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Multi-Criteria Screening of Organic Ethanolamines for Efficient CO_2 Capture Based on Group Contribution Method

Bin Liu, Yanan Yu, Hanlin Liu, Zhe Cui and Wende Tian *

College of Chemical Engineering, Qingdao University of Science & Technology, Qingdao 266042, China
* Correspondence: tianwd@qust.edu.cn

Abstract: Amine solvent has attracted much attention due to its high CO_2 capture level and wide application range, but its high energy consumption for recycling restricts its large-scale commercialization. In this work, a multi-objective optimization technology based on the group contribution method was used to select potential amine solvents for CO_2 capture. This computer-aided molecular design method considers the thermodynamic and kinetic properties of the candidate solvent and evaluates the influence of relevant parameters on solvent performance. Compared with previous experimental methods used to optimize solvent, this method selects potential solvents from a large number of solvent databases based on group contribution. Firstly, a corresponding classification database was established for various kinds of amine solvents. Then, the traditional experiments were used to verify and screen solvents. At the same time, the method was applied to 31 amine absorbents concerning solubility, molar volume, surface tension, heat capacity, viscosity, pKa, saturated vapor pressure, and so on, and seven solvents were found to have comparable performance to MEA, with higher absorption rates and solubility. This method provides guidance for screening CO_2 capture absorbents with economic viability, high efficiency, fast absorption rates, and low regeneration energy consumption.

Keywords: multi-criteria screening; CO_2 capture; group contribution; amine

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1. Introduction

In this modern era, the problem of global warming is becoming increasingly serious and has become one of the major factors threatening the sustainable development of mankind. Reducing greenhouse gas emissions to mitigate climate warming has become the focus of the international community. Relevant research shows that fossil energy will continue to be the most important energy source for mankind in the coming decades. To control global greenhouse gas emissions, carbon capture, utilization, and storage (CCUS) technology will play a significant role in improving energy efficiency, developing clean energy technology and improving the carbon sequestration capacity of natural ecosystems. The research and development of CO_2 capture technology with good industrialization prospects can realize the low carbon utilization of fossil energy, which is widely regarded as one of the most important technologies to cope with global climate change and control carbon emission. It can effectively solve the environmental problems such as air pollution caused by large amounts of CO_2 emissions.

CO_2 capture technology can be divided into three categories: post-combustion capture, pre-combustion capture, and oxygen-enriched combustion capture [1]. Post-combustion capture technology has good applicability to low partial pressure flue gases, so it does not require extensive modifications to existing power plants, and only additional CO_2 capture devices are required to achieve CO_2 removal. Optional post-combustion capture methods include adsorption, absorption, membrane separation, and cryogenic methods. Absorption is divided into physical absorption, chemical absorption, and physicochemical absorption, etc. However, in terms of industrial practicality, chemical absorption is considered the most promising CO_2 capture technology due to its fast absorption rate and high absorption capacity. In particular, chemical absorption with alkaline aqueous solution to selectively absorb CO_2 from flue gas is considered as the most versatile and flexible method, as well as being the cheapest. Typical types of absorbents include ethanolamine absorbers, ammonia absorbers, potassium carbonate absorbers, and amino acid salt absorbers. Among them, aqueous ethanolamine (MEA) solution is the most representative absorber.

Amine is a common CO_2 absorption solvent, and the process flow represented by ethanolamine (MEA) is shown in Figure 1. Firstly, the gas mixture enters the bottom of the absorber after dry desulfurization and then contacts with the lean amine solvent flowing down from the top of the tower, where the gas–liquid two phases undergo mass and heat transfer. Through a chemical reaction between the CO_2 and the amine solution, the CO_2 is effectively absorbed by the solvent while the remaining gas mixture is dried, purified, and ultimately discharged at the top of the tower. The absorbed CO_2-rich amine solution is fed to the desorber for regeneration through a heat exchanger. In the desorber, the rich amine solution counter-currently contacts with the steam generated by the reboiler at the bottom of the tower. After heating, CO_2 is removed from the rich amine solution and the water vapor is returned by the condenser at the top of the tower, resulting in high-purity CO_2.

