

RESEARCH ARTICLE

Thermodynamics and Molecular-Scale Phenomena

A general model for prediction of the CO₂ equilibrium solubility in aqueous tertiary amine systemsCheng Yu¹ | Hao Ling¹  | Zhigang Shen¹ | Hongyun Yang¹ |
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Abstract

We have developed a general model to predict CO₂ equilibrium solubility in aqueous tertiary amine solutions by relating the equilibrium constant (K_1) to all relevant parameters in a logical function form. Testing our model, we measured CO₂ equilibrium solubility data for N-methylmorpholine (NMM) and N-ethylmorpholine (NEM) across various conditions. Comparison with six existing models reveals our general model's superior predictive performance not only for NMM and NEM but also for an additional 10 tertiary amine solutions from literature, indicating its universality. Comprehensively considering the CO₂ equilibrium solubility, amine dissociation constant (pKa) and the CO₂ absorption heat, it is found that NMM and NEM may be promising desorption promoters enabling to reduce the energy cost. In short, it is expected the general model can be applied to more other tertiary amine systems.

KEYWORDS

carbon capture, CO₂ absorption heat, CO₂ equilibrium solubility, tertiary amine, thermodynamic models

1 | INTRODUCTION

The continuous rise in global temperatures has exacerbated the greenhouse effect, leading to a series of serious climate problems, including rising of sea levels and frequent extreme weather events. The massive emission of carbon dioxide (CO₂), as one of the major greenhouse gases, has become a major contributor to global warming.^{1,2} Currently, fossil fuels still are one of the most reliable and stable energy sources. Their combustion process releases large amounts of CO₂ directly into the atmosphere.³ Therefore, reducing CO₂ emissions has become a priority in the 21st century. At present, CO₂ capture and utilization technology has become the most effective means of mitigating carbon emissions and decarbonizing the economy.⁴

The CO₂ capture technologies are mainly divided into three categories: pre-combustion, post-combustion and oxygen-enriched combustion.⁵ Among them, post-combustion capture technologies cover a variety of methods such as chemical absorption,^{6–9} physical adsorption,^{10,11} and membrane separation.¹² These technologies were widely used in coal-fired power plants, and their advantage is that they do not require modification of the existing combustion system and power generation equipment processes, and are therefore considered to be the most promising technology for the realization of clean energy utilization. In particular, the amine-based chemical absorption method is favored for its large absorption capacity, fast absorption rate and high removal rate.^{13,14} In the past decades, many investigators have conducted in-depth studies on organic amine absorbers, including primary amines (e.g., monoethanolamine, MEA),

secondary amines (e.g., diethanolamine, DEA), and tertiary amines (e.g., methyldiethanolamine, MDEA). The reaction of primary and secondary amines with CO₂ involves two steps of carbamate generation and amine protonation, and has a fast absorption rate, but the high stability of carbamate leads to high energy consumption in the regeneration process.¹⁵ Tertiary amines are usually used as alkaline catalysts to convert CO₂ to bicarbonates and carbonates, which has lower energy consumption but suffering from slower absorption rates due to the weaker C–O bonds in bicarbonates and carbonates compared to the C–N bonds in carbamates.¹⁶ It is worth mentioning that MEA, as a representative of organic amines, has been successfully put into industrial-scale demo plants worldwide due to its good reaction kinetics and low cost, thus making organic amine absorption method to be one of the most effective and mature CO₂ capture technologies at present.^{17,18}

Although the remarkable progress has been made in carbon capture technology, organic amine absorbents still face a series of challenges in long-term recycling, including high energy consumption for solvent regeneration, susceptibility to degradation, and equipment corrosion, which are bottlenecks restricting their widespread applications.^{19,20} As a result, many researchers have turned their attention to the development of new absorbers with low energy consumption and low corrosion. Recent studies have shown that some novel absorbents, such as morpholine (MOR) and N-methylmorpholine (NMM), have slow corrosion rates on carbon steel (XC38) and stainless steel (304Ti). Sandrine Martin et al.²¹ experimentally demonstrated that MOR and NMM are less corrosion than conventional MEA for equipment. In fact, the corrosion phenomena are closely related to degradation, since these substances such as chlorides and fluorinated acids in MEA degradation products would accelerate the rate of metal corrosion.^{22,23} Some studies indicate that morpholinoids, especially cyclic amines, have excellent thermal stability.²⁴ It is reported that morpholine is the most stable cyclic amine relative to other absorbents, and it exhibits excellent performance in CO₂ capture.²⁵ This advantage was confirmed, since the degradation rate of MEA was 10 and 5 times higher than that of MOR and NMM, respectively, under the same conditions.²¹ In 2009, Davis and Rochelle²⁶ analyzed and tested the major degradation products and degradation rates of MEA by simulating the operating conditions of a desorption column and found that NMM is one of the degradation products of MEA. Ling et al.⁸ then added 13 degradation products of MEA, such as formic acid (FA), NMM, 2-methylpiperazine (2MPZ), and so forth, into 5 M MEA solution, and experimentally investigated the effect of each degradation product on the absorption and desorption performance of MEA solution. Despite the excellent performance of morpholino analogs in degradation and corrosion, it is still necessary to test the other properties in CO₂ capture.

The CO₂ equilibrium solubility of an organic amine solvent represents the maximum CO₂ uptake capacity under given conditions, and is therefore one of the key parameters in solvent screening.²⁷ Developing an accurate and universal thermodynamic model to predict the CO₂ equilibrium solubility is critical for the design, process simulation and optimization of an absorber tower. In 1976, Kent and

Eisenberg²⁸ proposed a semi-empirical thermodynamic model (i.e., the Kent–Eisenberg model) and well predict the CO₂ equilibrium solubility of MEA and DEA solutions for acidic gases (H₂S and CO₂). To improve the accuracy of the CO₂ equilibrium solubility, the Kent–Eisenberg model was further modified by Austgen,²⁹ Hu–Chakma,³⁰ Li–Shen,³¹ and Xiao et al.³² Besides, some other models, such as the electrolyte–non-random two-liquid model (e-NRTL),³³ the Deshmukh–Mather model,³⁴ and the artificial neural network (ANN) model,³⁵ were also proposed for predicting CO₂ equilibrium solubility. The introduction of these models has enriched the toolbox of researchers and provided diverse options for prediction of the CO₂ equilibrium solubility. However, the evaluation criterium of a model is not only limited to the prediction accuracy, but also should have good universality. Actually, the above models have certain limitations in the universality. Therefore, developing a general model is significant for the thermodynamic investigations of amine–H₂O–CO₂ systems.

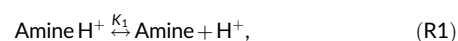
Here, we proposed a general thermodynamics model to predict the CO₂ equilibrium solubility in tertiary amine solution systems by considering all the related characteristic parameters to the model. We also experimentally measured the CO₂ equilibrium solubility in N-methylmorpholine (NMM) and N-ethylmorpholine (NEM) systems in different conditions ($T = 298.15\text{--}323.15\text{ K}$, $P_{\text{CO}_2} = 7.5\text{--}100\text{ kPa}$, amine concentration 1.0–2.0 mol/L), because above analysis indicates that they may be potentially promising candidates for CO₂ absorption. The results indicates that the proposed general model can predict these data of NMM and NEM more accurately than the existing models, including the Kent–Eisenberg, Austgen, Helei–Liu^①,³⁶ Hu–Chakma, Li–Shen, and Helei–Liu^②³⁷ models. Importantly, the proposed general model also exhibits better the prediction accuracy and universality of the CO₂ equilibrium solubility in other 10 tertiary amine systems from literature, compared to six existing models. Finally, we also performed a comprehensive evaluation of NMM and NEM with other published amine solvents in terms of the CO₂ equilibrium solubility, pKa, and the CO₂ absorption heat.

