

Article

Machine Learning (ML) Modeling of CO₂ Liquid–Vapour Equilibrium (LVE) Absorption in Amine Aqueous Solutions

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Abstract

Predicting CO₂ absorption behavior in aqueous amine systems is a critical challenge for optimizing carbon capture technologies. This research develops a high-precision Artificial Neural Network (ANN) to simulate equilibrium data across various amine classes, including primary (MEA, DGA), secondary (DEA, DPA), and tertiary (MDEA) amines. The model architecture utilizes a Multi-Layer Perceptron (MLP) trained on a dataset split into 70% training, 15% validation, and 15% testing segments to prevent overfitting and ensure reliable generalization. By employing a Sigmoid activation function, the network achieved a coefficient of determination (R^2) exceeding 0.98 and an absolute average relative deviation (AARD) below 5%. Furthermore, this study evaluates the efficacy of classical isotherms (Langmuir, Freundlich, and Temkin) strictly as empirical curve-fitting correlations for liquid-phase behavior. Results indicate that while these models are traditionally surface-adsorption based, the Langmuir form provides a mathematically robust fit for the tertiary amine MDEA ($R^2 = 0.9673$). Experimental observations indicate that Monoethanolamine (MEA) maintains the highest capacity for CO₂ uptake. Since the model relies on categorical descriptors for amine types, it offers a rapid and efficient framework for assessing specific solvents in post-combustion capture infrastructure.

Keywords: CO₂; monoethanolamide (MEA); diethanolamine (DEA); diglycolamine (DGA); methyl diethanolamine (MDEA); dipropylamine (DPA)

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1. Introduction

Global CO₂ emissions from fossil fuels have shown significant fluctuations in recent years, with a 5.4% decrease observed in 2020 due to the COVID-19 pandemic [1].

According to recent data, atmospheric CO₂ is the primary contributor to global warming, accounting for 76% of greenhouse gas effects, and to mitigate these impacts and

limit the global average temperature increase to 2 °C, carbon capture and storage (CCS) technology is essential [2].

From the point of view of CO₂ emissions levels and concentrations, the largest sources of stationary emissions are burning fossil fuels for energy production in oil refineries and petrochemical plants (24.2%), followed by transport activity (16.2%) [3].

Recent publications estimate that atmospheric carbon dioxide accounts for 76% of global warming, followed by methane at 12% and nitrous oxide at 11% [3].

Therefore, in the last decade, the capture of CO₂ from flue gases has become a central theme of Romanian chemical engineering research because the European Community has decided that the oil and gas industry of Romania will store 10 million tons of CO₂ from 2030.

The technology of carbon dioxide capture and storage is an integrated process involving the capture of CO₂ from burning gases resulting in significant emission points (power plants powered by fossil fuels, operators in the cement industry, steel industry, petrochemical industry, etc.), transport to the storage site, and storage of CO₂ in stable geological formations where it can be isolated for the long term.

However, CO₂ capture is technically and economically viable for sources that generate an annual amount of CO₂ exceeding 100.000 t [4].

The European Union has adopted ambitious targets for reducing greenhouse gas emissions, which cannot be met without significantly reducing CO₂ emissions from fossil fuels [5].

This reduction is technically possible by applying three types of measures [6]:

- Improving energy efficiency;
- The use of renewable energy sources;
- The capture and storage of the currently emitted carbon dioxide.

CO₂ capture and storage prevent carbon dioxide from the burning of fossil fuels from entering the atmosphere.

Since carbon dioxide is an important greenhouse gas, the Intergovernmental Panel on Climate Change (IPCC) believes that CO₂ capture and storage technology could contribute to limiting greenhouse gas emissions by 15 ÷ 55% and, therefore, combat climate change [7].

Efforts to capture CO₂ must focus on the combustion gases from fossil fuels (coal, natural gas, and oil) generated by electrothermal plants.

Depending on the fuel, the resulting gases contain 13–15% vol. CO₂ and have very high flow rates.

A comparative analysis of methods for separating CO₂ from such gases indicates that chemical absorption is the most effective.

The method can be implemented in various procedures, depending on the chemical solvent used.

Currently, there are three technological variants in competition [3]:

- Absorption in activated potassium carbonate solutions,
- Absorption in ammonia solutions,
- Absorption in amine solutions.

Several articles and experiments have sought to determine the absorption efficiency in amine solutions.

However, neural networks have been little used to demonstrate the effectiveness of this carbon dioxide reduction technique.

Salooki conducted the first simulation to demonstrate the process's efficiency in predicting reflux and CO₂-amine contact temperatures [8].

Saghatoleslami and Adib developed a similar algorithm and provided temperature and reflux-flow data for a CO₂-amine contact column [9].

Also, Sipöcz et al. modeled CO₂ absorption from flue gases in MEA solution [10].

Zhou and Daneshvar present simulation work that models flue gas absorption processes with fuzzy systems based on ANN sensitivity [11].

While this study focuses on optimizing the absorption stage, the ultimate goal of carbon management often involves the efficient conversion of captured CO₂ into value-added chemicals.

Recent breakthroughs in catalysis have highlighted that the structural architecture of catalysts plays a decisive role in these processes.

Specifically, the controlled creation, selective exposure, and activation of more basal planes—while simultaneously minimizing the generation and exposure of edge sites—are crucial for accelerating methanol synthesis from CO₂ hydrogenation over MoS₂ catalysts. To address current bottlenecks, recent research has reported a facile method to fabricate heteronanotube catalysts, where single-layer MoS₂ coaxially encapsulates carbon nanotubes (CNTs@MoS₂) through host–guest chemistry [12].