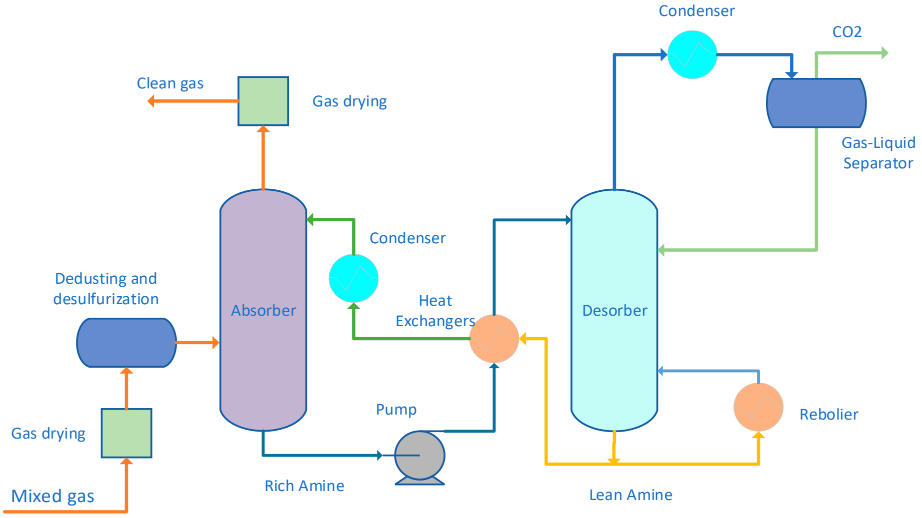

Figure 1. Process flow diagram of CO_2 absorption by amine solution.

However, there are still some shortcomings in using traditional amine solvents, such as low absorption capacity, high energy consumption for desorption, and easy dissolution and corrosion of equipment. Singh et al. [2] conducted experiments to investigate the relationship between the structure and activity of amine solvents in the uptake of CO_2. The results show that an increase in the number of amine groups in amine solvents increases the ability of amines to absorb CO_2. Volatility of amines is an important criterion for evaluating the performance of amine solvents. Du et al. [3] determined the Henry's law constant of 24 amine solvents in water using the hot gas FTIR method, and their experimental results showed that 14 of the amine solvents had a Henry's law constant smaller than that of AMP solvents. Aronu et al. [4] found that 1.0 M tetraethylenepentamine (TEPA) and 5.0 M MEA exhibited high uptake rates in the amine uptake and desorption CO_2 experiments. In addition, 1.5 M Bis-(3-dimethylaminopropyl) amine (TMBPA) had a strong desorption ability and larger adsorption capacity. Chowdhury et al. [5] compared AMP and MDEA as basic solvents with nine new amines synthesized in their experiments. Their results show that the three high performance amines have higher absorption rates and lower heats of reaction compared to AMP and MDEA.

The advantage of the experimental method is its ease of application, and the experimental data can truly reflect the performance parameters of the substance, which can provide a realistic basis for theoretical derivation. However, the use of experimental methods for solvent screening is, to some extent, limited by the high cost of the experiments, the harsh operating conditions, the inability to give a good prognosis of a large range, and the tendency to cause harm to the environment and the experimenter.

The group contribution method was first proposed by Macleod to calculate the isobaric heat capacity of liquids [6]. The group contribution method is a very effective method in the study of quantitative structure–property relations of compounds, which can be attributed to the qualitative structure property relations (QSPR) method [7]. The method decomposes the structure of the compound into several groups, and applies the thermodynamic principle and a large number of data fitting regression to obtain the contribution value of molecular groups to the properties of the compound. Gina et al. [8] successfully estimated the properties of various substances, including physical properties and thermodynamic properties, using group contribution method. In addition, the group contribution method can also predict the thermodynamic properties of mixtures, such as activity coefficients, so it began to receive widespread attention. Nowadays, the mature development of the group contribution method has greatly optimized the calculation process and improved the experimental efficiency, as well as saving time and economic costs. It is possible to screen the CO_2 absorbers with better performance from a wider range.

A lot of traditional aqueous amine solutions are used to capture CO_2, including monoethanolamine (MEA), methyldiethanolamine (MDEA), and diethanolamine (DEA). MEA is regarded as the standard solvent by scholars in various countries because of its high activity against CO_2. Due to the high temperatures required to regenerate amine solvents, they account for two-thirds of the total cost of regeneration. The disadvantages of the solvent used in this technology, such as easy oxidative degradation and evaporation, high corrosiveness and high energy consumption for regeneration, limit its further promotion and application. Therefore, the rapid identification of efficient, energy-efficient, and environmentally friendly CO_2 capture solvents is of great value in the development of cost-effective and benign absorbents. Over the years, a great deal of research work has focused on the development of new solvents to replace the traditional solvent ethanolamine (MEA).

In aiming to study the properties of the structures with various amines, it is often time-consuming and laborious to verify them experimentally. Therefore, it is necessary to develop rigorous predictive models for molecular states. For example, Cleeton et al. [9] used the ePC-SAFT equation of state to predict the absorption partial pressures of CO_2 and H_2S in aqueous solutions of methyl diethanolamine (MDEA). Alkhatib et al. [10] used a soft-SAFT prediction model based on the equation of state of the molecule to simulate the results of CO_2 capture in aqueous amine and non-aqueous amine solutions for absorption. The results show that the total heat of regeneration is reduced by one-third for non-aqueous amine solvents compared to aqueous amine solvents for the same amine mass concentration. The experimental results validate the effectiveness of the molecular modeling approach. Lepaumier et al. [11] examined the degradation of five tertiary amines (including diamines and triamines) in the presence of CO_2 or O_2. The aim was to investigate the relationship between amine properties and alkyl chain length as well as the main degradation mechanisms.

