5 are obtained by associating Equations (9)–9)–(22) in a software to obtain the concentration of each component. By taking the values of K_1–K_8 into Equation (28), $[H^+]$ could be obtained.

$$\begin{aligned}&[HMDA]_t + [DEEA]_t \\ &= \frac{K_6\cdot[CO_2]}{[H^+]} + \frac{2\cdot K_6\cdot K_7\cdot[CO_2]}{[H^+]} + \frac{K_8}{[H^+]} \\ &\quad + \frac{K_1\cdot[DEEA]_t}{K_1+[H^+]} + \frac{K_2\cdot[HMDA]_t}{[H^+]^2 + K_2\cdot[H^+] + K_2\cdot K_3\cdot[CO_2] + \frac{K_2\cdot K_3\cdot K_5\cdot[CO_2]^2}{[H^+]}} \\ &\quad \cdot\left(2\cdot[CO_2]\cdot K_3 + \frac{3\cdot K_3\cdot K_5\cdot[CO_2]^2}{[H^+]} + \frac{[H^+]\cdot[CO_2]}{K_4}\right) - [H^+]\end{aligned} \quad (28)$$

By bringing $[H^+]$ into Equation (29), the calculated value of CO_2 equilibrium solubility α_{cal}, could be presented as following.

$$\alpha_{cal} = \frac{[CO_2]}{([HMDA]_t + [DEEA]_t)}\cdot\left[1 + \frac{K_6}{[H^+]} + \frac{K_6\cdot K_7}{[H^+]} + \frac{K_2\cdot K_3\cdot[HMDA]_t}{[H^+]^2 + K_2\cdot[H^+] + K_2\cdot K_3\cdot[CO_2] + \frac{K_2\cdot K_3\cdot K_5\cdot[CO_2]^2}{[H^+]}}\left(1 + \frac{K_5\cdot[CO_2]}{[H^+]} + \frac{[H^+]}{K_4}\right)\right] \quad (29)$$

The developed models were evaluated by the presentation of AARD.

Finally, the developed models were fully compared and analyzed to determine the effect of parameters on the prediction accuracy of the thermodynamic models. In addition, parameter importance analysis was comprehensively performed by observing the effect of the introduced parameters on AARDs to obtain proper thermodynamic models that could represent thermodynamic models accurately. A framework of all processes for development of accurate and proper thermodynamic models was fully presented in Figure 2.

3 | EXPERIMENTAL SECTION

3.1 | Experimental materials

In this work, DEEA (99% purity) and HMDA (98% purity) as presented in Figure 3 were purchased from Shanghai Maclean Biochemical Technology Co. Different concentrations of amine solution and hydrochloric acid were prepared by adding deionized water.

3.2 | CO_2 solubility

The device of CO_2 solubility measurement for the DEEA-HMDA system was shown in Figure 4. The process is simply described as follows: First, a quantity of mixed amine solution was loaded into the reactor and immersed into a water bath with a controlled temperature (purchased from Changzhou Fipu Experimental Instrument Factory). The gas stream of CO_2 and N_2 cylinders (with a purity of 99.9% purchased from Beijing Wan Sheng Da Feng Co) was controlled to obtain the required CO_2 partial pressure by using the mass flow meter (purchased from Beijing Qi Xing Hua Chuang Flowmeter Co Ltd). The mixed gases are moistened through a water saturator and then fed into the reactor to react with the amine. The off gas passed through a water condenser to condense the amine solution in the exhaust gas After 6-h reaction, the sample was taken and analyzed by using the titration apparatus in previous work.[3] It is considered to the vapor–liquid equilibrium was identified once the CO_2 loading is stable, which could be determined as the equilibrium solubility of CO_2. This experimental set-up was valeted by using 2M MEA were obtained at 313 K with an AARD of 1.06% as indicated in Figure 5.[24] Among them, the error between the experimental value and the literature value at 76 kPa was slightly larger, 2.2%, which was within a reasonable error range, so the data was reliable (see Table S1 of supporting data for specific data).

4 | RESULTS AND DISCUSSION

4.1 | CO_2 solubility in DEEA-HMDA solution

In this work, CO_2 equilibrium solubility data (Table S2) were obtained for 2M DEEA:1M HMDA, 1.5M DEEA:1.5M HMDA, and 1M DEEA:2M HMDA at temperature range of 298–333 K and pressure range of 8–100 kPa, which were presented in Figure 6.

The graph showed that the CO_2 equilibrium solubility increased as CO_2 partial pressure increased and decreased as temperature increased. When pressure increased, the driving force of the gas increased, which resulted in an increase of CO_2 solubility. With the increase of temperature, the movement of CO_2 molecules in the solution was intensified, which leaded to the decreased of gas solubility. As the ratio of HMDA in the mixed solution system increased, equilibrium solubility of CO_2 showed an increasing trend at the same temperature

TABLE 1 Expressions of thermodynamic models.

Models	K_i expressions	
Empirical model	$P_{CO_2} = \exp\left[A \times \ln\alpha + \frac{a}{T} + b + \frac{B}{1+\exp(\frac{-c}{T}+d)\times\exp(-k_3\times\ln\alpha)} + C\times\ln[\text{Amine1}] + D\times\ln[\text{Amine2}]\right]$	(30)
KE model	$K_i = \exp\left(A + \frac{B}{T} + \frac{C}{T^2} + \frac{D}{T^3} + \frac{E}{T^4}\right)$	(31)
Austgen model	$K_i = \exp\left(B_1 + \frac{B_2}{T} + B_3\cdot\ln T + B_4\cdot T\right)$	(32)
Helei Liu model	$K_i = \exp\left(C_1 + C_2\cdot T + \frac{C_3}{T} + C_4\cdot\ln[\text{Amine}]\right)$	(33)
Hu–Chakma model	$K_i = \exp(D_1 + D_2\cdot T + D_3\cdot[CO_2(\text{aq})] + D_4\cdot\ln[\text{Amine}])$	(34)
Li–Shen model	$K_i = \exp\left(A_1 + \frac{A_2}{T} + \frac{A_3}{T^3} + C_1\cdot\alpha + \frac{C_2}{\alpha} + \frac{C_3}{\alpha^2} + C_4\cdot\ln[\text{Amine}]\right)$	(35)
Liu et al. model	$K_i = \exp\left(E_1 + E_2\cdot T + E_3\cdot[CO_2(\text{aq})] + E_4\cdot\ln[\text{Amine}] + \frac{E_5}{P_{total}}\right)$	(36)