2 | THEORIES

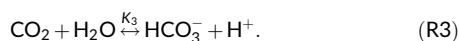
2.1 | CO₂ absorption mechanism and calculation method

Numerous studies have shown that CO₂ absorption by aqueous solutions of tertiary amines is consistent with a base-catalyzed reaction mechanism. In this mechanism, tertiary amine does not directly react with CO₂, but generates the reaction products such as carbonate and bicarbonate. The main chemical reaction of CO₂ absorption by aqueous tertiary amine solution can be expressed as follows.^{38,39}

Deprotonation of amines:



Formation of bicarbonate ion:



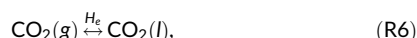
Dissociation of bicarbonate ion:



Dissociation of water:



CO₂ physical solubility:



where K_i stands for the equilibrium constant of chemical reaction i .

Under ideal conditions, the apparent equilibrium constants (K_1 , K_2 , K_3 , K_4 , and K_5) for these chemical reactions in the system of CO₂ absorption by aqueous tertiary amine solution are calculated by

$$K_1 = \frac{[\text{Amine}][\text{H}^+]}{[\text{AmineH}^+]} = \frac{([\text{Amine}]_t - [\text{AmineH}^+])[\text{H}^+]}{[\text{AmineH}^+]}, \quad (1)$$

$$K_2 = \frac{[\text{AmineH}^+][\text{HCO}_3^-]}{[\text{Amine}][\text{CO}_2]} = K_3/K_1, \quad (2)$$

$$K_3 = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{CO}_2]}, \quad (3)$$

$$K_4 = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]}, \quad (4)$$

$$K_5 = [\text{OH}^-][\text{H}^+], \quad (5)$$

where $[i]$ represents the molar concentration of component i (mol/L), and $[\text{CO}_2]$ represents the physical solubility of CO₂ (mol/L).

In addition to the chemical reaction equilibrium of the absorption process, we need to consider the amine balance, carbon balance and charge balance of the reaction system, mainly including the following equations.

Amine balance:

$$[\text{Amine}] + [\text{AmineH}^+] = [\text{Amine}]_t. \quad (6)$$

Carbon balance:

$$[\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{CO}_2] = \alpha \times [\text{Amine}]_t. \quad (7)$$

Charge balance:

$$[\text{AmineH}^+] + [\text{H}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-], \quad (8)$$

where $[\text{Amine}]_t$ represents the total concentration of amine solution (mol/L), and α represents CO₂ loading (mol CO₂/mol amine).

By Henry's law, we can get the physical solubility of CO₂ with the help of Equation (9).

$$P_{\text{CO}_2} = H_e[\text{CO}_2], \quad (9)$$

where P_{CO_2} represents the partial pressure of CO₂ in the gas phase (kPa), and H_e represents Henry's constant.

The expressions for the chemical reaction equilibrium constants K_3 , K_4 , K_5 and Henry's constant were taken from the relevant literature, given by²⁸

$$K_3 = \exp \left(-241.818 + \frac{298.253e^3}{T} - \frac{148.528e^6}{T^2} + \frac{332.648e^8}{T^3} - \frac{282.394e^{10}}{T^4} \right), \quad (10)$$

$$K_4 = \exp \left(-294.74 + \frac{364.385e^3}{T} - \frac{184.158e^6}{T^2} + \frac{415.793e^8}{T^3} - \frac{354.291e^{10}}{T^4} \right), \quad (11)$$

$$K_5 = \exp \left(39.5554 - \frac{987.9e^2}{T} + \frac{568.828e^5}{T^2} - \frac{146.4561e^8}{T^3} + \frac{136.146e^{10}}{T^4} \right), \quad (12)$$

$$H_e = \exp \left(22.2819 - \frac{138.306e^2}{T} + \frac{691.346e^4}{T^2} - \frac{155.895e^7}{T^3} + \frac{120.037e^{10}}{T^4} \right) / 7.50061, \quad (13)$$

where T stands for temperature (K).

According to Equations (1)–(8), the concentrations of all substances in the amine–CO₂–H₂O system can be expressed in terms of apparent equilibrium constants and hydrogen ion concentrations $[\text{H}^+]$ by substitution elimination, as shown in Equations (14)–(17):

$$[\text{Amine}] = \frac{[\text{Amine}]_t K_1}{K_1 + [\text{H}^+]}, \quad (14)$$

$$[\text{CO}_3^{2-}] = \frac{[\text{CO}_2] K_3 K_4}{[\text{H}^+]^2}, \quad (15)$$

$$[\text{HCO}_3^-] = \frac{[\text{CO}_2] K_3}{[\text{H}^+]}, \quad (16)$$

$$[\text{OH}^-] = \frac{K_5}{[\text{H}^+]}. \quad (17)$$

Combining these Equations (6)–(8) and (14)–(17), Equation (18) can be obtained, given by

$$\frac{K_3}{[H^+]} + \frac{K_3 K_4}{[H^+]^2} + 1 = \frac{\alpha \times [Amine]_t}{[CO_2]}. \quad (18)$$

By solving Equation (18) with MATLAB software, the hydrogen ion concentration can be obtained and further the dissociation constant of protonated organic amines in the amine–CO₂–H₂O system (i.e., K_1) can be obtained. The polynomial expression of K_1 is obtained by correlating K_1 with the experimental parameters in different thermodynamic models. In different thermodynamic models, K_1 expressions are different, and the values of the coefficients A_i in the polynomials can be determined by fitting the polynomials to the calculated K_1 values.

In addition, the data are predicted by means of the joint Equations (8)–(9) and (14)–(17), which will form a polynomial (19) on the concentration of hydrogen ions as follows:

$$A([H^+]^*)^4 + B([H^+]^*)^3 + C([H^+]^*)^2 + D[H^+]^* + E = 0 \quad (19)$$

with

$$A = 1, \quad (20)$$

$$B = [Amine]_t + K_1^*, \quad (21)$$

$$C = -K_3[CO_2] + K_5, \quad (22)$$

$$D = -K_1^* K_3 [CO_2] - K_1^* K_5 - 2K_3 K_4 [CO_2], \quad (23)$$

$$E = -2K_1^* K_3 K_4 [CO_2], \quad (24)$$

where $[H^+]^*$ represents the hydrogen ion concentration calculated from the model (mol/L), and K_1^* represents the equilibrium constants obtained by the fitting of the model expression. In this equation, the known terms have temperature, organic amine concentration, partial pressure of CO₂, and the equilibrium constant K_1^* can be obtained by fitting. By solving Equation (19), the hydrogen ion concentration $[H^+]^*$ can be calculated. The calculated hydrogen ion concentration $[H^+]^*$ is substituted into Equation (18) to predict the CO₂ equilibrium solubility in aqueous tertiary amine systems.

Fitting the coefficient A_i value of the K_1 expression is the key of thermodynamic model for accurate prediction. Here, the equilibrium constants K_i and hydrogen ion concentration of each reaction are calculated from the experimental parameters to obtain the concentration of each component in the solution, and then the value of the optimized K_1 expression coefficient A_i is fitted using MATLAB. Finally, the predicted the CO₂ equilibrium solubility is obtained. The main calculation process is shown in Figure 1.

The average absolute deviation (AAD, %, Equation 25) was used to assess the predictive accuracy of the different thermodynamic models. In general, a lower AAD indicates a better prediction.