Although rigorous mathematical models have important applications, the physicochemical problems involved in the models are very complex. The analysis is often performed by a combination of multiple mathematical models and excludes the human and financial resources consumed in the model design process. In screening and design, thermodynamic properties and reaction kinetic properties are usually considered in a comprehensive manner. The predictive models mentioned above cause the physical performance of the solvents to be limited only to the indexes examined, so that few solvents can be selected among all the promising compounds.

Computer-aided molecular design (CAMD) is a method that combines performance prediction models with computer-aided searches in the design of various chemical products. The group contribution method, representing the relationship between the molecular structure and properties of a substance, combined with CAMD, leads to efficient screening of target solvents. This provides a new avenue for the screening and design of absorbents. Joback [12] demonstrated the specific application of CAMD, where an example of designing extraction solvents was used. The experiment was conducted using ethyl acetate instead of toluene as the extractant for phenol in wastewater, and the group parameters corresponding to ethyl acetate were obtained. This method improves the efficiency of the experiment to some extent, but it does not necessarily mean that it is the best choice for screening. However, the combination of the group contribution method and the optimal screening method was used based on thermodynamic principles and mathematical operations. They can be used to evaluate and screen the various substances in the solvent database to obtain the best performing solvent. The commonly used methods are artificial neural network method (ANN), fuzzy integrated evaluation, etc. Petersen et al. [13] firstly proposed the combination of group contribution method and ANN to predict the activity coefficients of compounds.

The group contribution method for predicting compound properties is a practical engineering method developed for representing molecular structure information, analyzing the available property data, and estimating the group contribution term in the property model function [14]. It is predictive in terms of the range of molecular structures that can be processed. This method is simple, easy to use, and has a high predictive power.

Therefore, the efficient and reliable screening of CO_2 capture solvents can be improved by using the group contribution method prior to conventional experimental validation. This study examines the various factors that influence the performance of amines and utilizes a combination of the group contribution method and multi-criteria optimization to predict and evaluate the efficacy of different substances in the solvent database. This results in the screening of CO_2-absorbing solvents with faster absorption rate, higher capacity, and more energy savings compared to the conventional solvent ethanolamine (MEA).

2. Method

In order to design specific methods for screening CO_2 absorbers, a detailed knowledge of the thermodynamics and kinetics of CO_2 absorption processes in solvents is required as a basis. The solvents are designed and evaluated using GC- and non-GC-based models to predict the parameters of each property that reflect the CO_2 capture capacity of the solvent. This provides a set of metrics for each property, linking the chemical structure of the solvent with thermodynamics and reaction kinetics to achieve efficient screening.

2.1. Problem Decomposition for Integrated Solvent Selection

In the first step, a database of amine solvents was established, and 31 amine solvents from published sources were collected in this work, as shown in Table 1.

In the second stage, a series of properties that affect the ability of the solvent to absorb CO_2 were classified. They were divided into thermodynamic and kinetic factors.

In the third stage, group splitting was first performed for all compounds. Depending on the contribution values of different groups to the properties, the group contribution method or software prediction method was used to calculate the performance parameters.

In the last stage, a multi-objective optimization method was used to comprehensively evaluate the solvent performance.

In this study, the objective hierarchy-based [15] multi-objective optimization method is used. First, we ranked the solvents according to the importance of their target properties, with the properties that have the greatest impact on CO_2 capture performance at the top and the properties that have the least impact at the bottom. Then, stepwise screening was performed according to the importance of the target property, screening out some suitable solvents to ensure that there were enough solvents available for the next screening step. That is, the candidate optimal set of solvents for the next target property was found based on the candidate optimal set of solvents for the previous target property. This is performed until the optimal solution i found for the p-th objective. Each optimal solution set is listed as R_1, R_2 … R_{p-1}, and let R_0 be the feasible solution set when solving the first objective property, R1 be the optimal solution set of the first objective property, and so on. The functional expressions are shown in Equation (1):

$$\begin{gathered} f_1(x) = \underset{x \in R_0}{\mathrm{Min}}\, f_1(x) \\ f_2(x) = \underset{x \in R_1}{\mathrm{Min}} f_2(x) \\ \cdot \\ \cdot \\ f_i(x) = \underset{x \in R_{i-1}}{\mathrm{Min}}\, f_i(x) \\ \cdot \\ \cdot \\ f_p(x) = \underset{x \in R_{p-1}}{\mathrm{Min}}\, f_p(x) \\ R_i = \left\{ x | f_i(x) < f_i(x^i) + a_i, x \in R_{i-1} \right\} \\ (i = 1, 2, \cdots, P-1, a_i > 0) \end{gathered} \tag{1}$$

where $f_i(x)$ represents each property of the amine solvent (e.g., T_m, Cp, pKa, etc.), P represents the number of sought properties, R represents the number of solvents remaining in the screening list at the current step, a_i is the tolerance limit to ensure the appropriate number of solvents are available in each screening, and x^i is the solvent in the set of optimal solutions of the previous objective property sought.