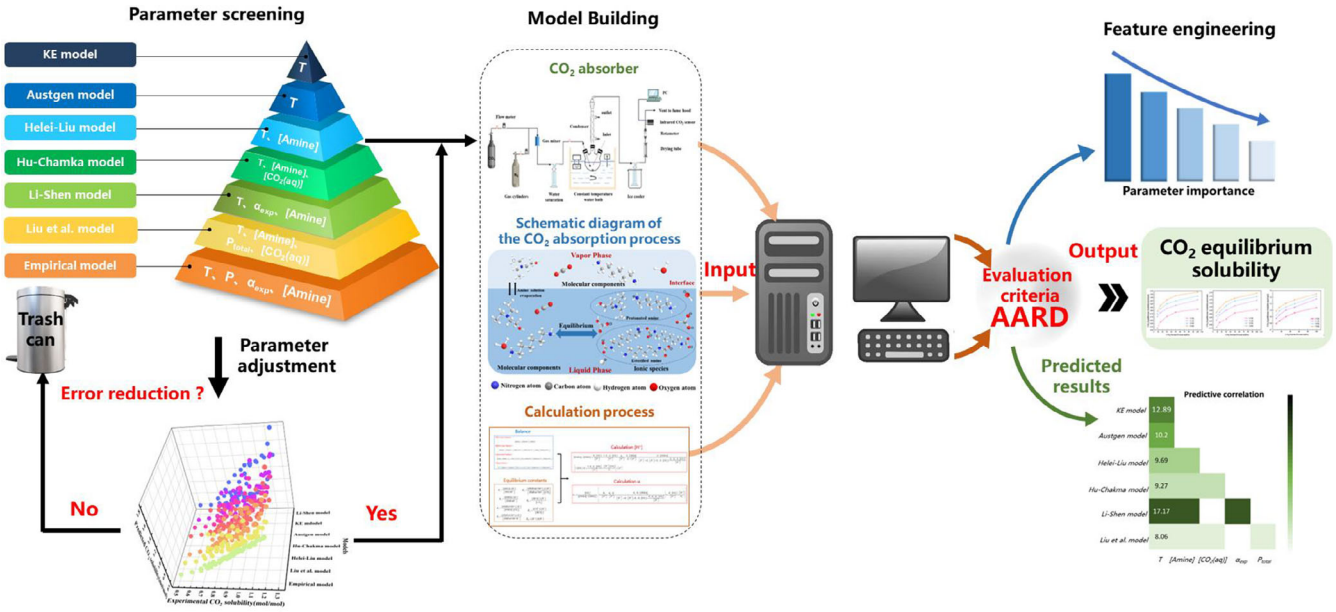

FIGURE 2 Diagram of thermodynamic model development for predicting the CO_2 equilibrium solubility.

and pressure. Increased ratio of HMDA with the present of two $-NH_2$ groups can effectively contribute to more free reactant $-NH_2$ the in the mixed solution, which resulted in the more CO_2 absorbed. However, it can be seen from Figure 7 that the equilibrium solubility of the 2M HMDA mixed system was like that of the mixed system with 1.5M HMDA under the same temperature and pressure. The reason was that HMDA was solid at room temperature. The high ratio of HMDA in the mixed solution leaded to precipitation of HMDA, which resulted in the loss of CO_2 capacity. As a result, the equilibrium solubility was not significantly improved. Although HMDA was cost-effective and had an excellent CO_2 absorption capacity, the precipitation behaviors should be considered before its industrial applications.

4.2 | Empirical model

The empirical model was the simplest thermodynamic model[25] as shown in Equation (23) in Table 1, where [Amine1] and [Amine2]

represent the concentration of each amine in the mixed solution, respectively. This model was used to correlate to experimental CO_2 solubility to obtain values of specific parameters as shown in Table 2. The obtained model was used to predict the CO_2 equilibrium solubility of DEEA-HMDA (Table S3). By comparing predicted results with the experimental results as shown in Figure 8. It can be seen from the that empirical model had a good prediction result with an AARD 1.90%. However, the shortcomings of this model, was that this model expression was developed with no practical theoretical significance. In response to this issue, many researchers have developed other thermodynamic models.

4.3 | KE model

Kent and Eisenberg established the KE model based on MEA and DEA absorption of acidic gases of CO_2 and hydrogen sulfide,[26] as presented in Equation (24) in Table 1. This model only related to the parameter of T was used to correlate to experimental CO_2 solubility to obtain specific values of model parameters as shown in Table 3. The obtained model was used to predict the equilibrium solubility of CO_2 in the mixed system (Table S4), which were compared with the experimental values, as shown in Figure 9.

From Figure 9, it could be seen that the total prediction deviation of the CO_2 solubility of the DEEA-HMDA system by using the KE model was 12.89%. It indicated that the CO_2 solubility data for the DEEA-HMDA system can be predicted with some extent, but it was not ideal. Temperature was an important factor affecting the equilibrium constant K_i, so 63% of the data points in the predicted dataset have good prediction effects. This was caused by the large errors of individual points, and the reasons were analyzed as follows: (1) DEEA-HMDA mixed system involved more reactions, which increased the complexity of the theoretical framework. (2) The K_i expression contained only T, making the expression relatively simple. T had a great impact on the prediction accuracy of the model. It was an indispensable parameter for the establishment of thermodynamic models. However, it was too simple and other factors should be considered.

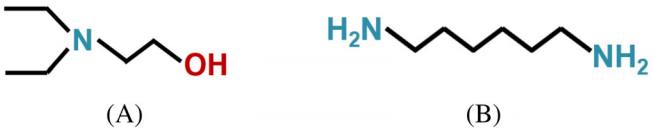

FIGURE 3 Chemical structures of (A) *N*,*N*-diethylethanolamine (DEEA) and (B) 1,6-hexamethyl diamine (HMDA).

4.4 | Austgen model

The Austgen model was initially proposed to represent the solubility of H_2S and CO_2 in monoamine and mixed amine solutions.[27] The expression was shown in Equation (25) in Table 1. The model with the correlation of T was used to represent the CO_2 equilibrium solubility, to obtain the specific parameter values of the model as shown in Table 4. The obtained model was used to predict the CO_2 equilibrium solubility (Table S5), which was compared with the experimental values as shown in Figure 10. For this model, the error from the predicted CO_2 equilibrium solubility for the DEEA-HMDA system was 10.20%. 78.3% of the predicted dataset had prediction errors of less than 15%.