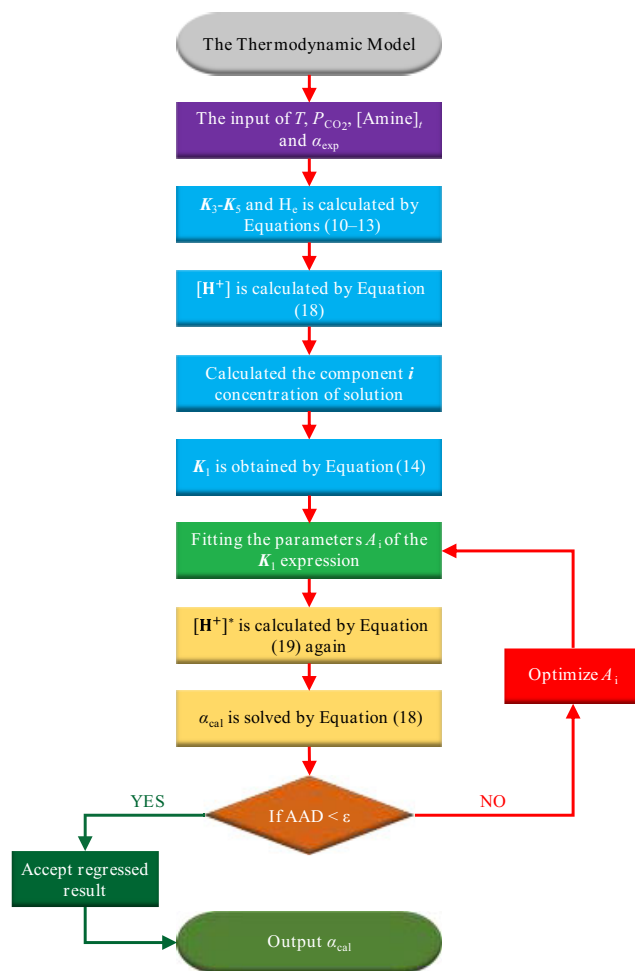


FIGURE 1 Thermodynamic modeling calculation process.

$$AAD = \frac{1}{N} \sum \left| \frac{\alpha_{exp} - \alpha_{cal}}{\alpha_{exp}} \right| \times 100\%, \quad (25)$$

where α_{exp} denotes the experimental value of CO₂ equilibrium solubility (mol CO₂/mol amine), α_{cal} represents its prediction value, and N denotes the data number.

2.2 | Determination of amine dissociation constants (pKa)

The magnitude of the amine dissociation constant not only reflects the protonation ability of the amine, but also determines the acidity or alkalinity of the aqueous solution of the organic amine, and is also one of the indicators for assessing CO₂ uptake in organic amines.^{40,41} The dissociation constant (pKa) of an organic amine is related to its absorption rate of CO₂. The higher the pKa of an organic amine solvent, the faster the reaction rate with CO₂.⁴² Here, the pKa values were determined by the method similar to that of Liu et al.⁴³ The equilibrium constant (K_a) was calculated by Equation (26), and the details on the calculation method was described in the Supporting Information, and its reliability was verified by using the MDEA solution (Figure S1).

$$K_a = [\text{H}^+] \left(\frac{[\text{Amine}] \cdot [\text{H}^+]}{K_w} - 1 \right), \quad (26)$$

where the molar concentration of the proton ($[\text{H}^+]$) is obtained from the experimentally tested pH, the molar concentration of the amine ($[\text{Amine}]$) is known for the experimental conditions, and the dissociation constant of water (K_w) is obtained from the experimental temperature. The relationship of the $\text{p}K_a$ and K_a is represented by Equation (27).

$$\text{p}K_a = -\log_{10}(K_a). \quad (27)$$

2.3 | CO₂ absorption heat

The CO₂ absorption heat is a key parameter for evaluating the CO₂ capture performance of organic amine solvents, as it directly affects the energy consumption of the regeneration process.⁴⁴ Typically, the CO₂ absorption heat can be calculated using a calorimeter or by following Clausius–Clapeyron equation.

$$-\frac{\Delta H_{\text{abs}}}{R} = \frac{d(\ln P_{\text{CO}_2})}{d(\frac{1}{T})}, \quad (28)$$

where R is the ideal gas constant (8.314 J/(mol·K)), and ΔH_{abs} is the CO₂ absorption heat (kJ/mol).

3 | EXPERIMENTAL

3.1 | Materials

The purity of experimental NMM and NEM was 99%, purchased from Shanghai Macklin Biochemical Co., Ltd, and their molecular structures were shown in Figure 2. Nitrogen and CO₂ with 99.99% purity were purchased from Hunan Zhongtai Hongyuan Gas, Co., Ltd. 36% hydrochloric acid was from Hunan Huihong Reagent Co., Ltd. All chemicals were used as received without further purification. Aqueous solutions of amines at different concentrations (1 and 2 mol/L) were prepared with ultrapure water.

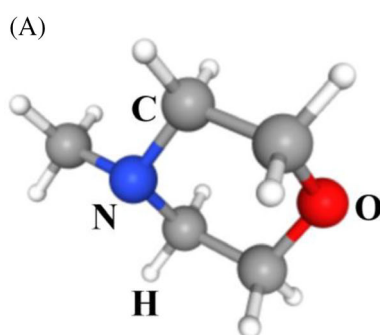
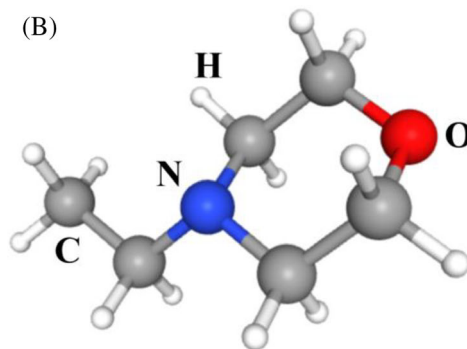


FIGURE 2 Molecular structures of (A) N-methylmorpholine (NMM) and (B) N-ethylmorpholine (NEM).



3.2 | Experimental measurement of equilibrium CO₂ solubility

The CO₂ equilibrium solubility test device for NMM and NEM aqueous solutions is shown in Figure 3, which mainly consists of two mass flow meters (D07, Seven Star, China), a bubbling gas–liquid absorption reactor, a water saturation device, a condensation system, and a constant-temperature water bath (FDLSC-40, accuracy: ± 0.05 K). In the experiments, high-purity nitrogen and CO₂ were controlled by a mass flow meter and mixed at a certain flow rate to form a simulated gas with the desired CO₂ partial pressure, which was water saturated by the water saturation device and then entered into the gas–liquid absorption reactor placed in the thermostatic water bath, and was finally discharged through the tail end of the condensation device to minimize the loss of amine and water under the operating conditions. Each set of experiments was carried out in a bubbling absorption reactor containing 25 mL of amine solution for more than 8 h. After 8 h, 2 mL of the loaded organic amine solution was taken at 30-min intervals and analyzed for CO₂ loading of the amine solution by titration using 1 mol/L hydrochloric acid using the Chittick apparatus.⁴⁵ When the CO₂ loading remains constant in three consecutive sampling titrations, it is determined that the system reaches equilibrium and the CO₂ loading is recorded as the CO₂ equilibrium solubility (mol CO₂/mol amine). The entire experimental procedure was carried out at atmospheric pressure. As shown in Figure S2, to verify the reliability of the equilibrium solubility device, the CO₂ equilibrium solubility data for 5 M MEA were compared with literature data, and the results were consistent (AAD were less than 1%).