Table 1. CAS number and molecular structure of the selected chemical solvent.

(A)

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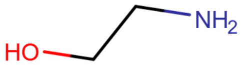
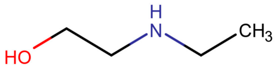
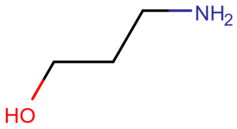
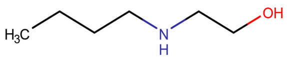
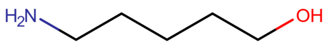
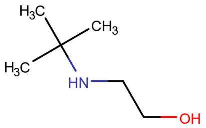
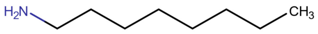
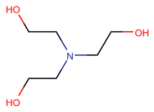
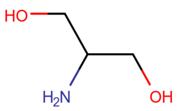
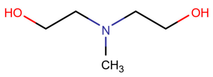
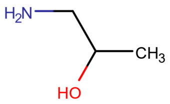
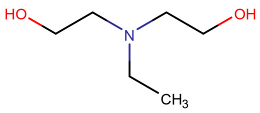
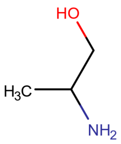
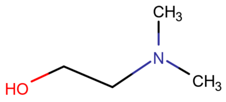
S1	141-43-5		S11	110-73-6	
S2	156-87-6		S12	111-75-1	
S3	2508-29-4		S13	4620-70-6	
S4	111-86-4		S14	102-71-6	
S5	534-03-2		S15	105-59-9	
S6	78-96-6		S16	139-87-7	
S7	6168-72-5		S17	108-01-0	

Table 1. *Cont.*

(A)					
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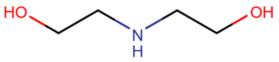
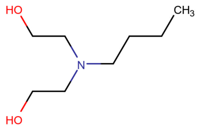
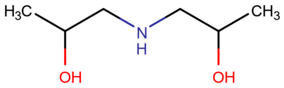
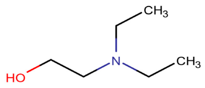
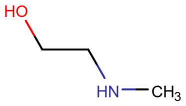
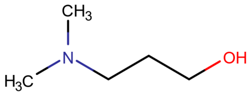
S8	111-42-2		S18	102-79-4	
S9	110-97-4		S19	100-37-8	
S10	109-83-1		S20	3179-63-3	

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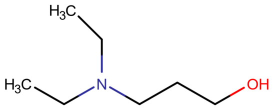
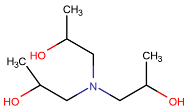
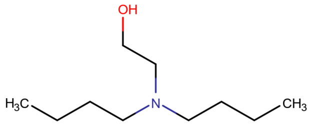
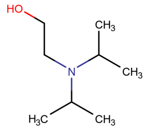
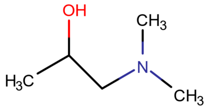
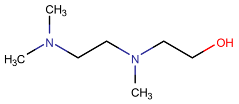
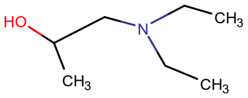
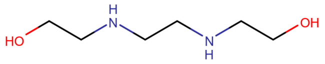
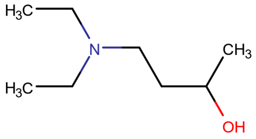
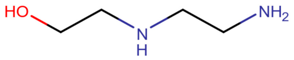
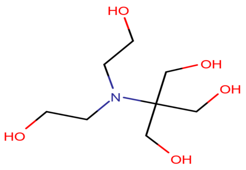
S21	622-93-5		S27	122-20-3	
S22	102-81-8		S28	96-80-0	
S23	108-16-7		S29	2212-32-0	
S24	4402-32-8		S30	4439-20-7	
S25	5467-48-1		S31	111-41-1	
S26	6976-37-0				

A block diagram of the process used to screen for quality solvents is shown in Figure 2.