The Austgen model also was only introduced with T. However, the prediction error was smaller than that of KE model. This may be caused by the different forms of K_i expression. The results showed that the Austgen model can be used to predict the equilibrium solubility of CO_2 to a certain extent. However, the K_i expression was only related to the T, which was too simple in the form to correlate well with experimental process. Beside temperature, there were more factors affecting the reaction process, such as pressure, amine concentration, and physical solubility. Therefore, these factors should be taken into account in the process of model development.

4.5 | Helei Liu model

The [Amine] in the mixed solution determined the amount of CO_2 absorption. Thus, [Amine] also reflected the equilibrium solubility of CO_2 to a certain extent. Some researchers introduced T, [Amine] into K_i expression to establish the Helei Liu model for predicting the CO_2

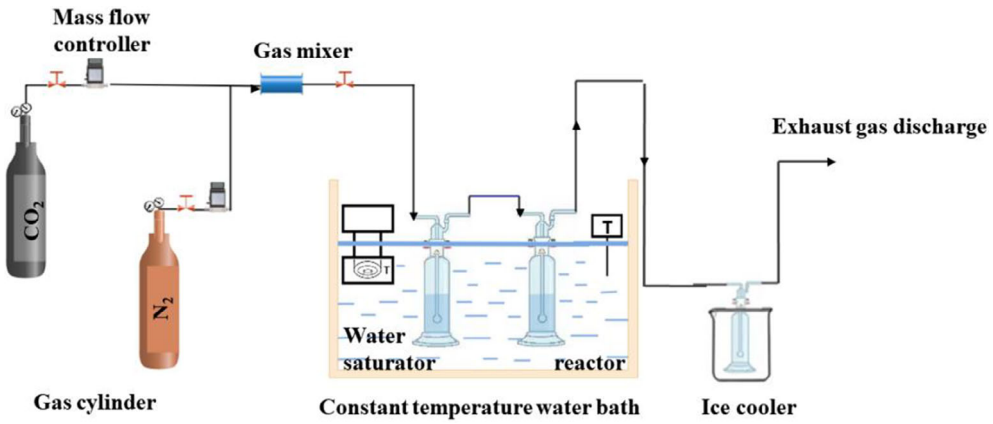

FIGURE 4 Diagram of CO_2solubility device.

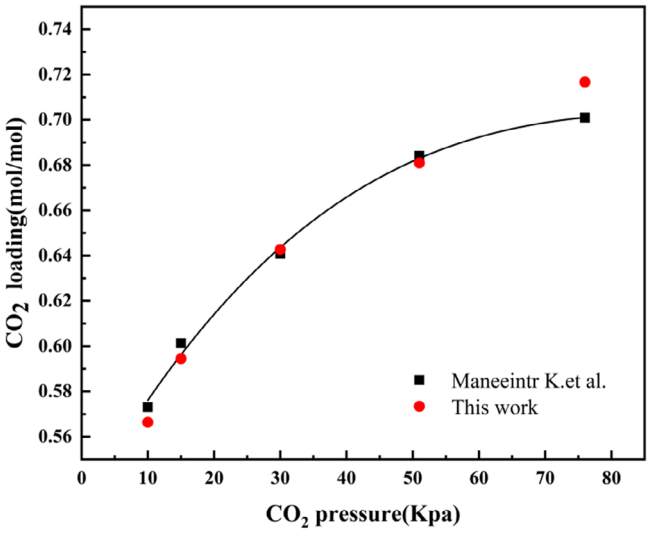

FIGURE 5 Equilibrium solubility of CO_2 in monoethanolamine (MEA) solution.

equilibrium solubility of 1DEA2P[22] as shown in Equation (26) in Table 1. The experimental conditions T and [Amine] were correlated with CO_2 equilibrium solubility to obtain the specific values of K_i expression parameters, as shown in Table 5. The developed model was used to obtain the predicted values of CO_2 equilibrium solubility (Table S6), which were compared with experimental values as shown in Figure 11.

As seen from Figure 11, the model can better predict the CO_2 equilibrium solubility for the DEEA-HMDA mixed system with an AARD of 9.69%. This observation indicated that [Amine] was a very critical parameter for predicting CO_2 equilibrium solubility, allowing 80% of the predicted datasets to have a prediction error of less than 15%. However, there were still some points with large errors. The reason was that HMDA accounted for a large proportion in the mixture of 1M DEEA:2M HMDA, which made a small amount of solid precipitated after absorbing a large amount of CO_2. This situation resulted in the loss of free amines so that they cannot absorbed CO_2. The [Amine] reflecting the CO_2 equilibrium solubility leaded to error. The introduction of [Amine] had more positive influence than negative influence on the model prediction results. This indicated that the [Amine] was an important parameter to make the more accurate prediction of CO_2 equilibrium solubility. It should be taken into account in the K_i expression.

4.6 | Hu–Chakma model

Hu and Chakma proposed a model to predict the equilibrium solubility of CO_2 in diethylene glycol amine solutions.[28] The researchers introduced T, [Amine] and [CO_2(aq)] parameters into the mathematical model expression of K_i, as shown in Equation (27) in Table 1. This model related to the three parameters was used to correlate to experimental CO_2 solubility to obtain specific values of model parameters