4 | RESULTS AND DISCUSSION

4.1 | Key factors influencing the equilibrium CO₂ solubility

The CO₂ equilibrium solubility of organic amine systems is a key parameter for assessing the CO₂ absorption performance of amine solvents, which represents the maximum capacity of organic amine solvents to absorb CO₂.²⁷ In the temperatures ranging from 298.15–323.15 K, the CO₂ partial pressures ranging from 7.5 to 100 kPa, and the amine concentration range of 1–2 mol/L, we

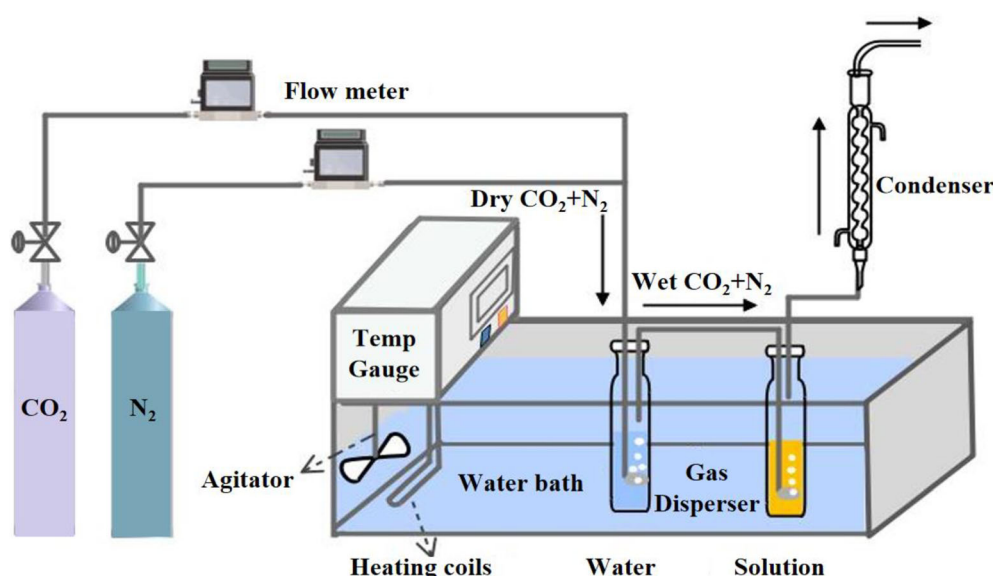


FIGURE 3 Experimental set-up of equilibrium CO₂ solubility measurement.

determined the CO₂ equilibrium solubility data in NMM and NEM solutions. Figure 4 illustrates all the experimental results, and detailed experimental data were listed in Tables S1 and S2 of Data S1.

Experimental results indicate that the CO₂ equilibrium solubility of both NMM and NEM solutions decrease with the increase of temperature, which is ascribed to the fact that the absorption of CO₂ by organic amines is a typical reversible exothermic reaction, and increasing the temperature will lead to the reaction equilibrium shifting to the reverse direction, unfavorable to the absorption of CO₂ by organic amines.⁴⁶ Besides, molecular motion is accelerated at high temperatures, making it more difficult for CO₂ molecules to bind to amine molecules in solution.⁴⁷ In contrast, the CO₂ equilibrium solubility in NMM and NEM solutions increases as the partial pressure of CO₂ increases, because the increase in CO₂ concentration enhances the mass transfer of CO₂ from the gas phase to the liquid phase. In addition, it is found that the CO₂ equilibrium solubility slightly decreases with the increase amine concentration, because the viscosity of the solution increases with the increase of amine concentration, which limits the mass transfer process in the reaction to a certain extent.

By comparing the CO₂ equilibrium solubility data of NMM and NEM solutions, it was found that the CO₂ equilibrium solubility of NEM was larger than that of NMM under the same conditions, which is attributed to the different chain lengths of the substituents (methyl and ethyl groups) on the nitrogen atoms. According to the base-catalyzed mechanism, the activity of CO₂ absorption by tertiary amines depends mainly on the ability of the nitrogen atom to capture protons, that is, on the magnitude of the electron density of the lone pair of electrons on the nitrogen atom. Since ethyl is a stronger electron-donating group than methyl and can enhance the reactivity of the nitrogen atom to bind protons, the substitution of ethyl rather than methyl is favorable to improve its CO₂ equilibrium solubility, which is consistent with the results of Narku-Tetteh et al. By studying the effect of alkanolamine chain length on CO₂ capture activity,^{48,49}

they pointed out that the longer alkyl chain substitution in alkanolamines can introduce higher electron density on the amino group, leading to higher pKa and therefore exhibits higher CO₂ equilibrium solubility. The pKa data obtained from the calculation in Section 4.3 can also prove the above conclusion. In fact, the pKa of the NEM is larger than that of the NMM, which has a stronger proton capture ability, and thus the NEM exhibits a superior CO₂ absorption performance than that of the NMM.

4.2 | Proposal of a general thermodynamic model

In order to improve the accuracy and universality of thermodynamic modeling for predicting the CO₂ equilibrium solubility in the amine-H₂O-CO₂ system, a series of empirical and semi-empirical models have been proposed, including Kent-Eisenberg, Austgen, Helei-Liu⁽¹⁾, Hu-Chakma, Li-Shen, and Helei-Liu⁽²⁾ models. By analyzing the existing models, it is found that the parameters of the equilibrium constant K_1 and the functional forms are the two key factors of determining the prediction accuracy. Since the chemical equilibrium constant is closely related to the chemical reaction, and experimental factors such as temperature, CO₂ partial pressure, and amine concentration play a crucial role in determining the chemical equilibrium constant for the amine-H₂O-CO₂ systems. Based on above analysis, we propose a general model by associating all the characteristic variables into the model. The K_1 expression of this model is given by.

$$K_1 = \exp \left(A_1 + \frac{A_2}{T} + A_3 \cdot \ln(P_{\text{CO}_2}) + A_4 \alpha + \frac{A_5}{\alpha} + \frac{A_6}{[\text{CO}_2]} + A_7 \ln[\text{Amine}] \right), \quad (29)$$

where T is the temperature, K, [Amine] is the free amine concentration, mol/L, α is the CO₂ loading, mol CO₂/mol amine, and A_1 – A_7 are polynomial coefficients.