In the screening design of amine absorbers, the ideal CO_2 absorber should have the characteristics such as being economical and efficient, fast absorption rate, low energy consumption for regeneration, environmentally friendly, high stability, antioxidant degradation and thermal degradation, low corrosiveness to equipment, etc. Therefore, the screening design of absorbents is a multi-objective optimization problem with three basic elements: variables, constraints, and objective functions. For the screening design of amine absorbents, the optimized variable is the molecular structure composed of a set of groups, the constraints refer to the group linkage satisfying structural feasibility and chemical feasibility, and the objective function refers to a series of relevant performance indicators of the predefined molecule, such as solubility, pKa, vapor pressure, etc. The solution to the problem is a series of candidate solvents that should first meet the following predetermined criteria: acidity coefficient (pKa) and density (ρ), whose higher values represent higher absorption properties of the solvent, relative energy difference (RED), heat capacity (Cp), vapor pressure (Pvp), viscosity (n), and surface tension (σ), which should be as small as possible as they contribute to mass and heat transfer.

T_m is the melting point of the solvent. The operating temperature of the absorber T_A should be greater than the melting point of the solvent to prevent the solvent from being involved in a solidification reaction in the absorber due to low temperature, which affects the absorption efficiency. T_b is the boiling point of the solvent, which should be greater than the desorption temperature of the desorber to avoid an evaporation reaction.

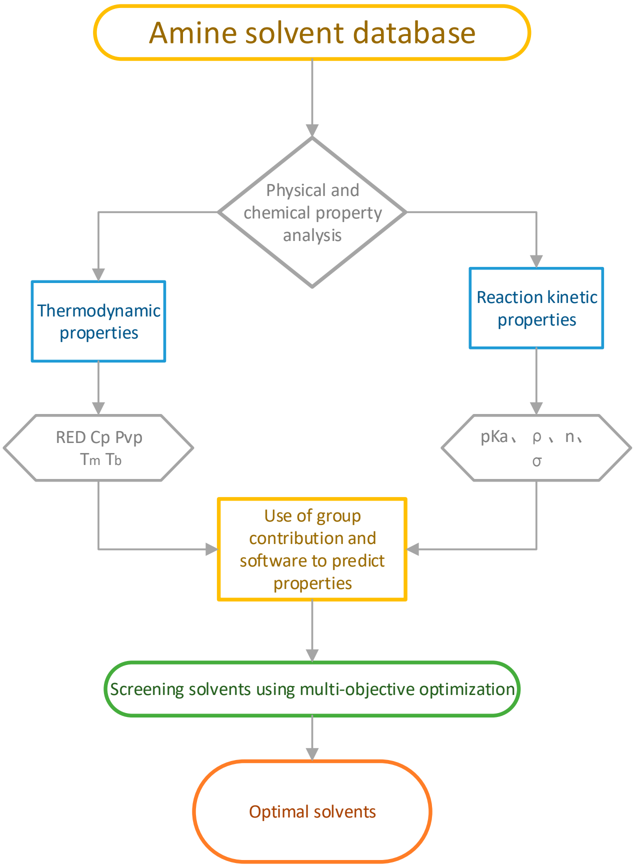


Figure 2. Flow chart for screening quality solvents.

2.2. Solvent Selection Criteria

Before initiating the specific selection process, it is crucial to fully comprehend the performance of the amine solvent as it will determine the direction of our work. The combination of different performance criteria enables us to choose a more reliable and better-performing solvent from a vast range of CO_2 candidate solvents. The performance criteria of amine solvents varies, and plays a crucial role in determining their CO_2 capture levels. To calculate the performance of amine solvents, we use the group contribution method, which considers the relationship between molecular structure and performance, to filter out useful candidates while excluding poor ones. The evaluation typically considers thermodynamic properties, reaction kinetic properties to look for solvents with fast uptake rates, high uptake capacity, and low environmental and equipment hazards in comparison to conventional solvents. These properties are summarized in Table 2.

Table 2. Effect of solvent performance parameters on CO_2 absorption process.

Solvent Performance	Impact on Industrial CO_2 Absorption
Solubility	Affects CO_2 absorption capacity and energy consumption for operation and recycling
Density	Influences flow rates and affects device performance and equipment size
Heat capacity	Influences tower plate efficiency and heat consumption
Vapor pressure	Influences solvent volatility
Acidity factor	Influences the rate of CO_2 absorption by the solvent
Viscosity	Influences gas–liquid mass transfer effect and tower plate efficiency
Surface tension	Influences gas–liquid mass transfer effect and tower plate efficiency
Melting point	Should be below the minimum process temperature to avoid curing
Boiling point	Should be above the maximum process temperature to avoid evaporation.