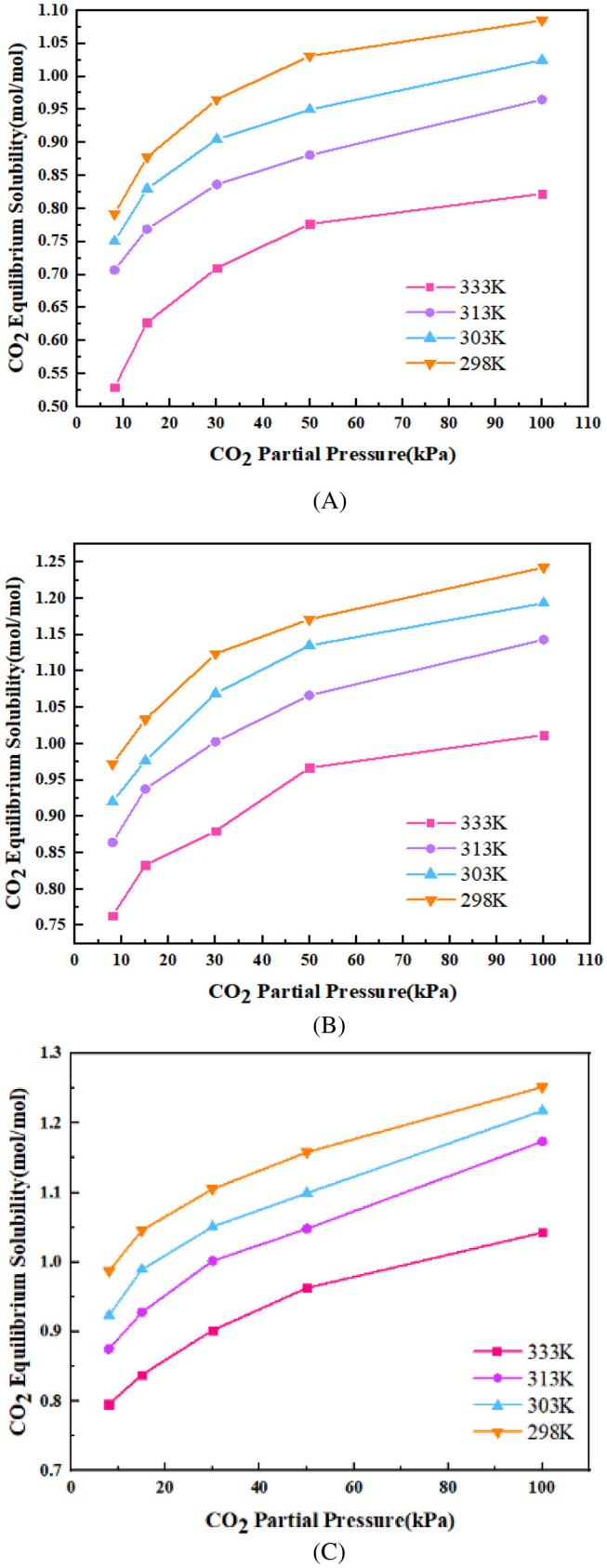

FIGURE 6 CO_2 equilibrium solubility of *N*,*N*-diethylethanolamine-1,6-hexamethyl diamine (DEEA-HMDA) at 298–333 K, 8–100 kPa.

as shown in Table 6. The obtained model was used to predict the CO_2 equilibrium solubility of DEEA-HMDA (Table S7). By comparing predicted results with the experimental results as shown in Figure 12.

The model achieved an AARD of 9.27% in the CO_2 equilibrium solubility for the DEEA-HMDA system. 88.3% of the data in the predicted dataset had prediction errors of less than 15%. This indicated the Hu–Chakma model was suitable to predict the CO_2 equilibrium solubility. And as the pressure increased, the [CO_2(aq)] increased and thus the CO_2 equilibrium solubility increased. Because the [CO_2(aq)] affected the CO_2 equilibrium solubility, the introduction of the parameter had a positive effect on the predicted results of the model. It indicated that [CO_2(aq)] was to be considered in the K_i expression.

4.7 | Li–Shen model

This model was a thermodynamic model established by Li and Shen to predict the CO_2 equilibrium solubility absorption in MEA-MDEA mixed solution.[29] Li and Shen introduced T, [Amine] and α_{exp} parameters into K_i expressions, as shown in Equation (35) in Table 1. This model related to the three parameters was used to correlate to experimental CO_2 solubility to obtain specific values of model parameters as shown in Table 7. The developed model was used to obtain the predicted values of CO_2 equilibrium solubility (Table S8), which were compared with experimental values as shown in Figure 13.

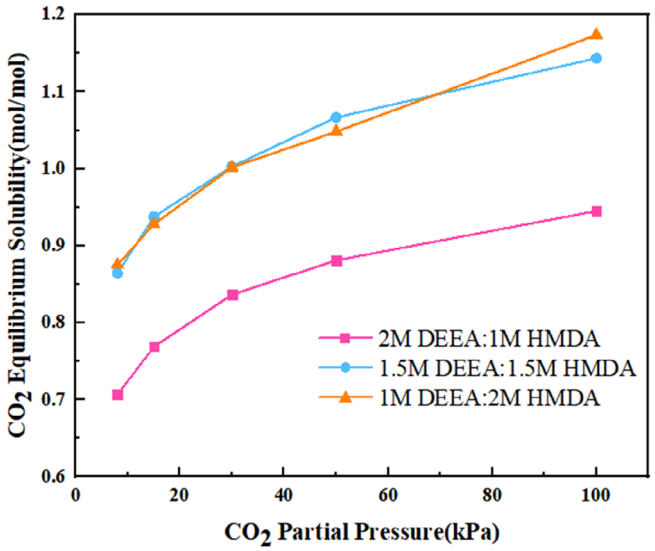

FIGURE 7 CO_2 equilibrium solubility of *N*,*N*-diethylethanolamine-1,6-hexamethyl diamine (DEEA-HMDA) at 313 K, 8–100 kPa.

The AARD of the predicted CO_2 equilibrium solubility of the DEEA-HMDA system using the model in this work was 17.17%. It indicated that the model cannot predict CO_2 equilibrium solubility in this the complex system very well. It was not a good idea to introduce α_{exp} parameter to improve the prediction accuracy of the model. This made 61.7% of the data in the predicted dataset with a prediction error of more than 15%. It is mainly due to the introduction of α_{exp} parameter in K_i expression, which was unsuitable for the DEEA-HMDA mixture system, caused a significant error. This observation was also confirmed by N other researchers with a large prediction error for DMAB, DPAB, HEMAB, and HEEAB, with AARD range of 15.3%–66.4%.[19] The research system of this work was complex, so significant prediction errors were also taken into account. The negative effect of introducing α_{exp} into the K_i expression was greater than the positive effect of introducing the [Amine] parameter. Therefore, the α_{exp} should not be included in the expression.

4.8 | Liu et al. model

In the process of building the thermodynamic model, *T*, P_{total}, [Amine], and [CO_2(aq)] were all key parameters for predicting the equilibrium solubility of CO_2. Therefore, Liu et al. constructed a new model by adding these four parameters in the K_i expression,[30] as shown in Equation (36) in Table 1. This model related to the four parameters was used to correlate to experimental CO_2 solubility to obtain specific values of model parameters as shown in Table 8. The developed model was used to obtain the predicted values of CO_2 equilibrium solubility (Table S9), which were compared with experimental values as shown in Figure 14.