Integrating such high-efficiency conversion pathways with the high-accuracy ANN modeling of absorption equilibrium presented in this work is essential for the future development of fully optimized carbon capture and utilization (CCU) systems [13].

2. Materials and Methods

Absorption of acid gases into alkanol amines is a process long used in industrial applications.

Alkanol amines are chemicals containing at least one hydroxyl group, which reduces vapor pressure and increases water solubility, and one amino group, which provides the alkalinity necessary for CO₂ absorption.

The amines of commercial interest studied in this work include:

- Monoethanolamine (MEA): a primary amine with the highest alkalinity and fast reaction rates.
- Diethanolamine (DEA): a secondary amine often used for refinery gas purification.
- Methyl diethanolamine (MDEA): a tertiary amine known for selective H₂S removal and low regeneration energy.
- Diglycolamine (DGA) and Dipropylamine (DPA).

The relationship between the concentration of CO₂ in the liquid phase and its partial pressure in the gas phase—known as CO₂ loading (mol CO₂/mol amine) or absorption capacity—is essential for plant design.

In the design of gas treatment plants, it is essential to understand the relationship between the concentration of acid gases in amine solutions and their partial pressures in the gas phase, i.e., solubility (or liquid–vapor equilibrium) data.

Selective absorption of H₂S from streams containing both acid gases is achieved by sizing the absorbers so that their contact area allows the reaction and absorption of H₂S but is insufficient to absorb a significant proportion of the CO₂.

The primary, secondary, and tertiary amines used in gas purification processes exhibit distinct physical characteristics that influence their selection for industrial applications. Key properties such as molar mass, density, and boiling point are detailed in Table 1 below.

Table 1. Amine properties of CO₂ loading (mol CO₂/mol amine).

Property	MEA	DEA	MDEA	DPA
Molar mass	61.12	105.22	119.18	133.21
Density at 20 °C (g/mL)	1.013	1.099	1.037	1.005
Boiling point °C				
750 mm Hg	172	272	245	249
50 mm Hg	99	188	163	166
10 mm Hg	68	153	131	134
Vapor pressure at 20 °C (mm Hg)	0.35	0.01	0.01	0.01
Freezing point, °C	10.4	28.1	−20	41.0
Solubility in water, % at 20 °C	100	96.8	100	88
Refractive index at 20 °C	1.44	1.47	1.46	1.45

The specified literature describes several experimental tests of CO₂ absorption in an amine solution [14–16].

The use of aqueous alkanolamines, specifically monoethanolamine (MEA), remains the industrial benchmark for post-combustion CO₂ capture due to its high reactivity and low solvent cost. However, optimizing the process requires a deep understanding of the complex interaction between chemical kinetics and phase equilibria.

Shen and Li [14] provided fundamental insights into the reaction mechanism, establishing the kinetic constants for CO₂ absorption into aqueous MEA and blends. Their work emphasized the dominance of carbamate formation in primary amines, which dictates the theoretical loading capacity. Building on these kinetic foundations, Lee and Lin [14] focused on the thermodynamic challenges by developing rigorous vapor-liquid equilibrium (VLE) models. By utilizing the electrolyte-NRTL framework, they successfully predicted the CO₂ partial pressure over loaded MEA solutions, a critical parameter for determining the energy required in the stripper section.

The transition from lab-scale kinetics to industrial-scale application was further bridged by Jones et al. [15]. They developed a rate-based model that accounts for mass and heat transfer resistances, rather than assuming simple equilibrium. Their research highlighted the “temperature bulge” phenomenon within the absorber—a result of the exothermic nature of the amine reaction—which can significantly inhibit absorption efficiency if not properly managed through inter-cooling. Furthermore, more modern computational approaches have sought to simplify these complex simulations; for instance, Sipöcz et al. [10] and Zhou and Daneshvar [11] demonstrated that Artificial Neural Networks (ANN) and fuzzy systems can predict column performance with high accuracy while significantly reducing the computational time compared to traditional rate-based models.

The most frequently cited experiments are those given in Table 2.

Table 2. Literature experience of CO₂ loading (mol CO₂/mol amine).

References	Temperature, °C	CO ₂ Loading (mol CO ₂ /mol Amine)	Number of Interval Points of Experiments	Partial Pressure of CO ₂ , kPa
Shen and Li [14]	40	15.7–2550.0	0.561–1.049	13
Jones [15]	40	0.3–120.7	0.412–0.713	8
Lee [12]	40	2.0–488.0	0.460–0.989	11
Less [16]	40	1.0–1316.0	1.000–1316.0	8

New laboratory experiments were conducted at a consistent temperature of 40 °C. Pure CO₂ (99.9%) was passed through aqueous solutions of MEA, DEA (2M and 4M), and MDEA.

The CO₂ partial pressure was varied while measuring the gas flow rate and concentration at the inlet and outlet of the reactor, to determine the amount of CO₂ absorbed.

These results were compared with equilibrium data sourced from specialized literature.

The experiment was designed to pass a stream of pure CO₂ through various amine solutions, including MEA, DEA 2M, DEA 4M, and MDA, each chosen for their unique properties and potential in CO₂ absorption.

Our experiment aimed to discover mathematical relationships between each research study and data obtained in the literature to define the partial pressure of CO₂ versus the amine loading capacity (moles CO₂/moles amine).

A local manufacturer supplied (Dafcochim, Romania) pure CO₂, and installation created for this experiment consisted of passing CO₂ through an amine solution in a reactor at temperatures of 40 °C.