Solubility: The solubility parameter plays a critical role in determining the ability of amine solvents to capture CO_2 and serves as an essential criterion for selecting a suitable CO_2 capture solvent. Hansen solubility parameters [16] are widely used to select a suitable solvent for a given solute. If the strength of molecular forces between amine solvent molecules and CO_2 molecules are comparable, the solvent is usually considered to be an excellent solvent for capturing CO_2. In the absorption of CO_2 by amine solvents, the solubility of the solvent is crucial to CO_2, which is mainly reflected in the relative energy difference (RED) [17]. As the Hansen solubility differential between amines and CO_2 rises, the amount of energy required to dissolve CO_2 from a particular amine solvent increases. Usually, solvents with RED < 1 are regarded as favorable for the dissolution of specific solutes, and the larger the RED, the lower the solvent solubility. Hansen solubility parameters can be derived by the group contribution method.

Vapor pressure: The saturation vapor pressure (Pvp) is an important thermodynamic parameter of liquid substances, which affects the volatility of solvents. It is generally believed that the lower the saturation vapor pressure of a solvent, the smaller the loss of the solvent when absorbing CO_2. Traditional experimental methods include the static method, which is a direct determination of the vapor pressure in the equilibrium state of the gas–liquid two-phase process. Our method uses the group contribution method [18] to find the saturation vapor pressure.

Liquid heat capacity: The molar heat capacity of a liquid is a key thermodynamic parameter considered in chemical production calculations, which is the key not only to chemical engineering design, but also to the development of thermodynamic theory. Better-performing solvents tend to exhibit a lower calorific value for regeneration, which includes the heat required in the absorption and desorption of CO_2. In addition, solvents with a lower heat capacity tend to absorb CO_2 at a faster rate [19].

Density: The solvent density chosen should be as high as possible to obtain a lower flow rate, which helps to increase the solvent–CO_2 contact time, thus, improving the absorption rate. By increasing the liquid density, it can reduce the impact force and wear of droplets on the tower plate, but also improve its holding capacity and reduce the tumbling, overflow, and corrosion of droplets on the tower plate. The density of the liquid can be calculated from the molar volume of the liquid.

Viscosity and surface tension: In a CO_2 absorber, viscosity and surface tension mainly affect the gas–liquid mass transfer effect by influencing the merging of bubbles, and the small viscosity and surface tension of absorbent are conducive to reducing the merging of bubbles, thus, improving the mass transfer efficiency.

Acidity coefficient: The acidity coefficient (pKa) is an essential property to take into account when searching for new amine solvents, as it provides information about the amine reaction performance and the main chemical reactions among the critical factors needed to simulate and design absorption columns. Svendsen et al. [20] experimentally show that the pKa of the amine solution affects the rate of CO_2 uptake, and the reaction rate increases with increasing pKa. Therefore, an amine with high alkalinity is desirable. In addition, some scientists have made many efforts to find the connection between the pKa of amine solvents with CO_2 uptake capacity. For example, Puxty et al. [21] conclude from experimental results that the absorption capacity of tertiary amine solvents for CO_2 is more affected by pKa, the absorption capacity of mixed amines is less affected by pKa, and the absorption capacity of primary and secondary amines is almost unaffected by pKa.

2.3. Description of Group Contribution Method

The compound was initially divided into 13 groups, namely, CH_3-, -CH_2-, >CH, >C<, -OH, -CH_2-NH_2, -CH_2-NH-, -CH_2-N<, >CH-NH_2, >CHNH-, CH_3-NH-, CH_3-N<, and ≥C-NH_2. The group contribution method is used for calculations based on the number of occurrences of different groups in the compound. The relative energy difference (RED) is based on the method proposed by Stefanis [22]. The density (ρ) is based on the method proposed by Constantinou [23]. The heat capacity is adopted from the method proposed by Rayer [24]. The boiling point (T_b) is adopted from the method proposed by Joback [25]. Melting points (T_m) are calculated according to the method provided by Marrero [26]. pKa prediction uses Marvin Sketch (chemicalize.com, accessed on 5 January 2023) software. The data were processed using structured process language (SPL).

3. Results and Discussion

In this section, the amines in the solvent database are classified into primary, secondary, and tertiary amines and diamines according to their structures. (In Table 1, S1–S7 are primary amines, S8–S13 are secondary amines, S14–S28 are tertiary amines, and S29–S31 are diamines). The relationship between the properties of the solvents and the solvent structures is analyzed. Also, some solvents with better performance were screened and compared with the conventional solvent ethanolamine (MEA) at 313.15 K.

3.1. Method Validity Verification

Ethanolamine (MEA), diethanolamine (DEA), 2-(Ethylamino)ethanol (EMEA), and N-Methyldiethanolamine (MDEA) are selected to verify the effectiveness of the GC prediction method. The results of relevant performance parameters calculated by the prediction method are listed in Table 3 and compared with the experimental results in the published work [24,27–37]. It can be seen that the predicted values are in good agreement with the experimental values within the experimental temperature range. The relative error (δ) of each parameter is within the acceptable range, proving that the GC method can be used to predict the relevant performance parameters of the selected amines. The formula of δ is given as Equation (2):

$$\delta = \left(\frac{F(X)_{Predicted} - F(X)_{Experimental}}{F(X)_{Experimental}}\right) \times 100\% \tag{2}$$

where $F(X)_{predicted}$ represents the predicted value of each substance performance parameter, and $F(X)_{Experimental}$ represents the experimental value of each substance performance parameter.