The AARD of this model for the complex DEEA-HMDA system in this work was 8.06%. It showed that this model can predict the CO_2 equilibrium solubility in the complex system very well. The total pressure parameter, P_{total}, had an important influence on the vapor–liquid equilibrium process which made 91.7% of the predicted dataset with prediction errors less than 15%. However, there were still some large errors in individual points. The main reason was that the proportion of HMDA in the mixture was too high, precipitated solid. The concentration of free amine was reduced, which affected the CO_2 equilibrium solubility. The prediction results of this model were more accurate for the DEEA-HMDA system. Therefore, the Liu et al. model was more suitable for predicting CO_2 equilibrium solubility for the complex system. T, [Amine], [CO_2(aq)] and P_{total} had positive effects on improving the prediction accuracy of the models. They were indispensable important factors in the establishment of thermodynamic models.

TABLE 2 Values of the parameters fitted by the Empirical model.

Parameters	*A*	*B*	*C*	*D*	*a*	*b*	*c*	*d*	k_3
Values	8.35	0.68	−5.28	−7.78	−4643.14	22.94	−133973.35	−445.42	42.45
AARD (%)	1.9								

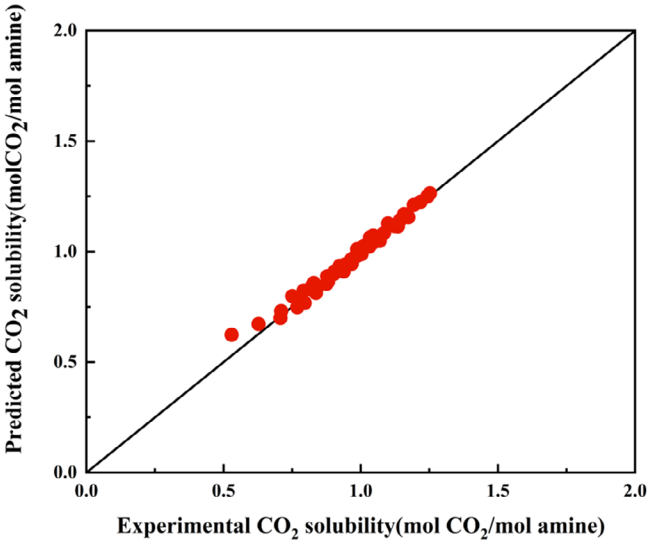

FIGURE 8 Parity plot of predicting the equilibrium solubility of CO_2in *N*,*N*-diethylethanolamine-1,6-hexamethyl diamine (DEEA-HMDA) solutions using Empirical model.

4.9 | Feature parameter analysis

In this work, different thermodynamic models were developed to predict the CO_2 equilibrium solubility for the DEEA-HMDA system. The comprehensive feature parameter analysis of models was presented in terms of prediction performance the distribution of data errors, the correlation between the parameters and the model, and the contribution of each parameter, which was were shown in Figure 15.

The empirical model had the minimum AARD of 1.90%. However, this model was only a simple fitting of experimental conditions and experimental results, instead of basing on reaction theory. Therefore, some researchers had developed thermodynamic models based on reaction processes. Only the *T* was introduced in the K_i expressions of the KE model and Austgen model. By comparison, Austgen model had a less prediction error, as shown in Figure 15A. The distribution range of the Austgen model prediction dataset errors as shown in Figure 15B was significantly smaller than that of the KE model. The difference in the form of K_i expressions led to differences in the prediction errors of the two models. It also indicated that the K_i expression of the Austgen model was more suitable for the complex DEEA-HMDA system in this work than that of the KE model. Although these two models can predict the CO_2 equilibrium solubility of the complex system DEEA-HMDA to some extent, the prediction results were not satisfactory. In order to make the prediction of the model more accurate, [Amine] parameter was introduced into the Helei Liu model in the presence of T parameter. As can be seen from Figure 15A, the prediction accuracy of this model was further improved compared with the previous two models. It can also be seen from Figure 15B that more of the data errors in this model were more concentrated in a small area around the x-axis 0 than in the previous two models. The [Amine] can reflected the reactant concentration from the side, which made the K_1, K_3, and K_5 values more correctly

TABLE 3 Values of the parameters fitted by the Kent and Eisenberg (KE) model.

	Parameters				
K_i	*A*	*B*	*C*	*D*	*E*
K_1	−20.67	−263.64	−1.33E-04	0	0
K_3	18.69	−6121.78	14.20	4.52	0
K_5	−6.20	166.24	−1.63E-04	−1.84E-04	0
AARD (%)	12.89				

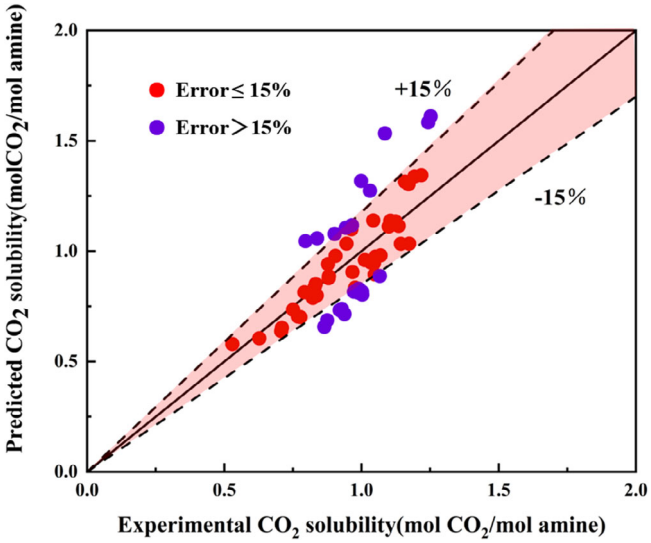

FIGURE 9 Parity plot of predicting the equilibrium solubility of CO_2 in *N*,*N*-diethylethanolamine-1,6-hexamethyl diamine (DEEA-HMDA) solutions using Kent and Eisenberg (KE) model.