The partial pressure of CO₂ was changed, determining the gas flow into and out of the reactor, and the gas concentration was also determined at the inlet and outlet.

3. Results

Five experiments were performed to determine the equilibrium curves for CO₂ absorption in aqueous solutions of MEA, 2M DEA, 4M DEA, and MDEA (Table 3).

Each experiment was conducted under the same laboratory conditions (99.9% CO₂ in pure gas and 1% water) and at a reactor temperature of 40 °C.

Also, the concentration and flow rate of the gases entering and leaving the reactor were measured.

The amount of CO₂ absorbed by the amine was determined numerically for each component in the experimental setup, based on the inlet and outlet flow rates.

The data collected from the experiment are shown in Table 2 and Figure 1.

Figures 2 and 3 show the data on CO₂ absorption in amine solution, taken from Table 3.

A logarithmic relationship was determined for each experiment, which enabled calculation of the CO₂ absorption process in amine solutions (Figure 4, Tables 4 and 5).

In this paper, for the development of the Artificial Neural Network (ANN) Model, to model the non-linear relationship between amine type, concentration, temperature, and CO₂ loading, a Multi-Layer Perceptron (MLP) architecture was employed.

The network consists of an input layer with four variables (CO₂ partial pressure, temperature, amine type, and concentration), one hidden layer with 10–15 neurons, and a single output layer for predicted CO₂ loading.

The dataset, comprising 75 experimental and literature points, was divided into 70% for training, 15% for validation, and 15% for independent testing, to ensure model generalizability.

Table 3. CO₂ loading (mol CO₂/mol amine), experiments of Petroleum Gas University.

Partial Pressure CO ₂ , kPa	CO ₂ Loading (mol CO ₂ /mol Amine) MEA	CO ₂ Loading (mol CO ₂ /mol Amine) DEA 2M	CO ₂ Loading (mol CO ₂ /mol Amine) DEA 4M	CO ₂ Loading (mol CO ₂ /mol Amine) MDEA
0.02				0.00201 ± 0.0005
0.03				0.0105 ± 0.0005
0.1	0.22 ± 0.0005	0.171 ± 0.0005	0.091 ± 0.0005	0.0058 ± 0.0005

0.5	0.44 ± 0.0005	0.279 ± 0.0005	
0.7	0.45 ± 0.0005		0.0608 ± 0.0005
0.9		0.282 ± 0.0005	
1.0	0.47 ± 0.0005	0.321 ± 0.0005	
2.6	0.55 ± 0.0005		0.135 ± 0.0005
4.5	0.66 ± 0.0005		
5.3		0.458 ± 0.0005	0.442 ± 0.0005
10.7		0.539 ± 0.0005	0.563 ± 0.0005
13.3			0.287 ± 0.0005
32.1		0.599 ± 0.0005	0.591 ± 0.0005
53.8		0.664 ± 0.0005	0.634 ± 0.0005
83.4			0.712 ± 0.0005
106			0.715 ± 0.0005

Overfitting was mitigated through the “Early Stopping” method, where training is halted once the validation error begins to rise, despite a falling training error.

Model performance was evaluated using R^2 and Absolute Average Relative Deviation (AARD).