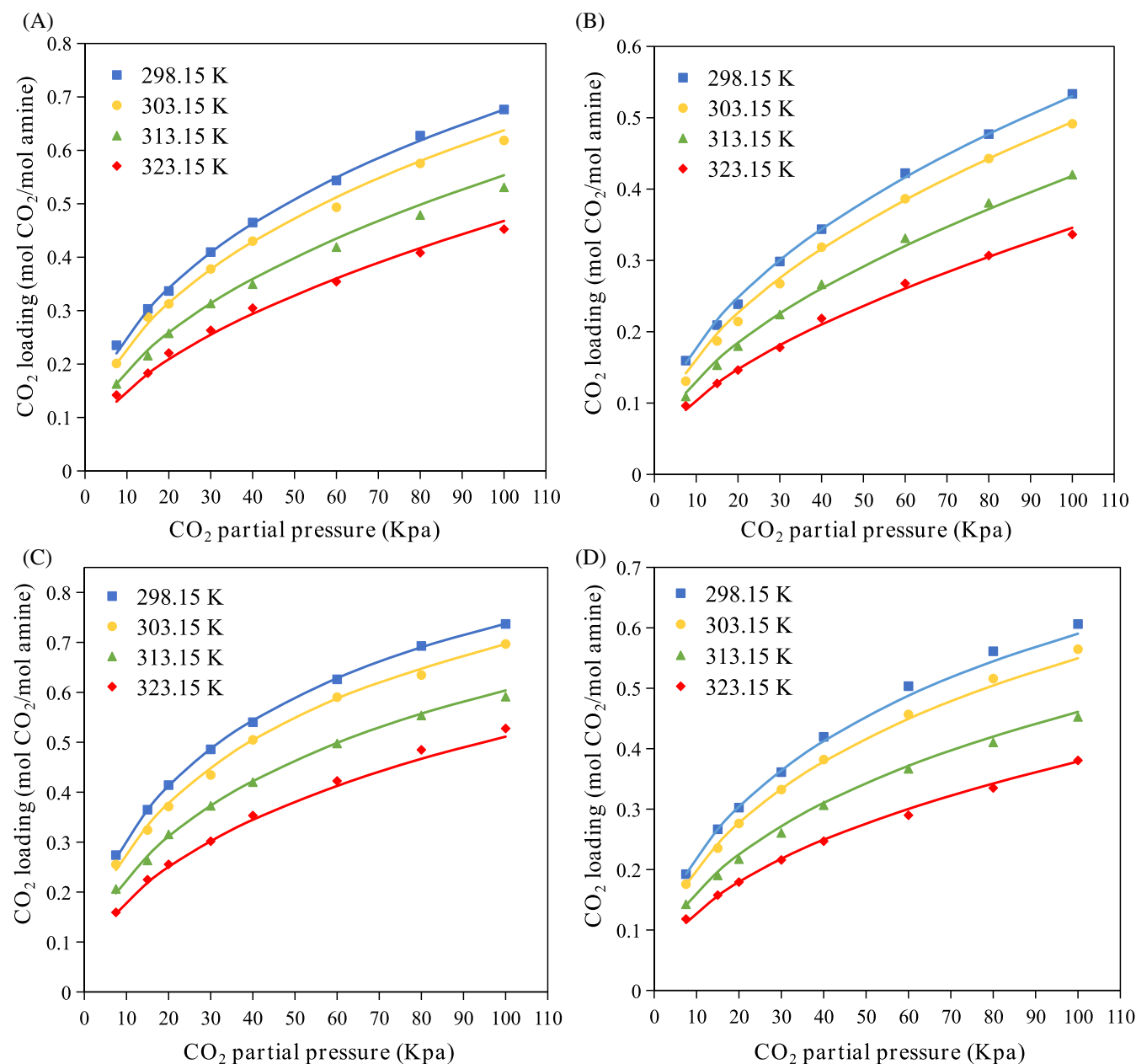


FIGURE 4 The CO₂ equilibrium solubility of (A) 1 M NMM (B) 2 M NMM solution and (C) 1 M NEM (D) 2 M NEM solution (dots: experiments, lines: predictions).

To confirm the accuracy and universality of the proposed model, we compared the prediction results of the CO₂ equilibrium solubility in NMM and NEM systems from the proposed model and six existing models. The K_1 expressions of six existing models were listed in Table 1. The parameters A_i of the K_1 expression in all seven models were obtained by fitting the K_1 values in different conditions using a nonlinear regression method. The detailed expressions were listed in Tables 2 and 3. The prediction results of the CO₂ equilibrium solubility in NMM and NEM systems are shown in Figures 5 and S3. The results show that the newly proposed general model has a lower average absolute deviation (AAD) in the prediction of the CO₂ equilibrium solubility in NMM and NEM solutions than other six existing models,

which are 0.98% and 0.77%, respectively, and 79.79% and 82.50% lower than the early proposed Kent-Eisenberg model. This observation further validates the accuracy of the general model. The specific data of Figure 2A,B are presented in Tables S13 and S14, respectively.

In the aspect of the prediction accuracy, Kent-Eisenberg and Austgen models have no obvious difference, probably because they only associate one parameter of temperature (T). In contrast, the Helei-Liu^①, Hu-Chakma, Li-Shen, and Helei-Liu^② models gradually introduced new variables such as free amine concentration ($[Amine]$), physical solubility of CO₂ ($[CO_2]$), CO₂ loading (α), and partial pressure of CO₂ (P_{CO_2}) to the K_1 expression, and thus improved their prediction accuracy. The observed discrepancy can be attributed to the limited

Model	K_1 expression
KE	$K_1 = \exp\left(A_1 + \frac{A_2}{T} + \frac{A_3}{T^2} + \frac{A_4}{T^3} + \frac{A_5}{T^4}\right)$
Austgen	$K_1 = \exp\left(A_1 + \frac{A_2}{T} + A_3 \ln T + A_4 T\right)$
Helei-Liu①	$K_1 = \exp\left(A_1 + A_2 T + \frac{A_3}{T} + A_4 \ln[\text{Amine}]\right)$
Hu–Chakma	$K_1 = \exp\left(A_1 + A_2 T + A_3 [\text{CO}_2] + A_4 \ln[\text{Amine}]\right)$
Li–Shen	$K_1 = \exp\left(A_1 + \frac{A_2}{T} + \frac{A_3}{T^2} + A_4 \alpha + \frac{A_5}{\alpha} + \frac{A_6}{\alpha^2} + A_7 \ln[\text{Amine}]\right)$
Helei-Liu②	$K_1 = \exp\left(A_1 + A_2 T + A_3 [\text{CO}_2] + A_4 \ln[\text{Amine}] + A_5 \alpha + A_6 P_{\text{CO}_2}\right)$

TABLE 1 The K_1 expression of thermodynamic models.

Model	Expression
KE	$K_1 = \exp\left(-6.69 - \frac{3337.06}{T} - \frac{5366.01}{T^2} - \frac{6}{T^3} + \frac{55.97}{T^4}\right)$
Austgen	$K_1 = \exp\left(7.98 - \frac{3968.01}{T} - 2.27 \ln T + 1.08 \times 10^{-3} T\right)$
Helei-Liu①	$K_1 = \exp\left(-26.75 + 0.03T - \frac{10.16}{T} + 0.07 \ln[\text{Amine}]\right)$
Hu–Chakma	$K_1 = \exp\left(-27.60 + 0.033T - 12.95[\text{CO}_2] + 0.08 \ln[\text{Amine}]\right)$
Li–Shen	$K_1 = \exp\left(-8.43 - \frac{2762.97}{T} - \frac{7985.12}{T^2} - 0.78\alpha + \frac{0.03}{\alpha} + \frac{2.78 \times 10^{-4}}{\alpha^2} - 7.44 \times 10^{-2} \ln[\text{Amine}]\right)$
Helei-Liu②	$K_1 = \exp\left(-28.55 + 0.036T + 8.58 \times 10^{-3} [\text{CO}_2] + 0.096 \ln[\text{Amine}] + 6.39 \times 10^{-5} \alpha - 3.95 \times 10^{-3} P_{\text{CO}_2}\right)$
This work	$K_1 = \exp\left(-23.59 + \frac{1114.74}{T} + 1.03 \ln(P_{\text{CO}_2}) - 5.11\alpha + \frac{0.24}{\alpha} - \frac{8.44 \times 10^{-5}}{[\text{CO}_2]} - 1.06 \ln[\text{Amine}]\right)$

TABLE 2 Thermodynamic model expressions for the NMM–H₂O–CO₂ system.