obtained in the modeling process. Thus, the prediction accuracy of the model was improved. In the presence of T, [Amine] parameters, the Hu–Chakma model introduced [CO_2(aq)] parameter into the K_i expression. This model had fewer data error points near the prediction error greater than 20% in Figure 15B. The total prediction error of equilibrium solubility was slightly reduced. This showed that [CO_2(aq)] had an important effect on the absorption of CO_2 into the amine solution. It can improve the prediction accuracy of CO_2 equilibrium solubility to a certain extent. [CO_2(aq)] indicated the concentration of CO_2 at the gas–liquid interface, which was correlated strongly with the mass transfer performance. Therefore, it affected the solubility of CO_2 in the amine solution. Subsequently, α_{exp} parameter was introduced into the Li–Shen model in the presence of T, [Amine] and [CO_2(aq)] parameters. It was obvious from the (B) that there were fewer error points in the data around x-axis 0, and the overall data distribution was wide. Most points were distributed after ±20% error, and the maximum error was close to 50%. The introduction of α_{exp} parameter made the prediction effect of the model the worst, and AARD was 17.17%. This suggested that introduction of α_{exp} in the K_i expression could improve the prediction accuracy for the DEEA-HMDA system. Based on the experience of the above model, α_{exp}

TABLE 4 Values of the parameters fitted by the Austgen model.

	Parameters			
K_i	B_1	B_2	B_3	B_4
K_1	−21.04	0.397	9.19E-04	−1.74E−03
K_3	−2.1E+04	5.81E+05	−5.66	3.64E+03
K_5	−4.48	1.71	−3.92E−03	−4.14E−03
AARD (%)	10.20			

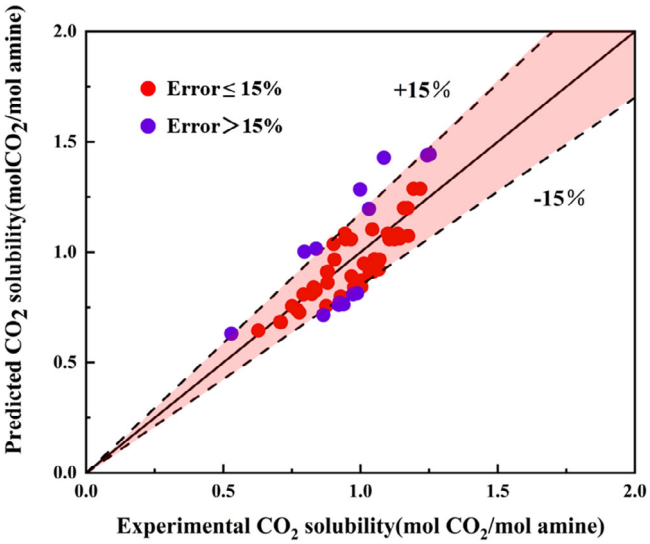

FIGURE 10 Parity plot of predicting the equilibrium solubility of CO_2 in *N*,*N*-diethylethanolamine-1,6-hexamethyl diamine (DEEA-HMDA) solutions using Austgen model.

TABLE 5 Values of the parameters fitted by the Helei Liu model.

	Parameters			
K_i	C_1	C_2	C_3	C_4
K_1	−18.27	−0.01	−3.01E−03	−7.01
K_3	−16.03	0.0494	−0.0142	3.52
K_5	0.71	−0.02	−0.013	−0.0122
AARD (%)	9.69			

was removed from the Liu et al. model and T, [Amine], [CO_2(aq)] and a new parameter P_{total} were introduced. In the (B) plot, the vast majority of points in the Liu et al. model was concentrated in the −10% to +10% range, with only a few points showing large deviations. This appears to be more concentrated than the data points in the other models. The introduction of all parameters made a prediction error of 8.06%, which was the minimum prediction error in this work. With another decrease in the error indicated that the introduction of the total pressure parameter was correct. It was necessary to include in the K_i expression. The theoretical system of reaction was complicated due to the large number of ionic components in the mixed solution.

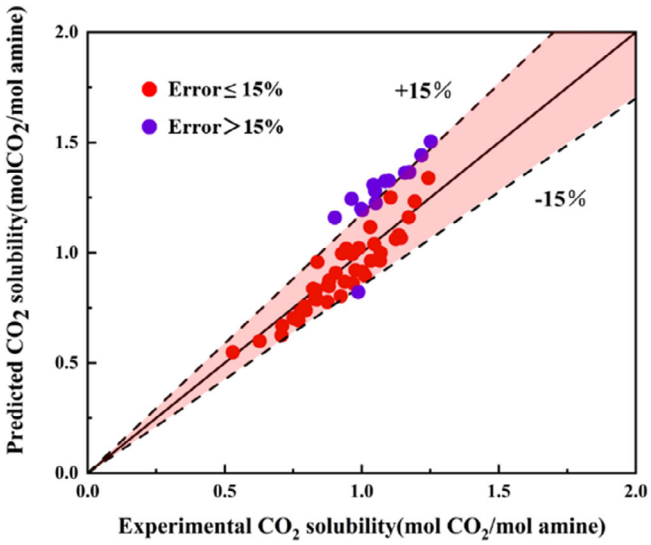

FIGURE 11 Parity plot of predicting the equilibrium solubility of CO_2 in *N*,*N*-diethylethanolamine-1,6-hexamethyl diamine (DEEA-HMDA) solutions using Helei Liu model.

TABLE 6 Values of the parameters fitted by the Hu-Chakma model.

	Parameters			
K_i	D_1	D_2	D_3	D_4
K_1	−21.71	−6.98E−04	−1.576	−0.0752
K_3	−8.59	0.032	−8.31	−3.16
K_5	−2.16	−6.20E-03	4.97	−3.27
AARD (%)	9.27			

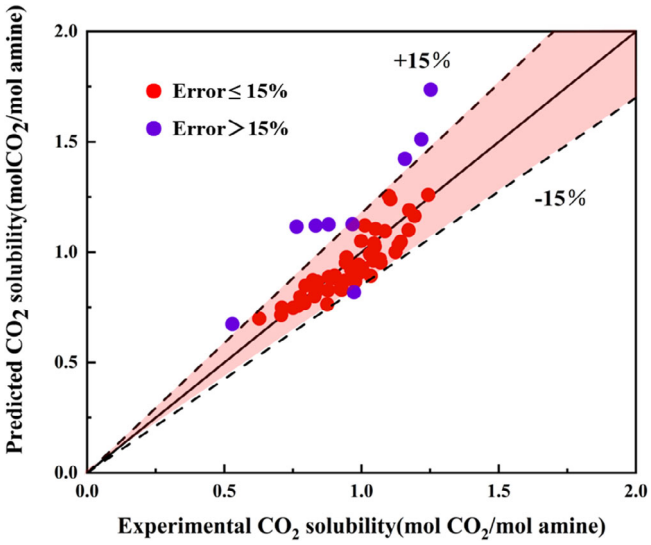

FIGURE 12 Parity plot of predicting the equilibrium solubility of CO_2 in *N*,*N*-diethylethanolamine-1,6-hexamethyl diamine (DEEA-HMDA) solutions using Hu-Chakma model.