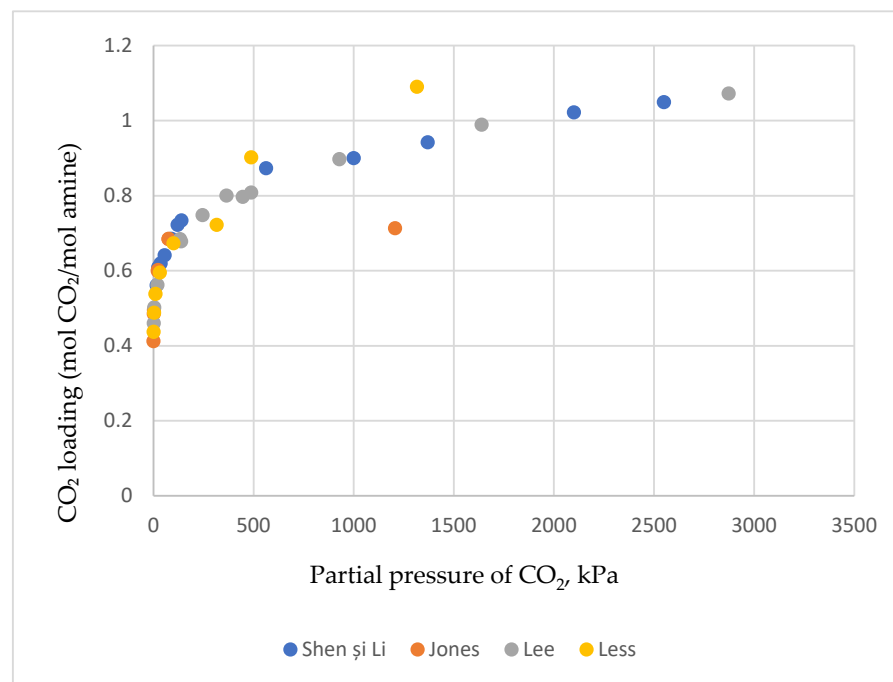


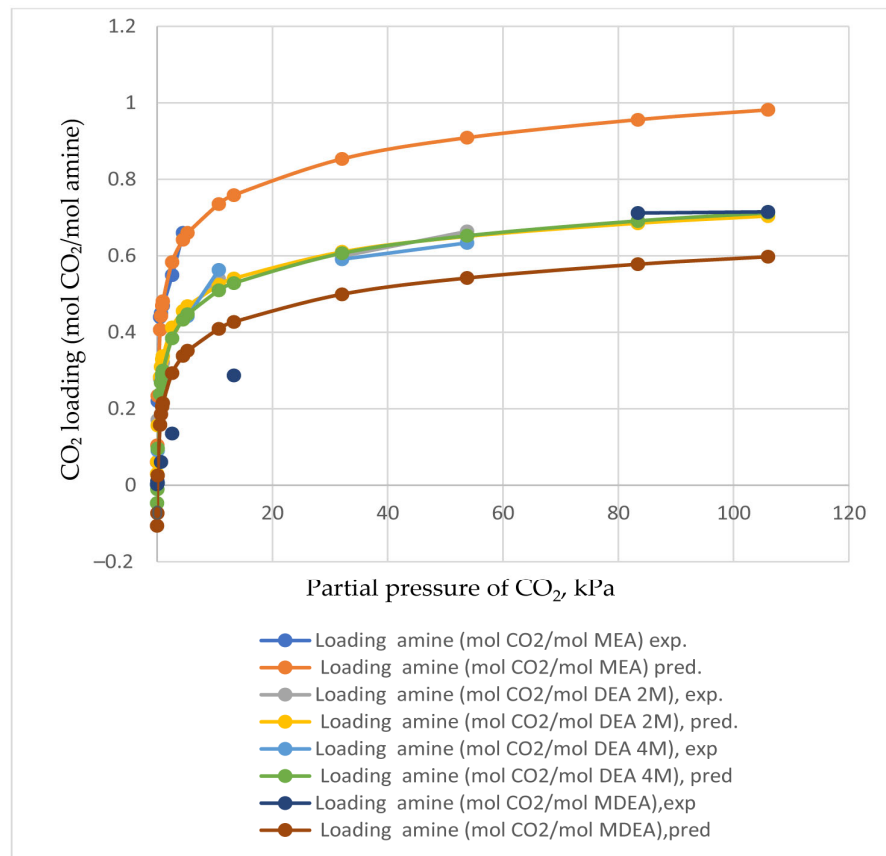
Figure 1. Absorption of CO₂ in monoethanolamide (MEA) [14–16].

Table 4. Equation of CO₂ absorption in amine with the 40 °C experiment temperature.

Type of Amine	Equation (x is Partial Pressure of CO ₂ , kPa, and y is CO ₂ Loading (mol CO ₂ /mol Amine))	R^2	%AARD	MPE
MEA	$y = 0.1074\ln(x) + 0.481$	0.9725	0.46857	0.46856
DEA 2M	$y = 0.0786\ln(x) + 0.3376$	0.9942	0.33368	−0.33367
DEA 4M	$y = 0.0885\ln(x) + 0.2998$	0.9839	0.97371	0.97372
MDEA	$y = 0.0821\ln(x) + 0.2148$	0.8311	12.5	12.5

Table 5. Equation of CO₂ absorption in MEA, (15.3% amine concentration) and 40 °C experiment temperature.

Type of Amine	Equation (x is Partial Pressure of CO ₂ , kPa, and y is CO ₂ Loading (mol CO ₂ /mol Amine))	R ²	%AARD	MPE
Shen and Li [14]	$y = 0.0808 \ln(x) + 0.3711$	0.9848	3.2878	3.2878
Jones [15]	$y = 0.0408 \ln(x) + 0.4708$	0.9360	0.2425	0.2425
Lee [12]	$y = 0.0785 \ln(x) + 0.3525$	0.9279	0.0577	0.0577

**Figure 2.** Absorption of CO₂ in MEA, DEA 2M, DEA 4M, and MDEA, experimental data and prediction data.

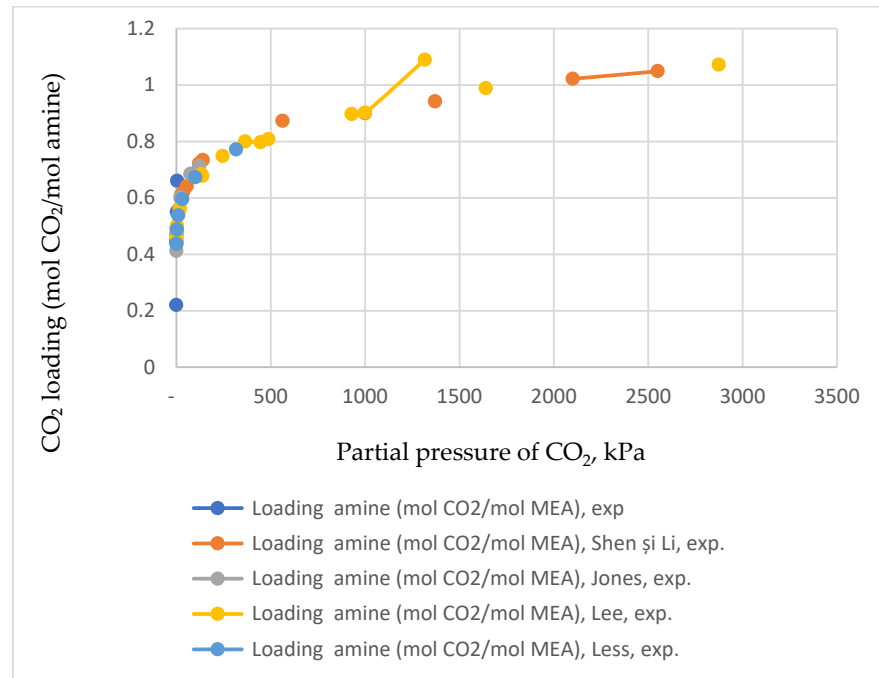


Figure 3. Absorption of CO₂ in MEA, experimental data and literature analysis.