Model	Expression
KE	$K_1 = \exp\left(-5.61 - \frac{3812.82}{T} - \frac{5315.13}{T^2} - \frac{6}{T^3} + \frac{50.84}{T^4}\right)$
Austgen	$K_1 = \exp\left(8.86 - \frac{4401.04}{T} - 2.22 \ln T + 9.9 \times 10^{-4} T\right)$
Helei-Liu①	$K_1 = \exp\left(-30.2 + 0.04T - \frac{7.36}{T} + 0.12 \ln[\text{Amine}]\right)$
Hu–Chakma	$K_1 = \exp\left(-29.59 + 0.038T - 9.04[\text{CO}_2] + 0.12 \ln[\text{Amine}]\right)$
Li–Shen	$K_1 = \exp\left(-7.098 - \frac{3370.76}{T} + \frac{0.25}{T^2} - 0.44\alpha + \frac{0.08}{\alpha} - \frac{8.46 \times 10^{-3}}{\alpha^2} - 2.07 \times 10^{-2} \ln[\text{Amine}]\right)$
Helei-Liu②	$K_1 = \exp\left(-28.53 + 0.035T + 0.108[\text{CO}_2] + 1.02 \times 10^{-3} \ln[\text{Amine}] - 0.64\alpha + 1.28 \times 10^{-4} P_{\text{CO}_2}\right)$
This work	$K_1 = \exp\left(-24.64 + \frac{1360.38}{T} + 1.09 \ln(P_{\text{CO}_2}) - 5.27\alpha + \frac{0.28}{\alpha} - \frac{7.63 \times 10^{-5}}{[\text{CO}_2]} - 1.12 \ln[\text{Amine}]\right)$

TABLE 3 Thermodynamic model expressions for the NEM–H₂O–CO₂ system.

consideration of variables in other models, which results in a decline in their prediction accuracy. Specifically, the key point of semi-empirical models in predicting CO₂ equilibrium solubility is the calculation of the hydrogen ion concentration within the solution. However, the hydrogen ion concentration derived from Equation (18) exhibits deviations from the actual concentration during CO₂ absorption. Through the corrective measures outlined in Equation (19) and subsequent adjustment of the fitting, the semi-empirical model achieves a

more precise depiction of the solution's actual state. Consequently, refining and adjusting the parameters associated with the K_1 expression emerges as a critical step in enhancing the model's accuracy. Comparing the Helei-Liu② model and the general model proposed in this study, it was found that the two models were basically the same in terms of the refinement of the experimental factors associated with the K_1 expression, but the prediction accuracies of the general model were improved by 69.18% and 63.18%, respectively, which may be

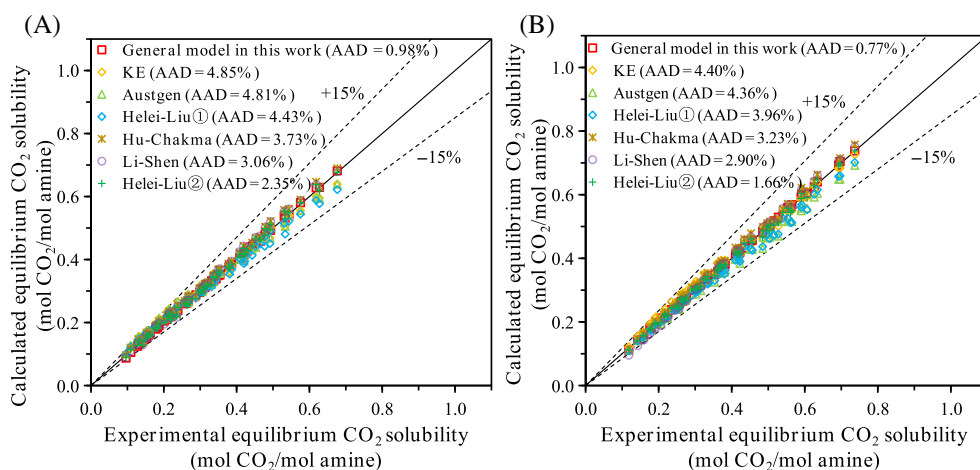


FIGURE 5 The comparison of the experimental results with the predicated data from thermodynamic models (A) NMM and (B) NEM.

caused by their difference in the functional form. So, optimization of the functional expansion form of each parameter in the K_1 expression is also another key to improve the prediction accuracy of the model.

4.3 | The universality of the proposed general model

In order to assess the universality of the proposed general model for the prediction of CO₂ equilibrium solubility in tertiary amines, we tested it by using literature data including 10 tertiary amine solvents, such as 1-(2-hydroxyethyl)-piperidine (1-(2HE)-PP),⁵⁰ 2-(dimethylamino)-2-methyl-1-propanol (2DMA2M1P),⁵¹ 2-[2-(dimethylamino)ethoxy]ethanol (DMAEE),⁵² N-methyl-4-piperidinol (MPDL),⁵³ 1-diethylamino-2-propanol (1DEA2P), 1-dimethylamino-2-propanol (1DMA2P), 4-diethylamino-2-butanol (DEAB), 4-(dimethylamino)-2-butanol (DMAB), 4-(ethyl-methylamino)-2-butanol (EMAB), and MDEA. The K_1 expressions for each tertiary amine were listed in Tables S3–S12, and the results predicted by different models were shown in Figure S4. For convenient observation and comparison, the AADs of different models for the prediction of the CO₂ equilibrium solubility in the above 10 tertiary amines are shown in Figure 6. Compared with the six existing models, the proposed general model still exhibits the smallest AAD in the prediction of the CO₂ equilibrium solubility in the 10 tertiary amine solutions mentioned above. Compared to the Kent–Eisenberg model, the AADs of the proposed general model significantly reduce by 93.27% (1-(2HE)-PP), 79.38% (2DMA2M1P), 69.98% (DMAEE), 95.12% (MPDL), 76.13% (1DEA2P), 80.77% (1DMA2P), 81.59% (DEAB), 71.08% (DMAB), 80.77% (EMAB), and 93.41% (MDEA), respectively. The above results show that the general model proposed here can predict the CO₂ equilibrium solubility of tertiary amine solvents more accurately than the other six models reported previously. The suitability of the general model for 10 tertiary amine systems suggests the

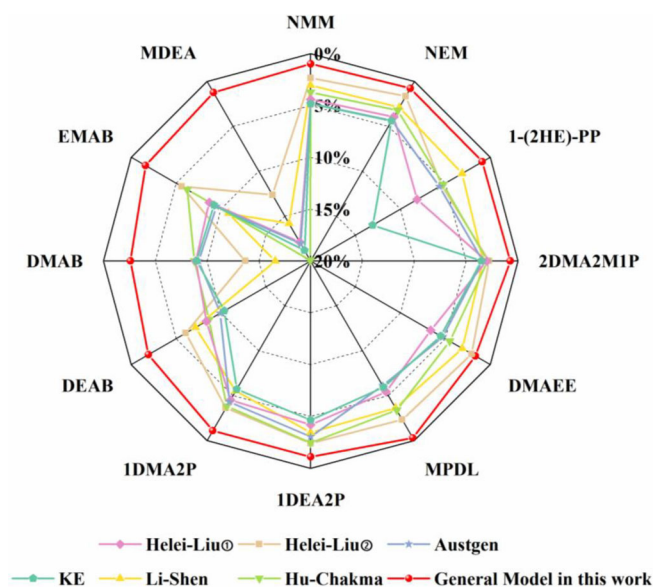


FIGURE 6 AAD comparisons of seven models in predicting the CO₂ equilibrium solubility in 10 tertiary amine systems, including 1-(2HE)-PP, 2DMA2M1P, DMAEE, MPDL, 1DEA2P, 1DMA2P, DEAB, DMAB, EMAB, and MDEA.

universality of the proposed general model in predicting the CO₂ equilibrium solubility of tertiary amine solvents. The specific data of Figure 6 are presented in Table S15.