TABLE 7 Values of the parameters fitted by the Li-Shen model.

	Parameters						
K_i	A_1	A_2	A_3	C_1	C_2	C_3	C_4
K_1	−17.48	−4.3E-03	−0.102	−0.0285	−0.346	−2.122	0.405
K_3	28.79	−1.87	−2.024	−35.56	−40.74	7.97	−2.431
K_5	−4.74	−5.79E-04	0.083	1.778	−0.746	−0.65	−0.0397
AARD (%)	17.17						

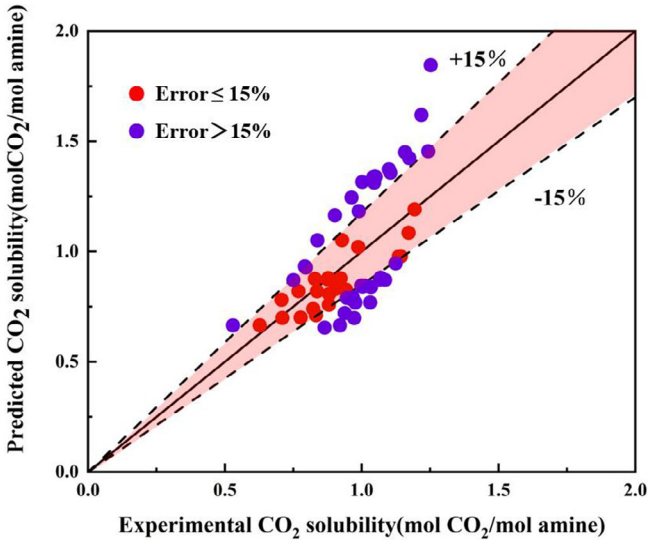

FIGURE 13 Parity plot of predicting the equilibrium solubility of CO_2 in *N*,*N*-diethylethanolamine-1,6-hexamethyl diamine (DEEA-HMDA) solutions using Li-Shen model.

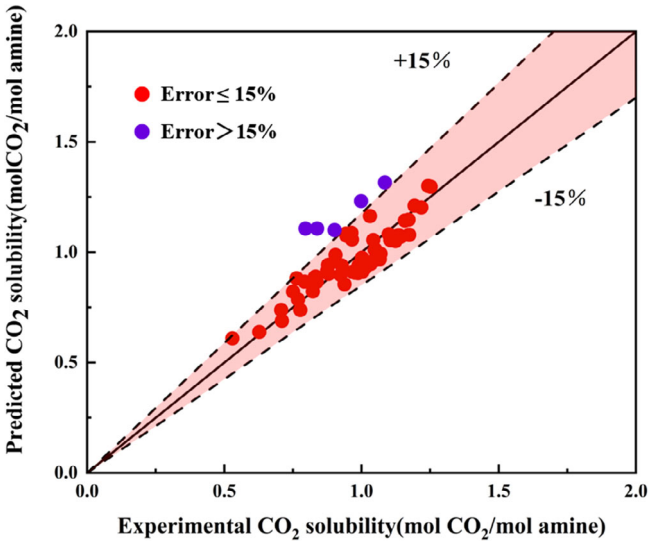

FIGURE 14 Parity plot of predicting the equilibrium solubility of CO_2 in *N*,*N*-diethylethanolamine-1,6-hexamethyl diamine (DEEA-HMDA) solutions using Liu et al. model.

TABLE 8 Values of the parameters fitted by the Liu et al. model.

	Parameters				
K_i	E_1	E_2	E_3	E_4	E_5
K_1	−15.04	−0.030	92.5	3.17	0.427
K_3	−5.96	0.0219	−15.55	−0.758	−10.054
K_5	−1.96	−0.0123	5.07	0.156	−0.0148
AARD (%)	8.06				

And the experimental data were affected by the precipitation of some amine solutions. So the AARD of 8.06% was a good result for the complex system. In summary, the introduction of *T*, [Amine], [CO_2(aq)], and P_{total} parameters can improv the prediction accuracy of the model. Liu et al.[19] model was more suitable for predicting CO_2 equilibrium solubility for the complex DEEA-HMDA system.

The introduction of *T*, [Amine], [CO_2(aq)], and P_{total} parameters all reduced the prediction error of the model, and only the introduction of α_{exp} made the prediction error increased significantly. The correlation between each parameter and model prediction was shown in Figure 15C. In addition, the contribution of each parameter to the model prediction accuracy was shown in Figure 15D. Among them, *T* was the biggest contributor, because the equilibrium constant was just a value associated with *T*. The concentration of free amines directly reflected the amount of CO_2 absorbed and was the parameter with the second-highest contribution after *T*. The total pressure of the system environment, P_{total}, can affected the vapor–liquid equilibrium process. It indirectly affected the solubility of the gas. [CO_2(aq)] was a small value, so it was understandable that it contributed less to prediction accuracy. Based on the above, *T*, [Amine], P_{total}, and [CO_2(aq)] were necessary parameters that can improve the prediction accuracy of thermodynamic models. Other factors accounted for a large proportion. This indicated that the prediction accuracy of the models had a large space to improve. In this work, the non-ideality of DEEA-HMDA complex system was not considered by thermodynamic models. To further reduce the prediction error of the CO_2 equilibrium solubility of the DEEA-HMDA complex system to a satisfactory level. It was necessary to develop activity coefficient model, UNIQUAC model, and NRTL model that considered the non-idealities of the solution. They were also to be considered in the subsequent work.