Table 3. Comparison of simulated and experimental values.

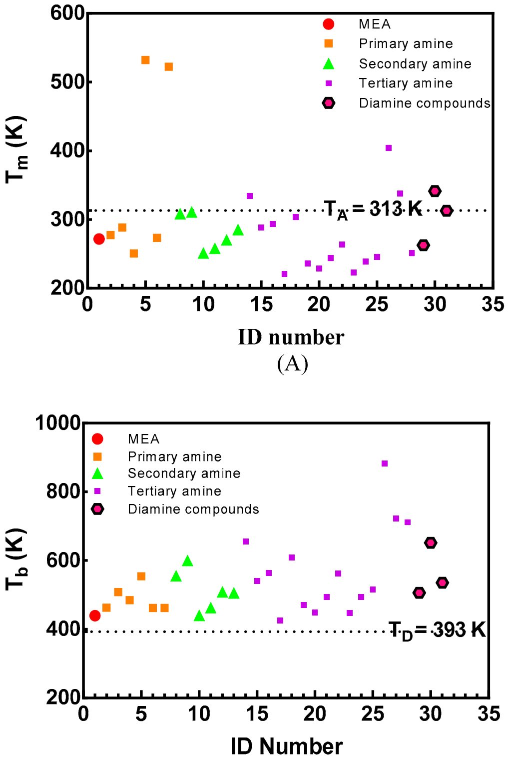
Properties	MEA	DEA	EMEA	MDEA
ρ_{pre} (g/cm^3)	16.53	10.47	10.02	9.27
ρ_{exp} (g/cm^3)	16.60 [27]	10.40 [28]	10.24 [29]	8.71 [30]
δ (%)	0.39	0.66	2.10	6.46
pKa_{pre}	9.14	8.85	9.45	8.32
pKa_{exp}	9.44 [31]	8.88 [31]	9.52 [31]	8.51 [32]
δ (%)	3.18	0.34	0.74	2.23

Table 3. *Cont.*

Properties	MEA	DEA	EMEA	MDEA
Cp_{pre} (J/(mol·K))	178.71	282.89	237.54	286.18
Cp_{exp} (J/(mol·K))	169.81 [33]	260.73 [33]	239.3 [24]	277.73 [34]
δ (%)	5.24	8.50	0.74	3.04
Tb_{pre} (K)	439.87	555.45	463.27	540.6
Tb_{exp} (K)	443.15 [35]	541.351 [35]	443.15 [35]	520.35 [35]
δ (%)	0.74	2.60	4.54	3.89
Tm_{pre} (K)	271.73	308.57	258.22	288.43
Tm_{exp} (K)	283.65 [35]	301.15 [35]	-	252.15 [35]
δ (%)	4.20	2.46	-	14.39
RED	3.77	5.32	2.90	5.28
Pvp_{pre} (Pa)	278.07	0.22	219.55	4.47
Pvp_{exp} (Pa)	-	-	219.77 [36]	3.42 [37]
δ (%)	-	-	0.10	30.92

3.2. Data Analysis

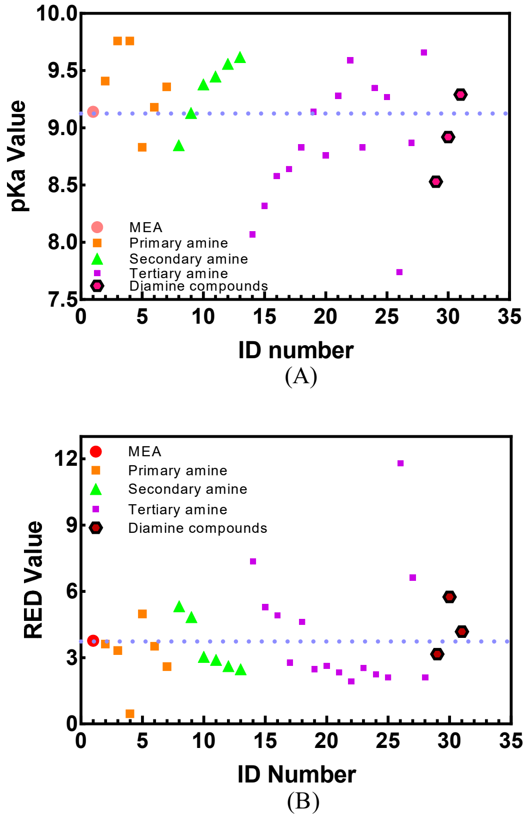
This subsection discusses the influence of the structures possessed by different types of amines on their properties and analyzes the conditions that should be met by a solvent with good performance. The values of the horizontal coordinates in Figures 3–5 represent the solvent ID numbers in Table 1. For example, ID 1 represents S1 (CAS 141-43-5), ID 2 represents S2 (CAS 156-87-6), ID 3 represents S3 (CAS 2508-29-4), and so on.