4.4 | Dissociation constants (pKa) in aqueous NMM and NEM solutions

The dissociation constant of amines (pKa) is an indicator of the alkalinity of organic amine solvents and can explain the kinetic mechanism of the reaction of amine solvents in absorption of acidic gases.⁴¹ In this study, the pKa values of NMM and NEM solvents were

determined in the temperature range of 298.15–333.15 K. As shown in Figure 7A, the pKa values in both systems decreased with increasing temperature, and the pKa values of NEM were higher than that of NMM under the same conditions (e.g., at 298.15 K, the pKa of NMM was 7.38, while it is 7.68 for NEM), which was consistent with the effect law of chain length on CO₂ capture performance of amine solvents proposed by Xiao et al.²⁰ The equilibrium constant K_a vs. temperature in aqueous solutions of NMM and NEM was calculated by linear regression analysis and shown in Equations (30) and (31), respectively. As shown in Figure 7B, the equation well correlates K_a with temperature with AAD of 0.04% and 0.06%, respectively. Therefore, this Equations (30) and (31) can well predict the equilibrium constant K_a of NMM and NEM aqueous solutions under different conditions, and the dissociation constant pKa can be further calculated from the value of K_a . The specific data of Figure 7 are presented in Table S16.

$$K_a = \exp\left(\frac{-6.441 \times 10^3}{T} + 4.61\right), \quad (30)$$

$$K_a = \exp\left(\frac{-7.469 \times 10^3}{T} + 7.37\right). \quad (31)$$

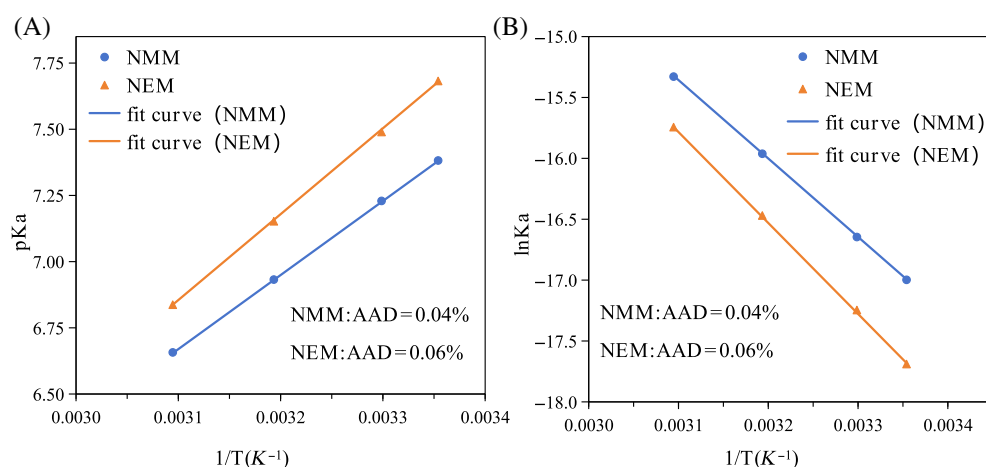


FIGURE 7 (A) The dissociation constant pKa and (B) the equilibrium constants K_a of NMM and NEM solutions at different temperatures.

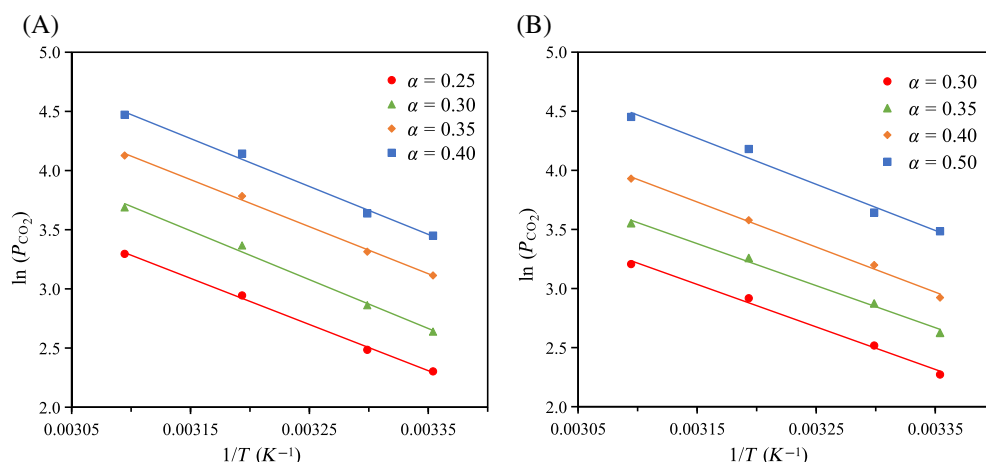


FIGURE 8 The plots of ln(P_{CO2}) vs. 1/T for (A) NMM and (B) NEM aqueous solution at different CO₂ loadings.

4.5 | Absorption heat of CO₂ in aqueous NMM and NEM solutions

Absorption heat of CO₂ in organic amine solvents is a critical factor for process operation and cost prediction. These data largely determine the energy consumption of the solvent regeneration process and are an important parameter in evaluating the performance of organic amine absorbents.⁴⁴ The CO₂ absorption heat was estimated by CO₂ equilibrium solubility data using the Clausius–Clapeyron equation (Equation 28). Previous investigations indicate that the CO₂ absorption heats of MEA,³¹ DEA,⁵⁴ and MDEA⁵⁵ estimated by the Clausius–Clapeyron equation were in good agreement with the experimental data of Carson et al.⁵⁶ using the calorimeter method, which proves that the CO₂ absorption heat obtained by Clausius–Clapeyron equation is acceptable and reliable.

In this study, the CO₂ absorption heat of 1 M NMM and NEM was calculated using Equation (28) based on the CO₂ equilibrium solubility predicted by the proposed general model. Plotting ln(P_{CO2}) vs. 1/T for the same CO₂ loading and fitting it to obtain the slope of the straight line is the CO₂ absorption heat for that CO₂ loading. In this study, four values can be obtained by fitting the slopes of the straight lines under four different CO₂ loading for each amine solvent (Figure 8). And the average value was used as the final CO₂

absorption heat in NMM and NEM solvents, which are -33.38 and -30.92 kJ/mol, respectively. Figure 10 demonstrates the relationship between different amines and CO_2 loading, where the reference amines are commonly used commercial amines including MEA,⁵⁷ DEA,⁵⁸ AMP,⁵⁹ PZ,⁶⁰ MDEA,⁵⁵ DMEA,⁶¹ DEAB,⁶² DEEA,⁶³ and DMAEE.⁵² It can be seen from Figure 10 that the CO_2 absorption heat in NMM and NEM solvents is lower than that of all reference amines. Among them, the CO_2 absorption heat of NMM and NEM was reduced by 60.26% and 63.19% compared to MEA and 33.24% and 38.16% compared to DMEA, respectively. For the conventional primary amines (MEA), secondary amines (DEA), space-site-resistant amines (AMP) and cyclic amines (PZ), their reaction mechanism is different with tertiary amines. Primary and secondary amines react with CO_2 to produce mainly carbamates with a high heat of reaction, whereas tertiary amines usually do not react directly with CO_2 but act as bases to catalyze the hydration of CO_2 . Therefore, primary and

secondary amines exhibit a higher CO_2 absorption heat than tertiary amines. In addition, the lower CO_2 absorption heat of NMM and NEM than other tertiary amines may be attributed to the presence of ether bonds and three alkyl substituents on the nitrogen atoms in the molecular structure of NMM and NEM, resulting in a weaker bonding strength with CO_2 . It is well known that the absorption and desorption processes of CO_2 by organic amine absorbents are inverse reactions, so the smaller the CO_2 absorption heat means the less energy consumption in the regeneration process and the lower the operating cost.⁴⁴ Therefore, NMM and NEM solvents possess apparent advantage in reducing regeneration energy consumption. The specific data of Figures 8 and 9 are presented in Tables S17 and S18, respectively.