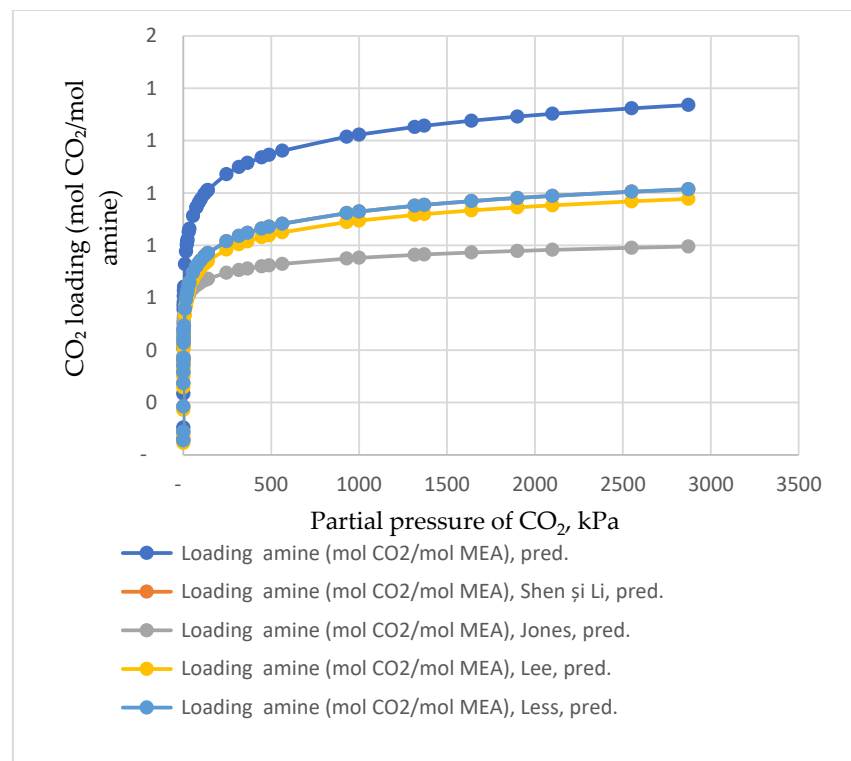


Figure 4. Absorption of CO₂ in MEA, prediction data.

In this research, we also sought to write the kinetic equations of absorption isotherms (Freundlich [17], Langmuir [18], and Temkin [19]). While the Freundlich, Langmuir, and Temkin models are historically derived for surface adsorption, they are utilized here strictly as empirical curve fits for liquid-phase behavior [20].

No physical interpretation regarding surface sites or monomolecular layer formation is intended.

The Freundlich model is based on empirical observations, and describes absorption on inhomogeneous surfaces according to the normal or modified equation (Tables 6–9) [17]:

$$y = K_f \cdot x^{\frac{1}{n}} \quad (1)$$

$$\ln(y) = \ln(K_f) \cdot \frac{1}{n} \ln(x) \quad (2)$$

where:

y : amine charge (mol CO₂/mol amine).

x : partial pressure of CO₂ (kPa).

K_f : Freundlich constant (absorption capacity).

$\frac{1}{n}$: absorption intensity factor (where n is a measure of heterogeneity).

The Langmuir model is based on adsorption on a homogeneous surface and the analysis of the formation of a monomolecular layer in the absence of lateral interactions between adsorbed molecules (theoretical model) [18].

$$y = \frac{y_{max} K_L x}{1 + K_L x} \quad (3)$$

$$\frac{1}{y} = \frac{1}{y_{max}} + \frac{1}{y_{max} K_L} \frac{1}{x} \quad (4)$$

where y_{max} is the maximum charge of the monolayer (mol CO₂/mol amine) and K_L is the Langmuir constant (linking the rate of absorption and desorption).

The Temkin model assumes that the absorption energy decreases linearly with surface coverage, according to the equations [19]:

$$y = \frac{RT}{b} \ln(A_T x) \quad (5)$$

$$y = \frac{RT}{b} \ln(A_T) + \frac{RT}{b} \ln(x) \quad (6)$$

where R is the universal gas constant, T is the absolute temperature (in K) and A_T is the Temkin constant.

The total loading of the mixture $Loading_{mix}$ at a given partial pressure (p_{CO_2} and temperature (40 °C) is given by:

$$Loading_{mix} \frac{mol CO_2}{mol amine} = Z_A Loading_A + Z_B Loading_B \quad (7)$$

where $Loading_A$ and $Loading_B$ are the CO₂ charge of Amine A and Amine B, respectively, calculated using the logarithmic equations, and Z_A and Z_B are the mole fractions of Amine A and Amine B in the mixture, respectively ($Z_A + Z_B = 1$).

$$Loading_{mix} = 0.5 (0.0786 \ln p_{CO_2} + 0.3376) + 0.5 (0.0885 \ln p_{CO_2} + 0.2998) \quad (8)$$

The equation shows the empirical DEA 2M/DEA 4M mixture model with a 50/50 ratio.

The above empirical model is NOT accurate for mixtures of amines (e.g., MEA + MDEA because of the following:

- Nonlinear Chemical Interactions: primary amines (MEA) and tertiary amines (MDE) react with CO₂ by different chemical mechanisms.
- When mixed, they can interact chemically (activation effect) or physically, changing the total capacity in a nonlinear manner.
- Kinetics: adding a fast amine (e.g., MEA) to a slow amine (e.g., MDEA) accelerates the uptake.