5 | CONCLUSION

In this work, CO_2 equilibrium solubility data were obtained for 2M DEEA:1M HMDA, 1.5M DEEA:1.5M HMDA, and 1 M DEEA:2M

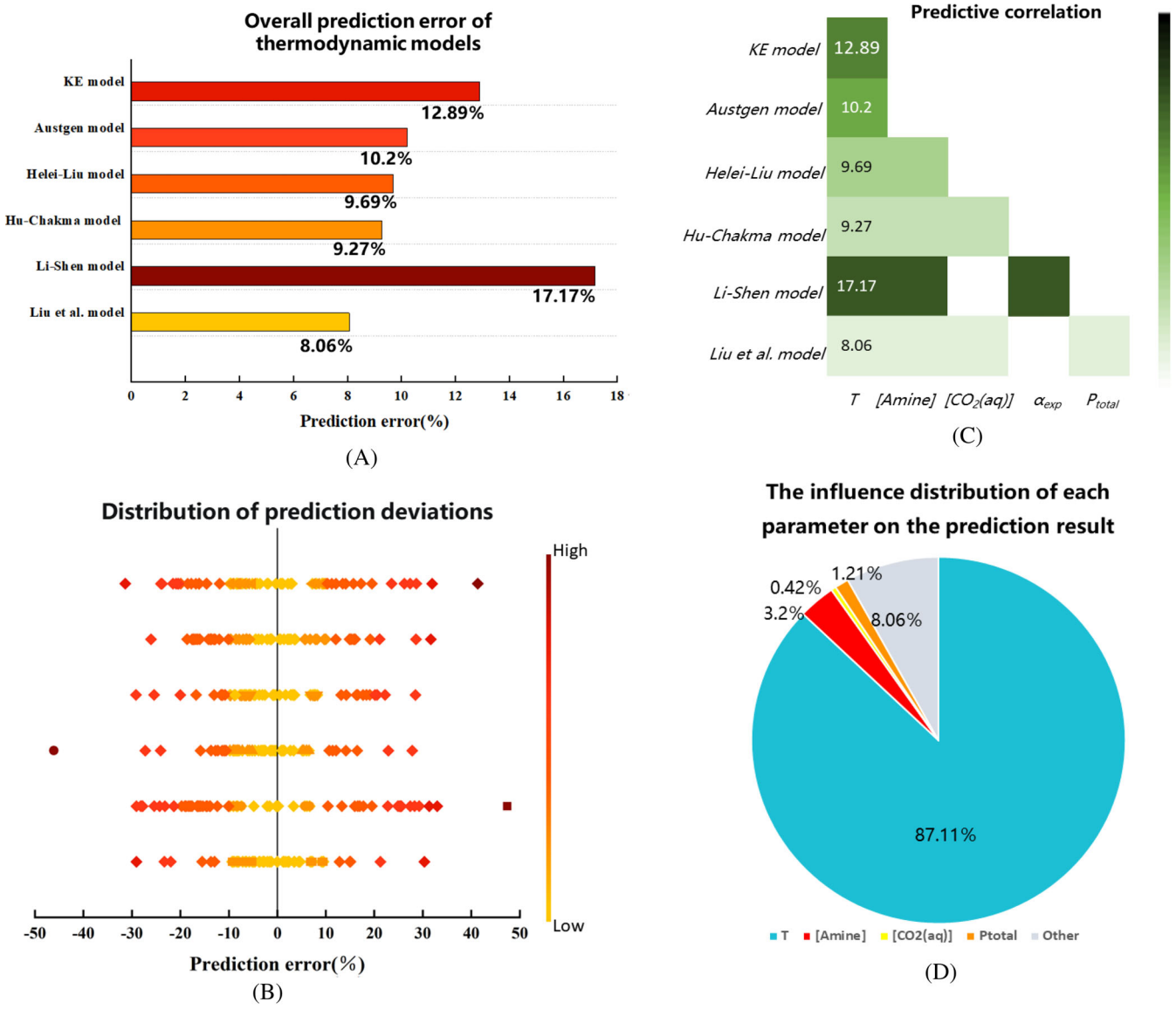

FIGURE 15 Comparison of model prediction results for CO_2 equilibrium solubility. (A) prediction results; (B) the distribution of data errors; (C) predictive correlation; (D) parameter contribution.

HMDA with the temperature range of 298–333 K and pressure range of 8–100 kPa. Seven thermodynamic models including the empirical model, KE model, Hu–Chakma model, Austgen model, Helei Liu model, Liu et al. model, and Li–Shen model, were used to predict the CO_2 equilibrium solubility of DEEA-HMDA. Liu et al. model had the best prediction ability for CO_2 equilibrium solubility of the target system, and AARD was 8.06%. This showed that the introduction of T, [Amine], P_{total} and [CO_2(aq)] parameters can improve the prediction accuracy of the model. At the same time, the influence of different parameters on the prediction results was given. The importance of parameters was ranked as T > [Amine] > P_{total} > [CO_2(aq)]. Therefore, it provided ideas and guidance for building thermodynamic models with excellent prediction ability. In order to further improve the prediction accuracy, it was necessary to consider the non-ideal factors of the complex system.

AUTHOR CONTRIBUTIONS

Dongfang Zhao: Conceptualization (lead); data curation (lead); formal analysis (equal); investigation (equal); software (lead); validation (lead); writing – original draft (lead); writing – review and editing (equal). **Xizi Xiao:** Conceptualization (equal); data curation (equal); formal analysis (supporting); investigation (equal); methodology (equal); writing – review and editing (equal). **Shuai Wang:** Conceptualization (equal); data curation (equal); investigation (equal); methodology (equal); resources (supporting); writing – original draft (supporting); writing – review and editing (equal). **Miyi Li:** Formal analysis (supporting); investigation (equal); methodology (supporting); supervision (equal); visualization (supporting); writing – review and editing (equal). **Helei Liu:** Conceptualization (lead); data curation (equal); formal analysis (lead); funding acquisition (lead); investigation (supporting); methodology (lead); supervision (lead); validation (equal); visualization

(equal); writing – original draft (supporting); writing – review and editing (lead).

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DATA AVAILABILITY STATEMENT

The numerical data from Figures 5-14 are tabulated in the Supplementary Data. CO2 equilibrium solubility data shown in Figure 6 are the average results of three titrations. Prior to generating data for the Mixed amine solvent that is the main topic of this paper, we have verified the experimental apparatus from which the data was obtained so that direct comparisons can be made with previous data from Maneeintr et al. A comparison between our measurements and these previous data, which shows there is good consistency with and between these prior measurements, is discussed in section Table S1 of the Supplementary Data. The other data that support the findings of this study are available from the corresponding author upon reasonable request.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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