4.6 | Comprehensive evaluation of amine

In order to comprehensively evaluate the potential for CO_2 capture applications, NMM and NEM were compared with other amines (e.g., MEA, DEA, AMP, PZ, MDEA, etc.)^{57–60,62,64} in terms of CO_2 equilibrium solubility, pKa, and the CO_2 absorption heat. The CO_2 equilibrium solubility reflects the maximum CO_2 absorption capacity of an aqueous amine solution, while the dissociation constants (pKa) of amines correlate with the reaction kinetics, and usually a higher pKa corresponds to a faster rate of absorption, while the CO_2 absorption heat reveals the energy requirement of organic amines in the solvent regeneration process. A comparison of CO_2 equilibrium solubility of NMM and NEM with that of other amines is shown in Figure 10A, where PZ and DEAB have higher absorption capacities and NMM and NEM show relatively low absorption capacities. PZ is a diamine with two amino groups, DEAB has two ethyl substituents on the nitrogen atom, while the hydroxyl group at the γ -position reduces the negative impact of the induction effect, and the methyl side chain provides a certain spatial site-blocking effect making hydrogen bonding not easy to be formed. On the contrary, the activity of NMM and NEM in reacting with CO_2 is greatly limited due to the presence of ether bonds in their six-membered rings.²⁰ In addition to high CO_2 equilibrium solubility, the ideal amine solvents should also have high

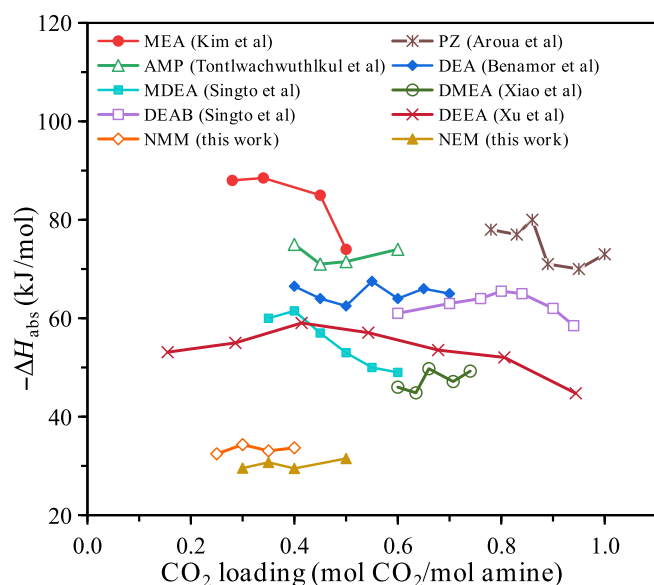


FIGURE 9 The plot of the CO_2 absorption heat with CO_2 loading for different amines.

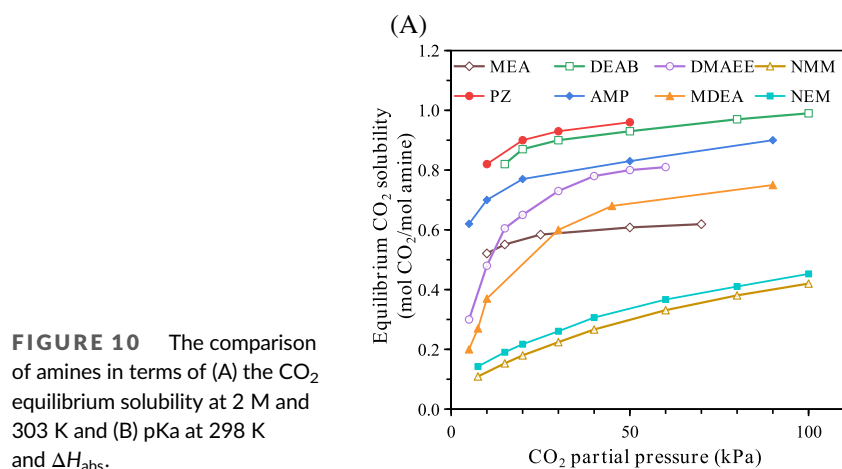


FIGURE 10 The comparison of amines in terms of (A) the CO_2 equilibrium solubility at 2 M and 303 K and (B) pKa at 298 K and ΔH_{abs} .

pKa and low CO₂ absorption heat. Figure 10B shows the pKa and the CO₂ absorption heat of the amine solvents. NMM and NEM have some deficiencies in CO₂ uptake and reaction rate, but have advantage in the CO₂ absorption heat. Considering the low pKa values, meaning faster desorption reaction rates, and low CO₂ absorption heat, NMM and NEM may be a promising desorption promoter. By introducing them into the organic amine solvent regeneration process, a more efficient and energy-saving CO₂ capture process may be realized. The specific data of Figure 10A,B are presented in Tables S19 and S20, respectively.

The above information and data in the text are presented in the Word, Data S1. The numerical data from Figures 5–10 are tabulated in the Excel, Data S2. And the numerical data from Figures S1–S5 are tabulated in the Excel, Data S3.

5 | CONCLUSIONS

In summary, we successfully constructed a general model for predicting CO₂ equilibrium solubility of aqueous tertiary amine solutions by associating all the characteristic variables including constant K_1 -related parameters and functional forms into the model. To confirm its prediction accuracy, we experimentally measured the CO₂ equilibrium solubility in aqueous NMM and NEM solutions under different conditions. By comparing with six existing models, the proposed general model not only presented better prediction accuracy for these data in NMM and NEM solutions, but also exhibited excellent universality for other 10 tertiary amine systems from literature. To comprehensively evaluate the amine system for CO₂ absorption, the CO₂ absorption heat was calculated by the Clausius–Clapeyron equation to be −33.38 and −30.92 kJ/mol for NMM and NEM, respectively. In terms of the CO₂ equilibrium solubility, pKa and the CO₂ absorption heat, NMM and NEM exhibited lower CO₂ absorption heat compared with other amines, which is expected to reduce the energy consumption of the solvent regeneration process. However, NMM and NEM as single solvents still have some shortcomings in terms of CO₂ absorption capacity and reaction rate. To solve these problems, they can be considered to be introduced into primary amines or polyamines. Besides, NMM and NEM may be promising absorbents for post-combustion CO₂ capture owing to the excellent resistance to degradation and corrosion.

AUTHOR CONTRIBUTIONS

Cheng Yu: Writing – original draft; validation; investigation; conceptualization; methodology; software; data curation; visualization. **Hao Ling:** Funding acquisition; writing – review and editing; project administration; resources; supervision; formal analysis; conceptualization; methodology; validation. **Zhigang Shen:** Writing – review and editing. **Hongyun Yang:** Writing – review and editing. **Dapeng Cao:** Writing – review and editing; funding acquisition; resources; validation; formal analysis. **Xiayi Hu:** Funding acquisition; writing – review and editing; resources.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT

All data mentioned in the text are presented in the supplementary material. Additional information and data mentioned in the manuscript are presented in the Word, Data S1. The numerical data from Figures 5–10 are tabulated in the Excel, Data S2. And the numerical data from Figures S1–S5 are tabulated in the Excel, Data S3. All the literature data are taken from publicly available literature in the Web of Science, as well as public data websites such as Pubchem to ensure the availability and reproducibility of the data.

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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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