- This kinetics is a synergistic effect that is not captured by a simple additive equilibrium model. Heat of Reaction: the heat of reaction of the mixture is not a simple average; it depends on complex thermodynamic equilibria, which are essential for regeneration.

Table 6. Equation models of CO₂ absorption in MEA (15.3% amine concentration) and 40 °C experiment temperature.

Models	Regression Forms	Equation	R ²
Logarithmic	$y \text{ vs. } \ln(x)$	$y = 0.1074 \ln(x) + 0.481$	0.9725
Freundlich	$\ln(y) \text{ vs. } \ln(x)$	$y = 0.967 \cdot x^{0.111}$	0.9582
Langmuir	$\frac{1}{y} \text{ vs. } \frac{1}{x}$	$y = \frac{0.578 \cdot 54.8 x}{1 + 54.8 x}$	0.8911
Temkin	$y \text{ vs. } \ln(x)$	$y = 0.1074 \ln(x) + 0.481$	0.9725

Table 7. Equation models of CO₂ absorption in 2M (DEA 2M) (15.3% amine concentration) and 40 °C experiment temperature.

Models	Regression Forms	Equation	R ²
Logarithmic	$y \text{ vs. } \ln(x)$	$y = 0.0786 \ln(x) + 0.3376$	0.9942
Freundlich	$\ln(y) \text{ vs. } \ln(x)$	$y = 0.383 \cdot x^{0.183}$	0.9601
Langmuir	$\frac{1}{y} \text{ vs. } \frac{1}{x}$	$y = \frac{0.698 \cdot 11.2 x}{1 + 11.2 x}$	0.8475
Temkin	$y \text{ vs. } \ln(x)$	$y = 0.0786 \ln(x) + 0.3376$	0.9942

Table 8. Equation models of CO₂ absorption in 4M (DEA 4M) (15.3% amine concentration) and 40 °C experiment temperature.

Models	Regression Forms	Equation	R ²
Logarithmic	$y \text{ vs. } \ln(x)$	$y = 0.0885 \ln(x) + 0.2998$	0.9839
Freundlich	$\ln(y) \text{ vs. } \ln(x)$	$y = 0.317 \cdot x^{0.214}$	0.9805
Langmuir	$\frac{1}{y} \text{ vs. } \frac{1}{x}$	$y = \frac{0.719 \cdot 2.1 x}{1 + 2.1 x}$	0.9201
Temkin	$y \text{ vs. } \ln(x)$	$y = 0.0885 \ln(x) + 0.2998$	0.9839

Table 9. Equation models of CO₂ absorption in MDA and 40 °C experiment temperature.

Models	Regression Forms	Equation	R ²
Logarithmic	$y \text{ vs. } \ln(x)$	$y = 0.0821 \ln(x) + 0.2148$	0.8311
Freundlich	$\ln(y) \text{ vs. } \ln(x)$	$y = 0.119 \cdot x^{0.379}$	0.9245
Langmuir	$\frac{1}{y} \text{ vs. } \frac{1}{x}$	$y = \frac{0.757 \cdot 0.39 x}{1 + 0.391 x}$	0.9673
Temkin	$y \text{ vs. } \ln(x)$	$y = 0.0821 \ln(x) + 0.2148$	0.8311

We also created an Artificial Intelligence (AI) model specific to CO₂ absorption in amine solutions, which would be an Artificial Neural Network (ANN) with excellent accuracy ($R^2 > 0.98$ and %AARD < 5%).

We completed this model using an ANN and discussed how it can be improved.

The ANN model is ideal for this field, as it can learn complex, nonlinear relationships between operating variables (inputs) and absorption capacity (output), without being limited by the simplifying assumptions of classical thermodynamic models (Langmuir, Freundlich).

The model inputs are the variables that the engineer can control or measure during the absorption process:

- CO₂ Partial Pressure (pCO₂): the main variable, expressed in kPa (or bar/psi).
- Solution Temperature (T): measured in °C or K. All experiments were at 40 °C, but including temperature makes the model universally predictive.
- Amine Type: this categorical variable (MEA, DEA, MDEA, DGA, and DPA) must be converted to a numeric format (e.g., One-Hot Encoding or a numeric scale based on molar mass or alkalinity).
- Amine Concentration (CAmine): expressed in mass or molar concentration (mol/L).

Network Architecture (Hidden Layer) is a simple Multi-Layer Perceptron (MLP) Neural Network structure.

Number of Hidden Layers: typically, one or two hidden layers are sufficient for chemical equilibrium problems.

Number of Neurons: the optimal number of neurons in the hidden layer is determined by iterative testing, often starting with 5–20.

Activation Function: Sigmoid or Rectified Linear Unit functions are frequently used to introduce the necessary nonlinearity in modeling kinetics and equilibria.

Output Variable (Output Layer): the model is trained to predict a single variable, namely the CO₂ Loading, expressed in mol CO₂/mol amine.

In the field of CO₂ capture, equilibrium behavior is traditionally described by thermodynamic models such as the Kent–Eisenberg or the Electrolyte Non-Random Two-Liquid (e-NRTL) models. While these classical approaches are grounded in physical chemistry, the ANN model developed in this work offers several distinct advantages and a few inherent limitations (Figure 5 and Table 10).

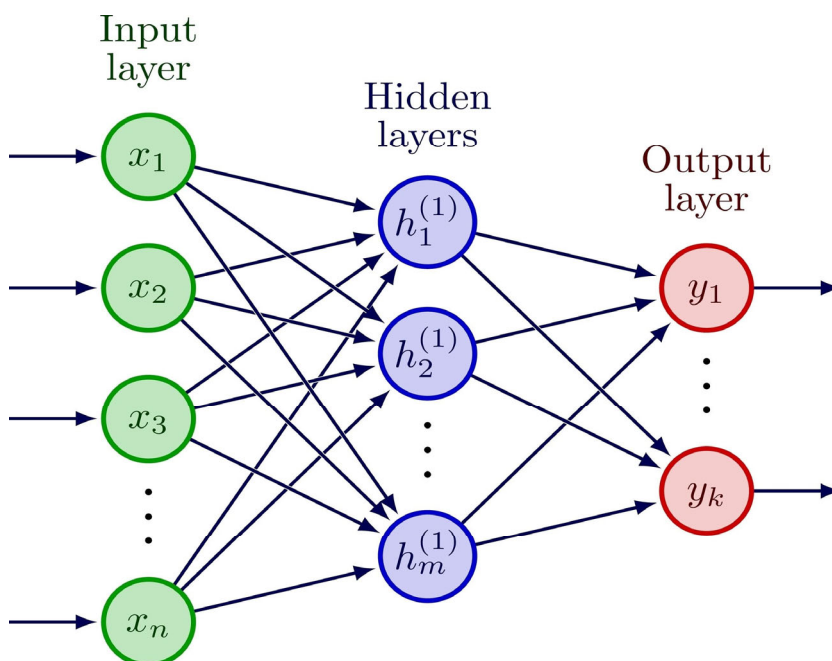


Figure 5. ANN Models presented in analysis.

1. Handling of Chemical Complexity

Classical models like e-NRTL require the determination of numerous parameters such as interaction energy and chemical equilibrium constants, which are often difficult to measure experimentally for complex amine blends.

In contrast, the ANN model functions as a data-driven tool that inherently “learns” the non-linear chemical interactions and synergistic effects (such as the activation effect when adding a fast primary amine to a slow tertiary amine) without requiring prior knowledge of the reaction mechanisms.

2. Accuracy and Predictive Power

As demonstrated in this study, the ANN model achieved a superior fit, with an R^2 of over 0.98 and an AARD below 5%. Classical models often struggle to maintain this level of precision across wide ranges of CO_2 partial pressure and different amine types (primary vs. tertiary) unless they are heavily modified with empirical parameters.

3. Computational Efficiency and Practical Application

From a practical engineering perspective, the ANN model is significantly faster to execute once trained, making it ideal for real-time process control and the rapid optimization of post-combustion CO_2 capture facilities. However, classical models remain superior for extrapolation; they rely on physical laws that allow them to predict behavior outside of the experimental data range, whereas the ANN is strictly limited to the boundaries of its training dataset.

Table 10. Comparison between the Artificial Neural Network (ANN) and classical thermodynamic models (such as the e-NRTL or Kent–Eisenberg models).

Model Type	Advantages	Limitations
Classical (Thermodynamic)	Physically meaningful parameters; reliable for extrapolation	Computationally intensive; requires complex chemical equilibrium constants
Machine Learning (ANN)	High accuracy in non-linear spaces; rapid execution; no need for prior chemical knowledge	Black-box nature; requires large datasets; limited extrapolation beyond training range.

4. ANN Mathematical Framework

The predictive engine developed in this study is a Multi-Layer Perceptron (MLP) that maps complex nonlinear input parameters to an equilibrium absorption output.

The fundamental operation of each neuron in the hidden layer involves calculating a weighted sum of inputs followed by the application of a bias and a non-linear activation function.

The activation h_j for a specific neuron j is defined as:

$$h_j = \sigma(\sum_{i=1}^n w_{ij}x_i + b_j) \quad (9)$$

where:

x_i represents the input vector (including CO_2 partial pressure, temperature, amine type, and concentration).

w_{ij} is the weight connecting input i to hidden neuron j .

b_j is the bias term for the hidden layer.

σ represents the Sigmoid activation function.

To capture the saturation-limited behavior of the absorption curves, particularly the flattening observed after 500 kPa, the Sigmoid function was utilized:

$$\sigma(z) = \frac{1}{1 + e^{-z}} \quad (10)$$

The final predicted CO_2 loading (y) is the resultant signal from the output layer, calculated as follows:

$$y = \sum_{j=1}^m w_j^{\text{out}} h_j + b_{\text{out}} \quad (11)$$

where:

m is the number of neurons in the hidden layer, optimized between 10 and 15.

w_j^{out} represents the weights connecting the hidden layer to the output layer.

y is the predicted CO₂ loading expressed in mol CO₂/mol amine.

The model was trained to minimize the deviation between experimental data and network predictions.

The primary metric for validation is the Absolute Average Relative Deviation (AARD):

$$AARD(\%) = \frac{100}{n} \sum_{k=1}^N \left| \frac{y_{exp,k} - y_{pred,k}}{y_{exp,k}} \right| \quad (12)$$

where:

$y_{exp,k}$ is the experimental loading observed at 40 °C.

$y_{pred,k}$ is the predicted value from the ANN.

N is the total number of data points used in the study ($N = 75$).

4. Discussion

A detailed analysis of the experimental absorption data for MEA solutions compared to those in the specialized literature reveals several key findings:

Comparative Data Analysis

- The experimental results align closely with existing literature values, particularly within the 0 to 500 kPa pressure range.
- Logarithmic models provide an accurate description of CO₂ absorption in amine solutions.
- Among the models tested, the predictions based on the study by Shen and Li show the highest proximity to the experimental data [4].
- Subsequent error analysis was performed for each relationship, to validate accuracy against experimental results.

Amine Performance and Behavior

MEA-type amines demonstrate the highest CO₂ absorption capacity.

Under specific partial pressures, MEA can achieve a loading of 1 mol CO₂/mol MEA.

MDEA amines exhibit the lowest overall absorption capacity among the solvents tested [8].

Both DEA 2M and DEA 4M exhibit nearly identical absorption behavior [9].

Technological Context

The removal of CO₂ emissions can be achieved through several established methods:

- Solid adsorption.
- Absorption in liquid solvents.
- Membrane separation.
- Physical or biological separation techniques.

Among these, gas–liquid absorption is recognized as one of the most mature and commercially viable technologies.

It is widely utilized in industrial chemical processes, such as ammonia and hydrogen synthesis.

Modeling Scope and Technical Specifications

While the Artificial Neural Network (ANN) and empirical models offer high precision, their theoretical boundaries must be clearly defined.

Empirical Nature of Isotherm Models

The Langmuir, Freundlich, and Temkin models are applied in this study strictly as empirical curve fits.

While these models originated from surface-adsorption theory, CO₂ capture in amines is actually a liquid-phase dissolution and chemical reaction process.

No physical interpretation regarding monomolecular layers or surface sites is intended.

The high correlation found for MDEA using the Langmuir model ($R^2 = 0.9673$) is purely a mathematical representation of its saturation-limited behavior.

ANN Technical Details and Reproducibility

To maintain model robustness, the following parameters were utilized:

- Dataset: a total of 75 experimental and literature data points covering MEA, DEA, MDEA, DGA, and DPA were used for training.
- Data Splitting: the data was divided into 70% training, 15% validation, and 15% testing, to prevent overfitting.
- Architecture: a Multi-Layer Perceptron (MLP) was used, featuring an input layer (pressure, temperature, concentration, and amine type), hidden layers with 10 to 15 neurons, and a single output layer for predicted loading.
- Training: the model utilized a Sigmoid activation function and a backpropagation optimizer to minimize the Absolute Average Relative Deviation (AARD).

Constraints on Generalizability

The current ANN employs categorical identity for amine types, rather than molecular structural descriptors.

Consequently, the model is highly precise for the specific solvents included in the study (MEA, DEA, MDEA, DGA, and DPA) but cannot be reliably extrapolated to new amine structures or proprietary mixtures without additional data and retraining.

5. Conclusions

The global imperative to mitigate climate change has positioned Carbon Capture and Storage (CCS) as a necessary technology.

Within this framework, chemical absorption is the preferred method for reducing CO₂ from flue gas streams.

This work successfully employed a machine learning-based approach, utilizing Artificial Neural Networks (ANNs), to model the equilibrium CO₂ absorption capacity (loading) across various alkanolamine solutions, including primary, secondary, and tertiary amines.

Technological Context and Carbon Capture

Capture Technologies: three primary CO₂ capture technologies are currently recognized: pre-combustion, oxy-combustion, and post-combustion.

Absorption Method: gas-liquid absorption is the most widely utilized technological and commercial method in the chemical sector.

Solvent Selection: the most commonly used solvents include monoethanolamine (MEA), diethanolamine (DEA), and methyl diethanolamine (MDEA).

Chemisorption Mechanism: this process involves a chemical reaction between CO₂ and the solvent to form a weakly bound intermediate, which can be regenerated, producing a relatively pure CO₂ stream.

Modeling Performance and Findings

The data-driven models developed in this study demonstrated high efficacy in predicting equilibrium CO₂ loading.

ANN Accuracy: the developed prediction model achieved a high coefficient of determination $R^2 > 0.98$ and an absolute average relative deviation (AARD) of under 5%.

Empirical Isotherms: while historically adsorption-based, the Langmuir model provided the most accurate empirical representation for the tertiary amine MDEA ($R^2 = 0.9673$), indicating a saturation-limited absorption capacity in the studied range.

Logarithmic Correlations: experimental datasets were successfully described by logarithmic equations:

- In the low-pressure range (0 to 10 kPa), absorption is best described by the relationship presented by Jones.
- In the high-pressure range (10 to 2873 kPa), the fit closest to experimental reality is described by Lee's experiment.

Absorption Behavior: modeling confirms that amines are strongly absorbing in the 0 to 500 kPa range, after which the absorption curve flattens.

Chemical Engineering Insights on Amine Performance

The comparison of absorption capacities at a consistent temperature of 40 °C revealed distinct chemical behaviors among the amine classes.

Primary (MEA) consistently demonstrated the highest absorption capacity in both low and high-pressure range. At 2873 kPa, loading can reach a 1:1 stoichiometric ratio (1 mol CO₂/mol amine).

Secondary (DEA)-DEA 2M solutions were found to be more absorbent than the higher-concentration **DEA 4M** solutions.

Tertiary (MDEA) exhibited the lowest absorption capacity [19]. However, this is offset by lower costs and reduced regeneration energy, due to its non-carbamate-forming mechanism.

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Abbreviations

The following abbreviations are used in this manuscript:

ANN	Artificial Neural Network models
CO ₂	Carbon dioxide
CS ₂	Carbon disulfide
COS	Carbon oxysulfide
DEA	Diethanolamine
DPA	Dipropylamine
MDEA	Methyl diethanolamine
MEA	Monoethanolamide
H ₂ S	Hydrogen sulfide

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