(A)

(B)

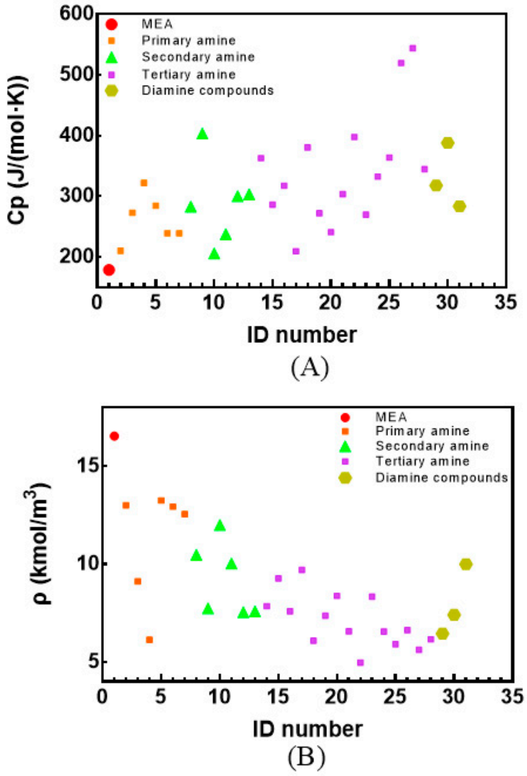
Figure 3. Melting point temperature (**A**) and boiling point temperature (**B**) of each candidate amine solvent.



(A)

(B)

Figure 4. Acidity coefficient (pKa) value (**A**) and relative energy difference (RED) value (**B**) of each candidate amine solvent.



(A)

(B)

Figure 5. Heat capacity (**A**) and density (**B**) of each candidate amine solvent.

In Figure 3, T_b indicates the boiling temperature of the solvent, while T_m signifies its melting temperature. T_A and T_D correspond to the lowest and highest temperatures involved in the operation of the tower, respectively. K represents Kelvin temperature.

In Figure 4, the pKa value represents the acidity coefficient value of the solvent and the RED value represents the relative energy difference value of the solvent.

In Figure 5, Cp represents the heat capacity of the solvent and ρ represents the density of the solvent.

The data of melting and boiling points are shown in Figure 3.

The melting and boiling points of solvents are two important parameters for determining whether solvents can normally react in the absorber and desorber. In chemical production, the minimum and maximum temperatures for absorption and desorption are generally T_A = 313 K and T_D = 393 K, respectively. To prevent solidification or excessive evaporation of the solvent due to a too low or too high reactor temperature, we usually specify $T_m < T_A$, $T_b > T_D$. It can be found from Figure 3 that the boiling points (T_b) of all the compounds in our selected solvents are in accordance with the conditions, while a few solvents are excluded in the melting point diagram due to high melting points (T_m). We find that in the primary amine group, the melting points of substances S5 and S7 increase significantly and abruptly, and in the tertiary amine group, the melting points of S26, S27, and S28 show a significant decreasing trend. After analyzing these data and the structures of the compounds, we discover that an increase in the number and change in the position of the hydroxyl groups substantially increases the melting points of the substances under the premise of structural similarity. In all, the melting and boiling points of other compounds basically show a steady increase with the growth of carbon chains and structural complexity.

The absorption rate of amine solvents is affected by the acidity coefficient (pKa), with a higher pKa resulting in a faster absorption rate. As can be seen in Figure 4A, primary and secondary amines have a significantly higher overall absorption rate than tertiary amines, but they generate carbamates, which leads to lower solvent regeneration. Tertiary amines have higher recovery rates but slower uptake rates [38].

The blue dashed line in Figure 4 separates solvents that have higher absorption than MEA from those with lower absorption. Based on the molecular structure and pKa data, we found that pKa tends to increase with increasing carbon chain length but is inhibited by the presence of hydroxyl groups near the amine group. According to S23, S24, and S25, it can be seen that the closer the hydroxyl group is to the amine, the more it affects the degree of ionization of the amine, leading to the decrease in pKa. In Figure 4A, S26 is the compound containing the most hydroxyl groups and its pKa value is also the smallest. Moreover, we can find that diamine solvent does not offer any advantage in terms of absorption rate.

The relative energy difference (RED) of different solvents for CO_2 can be used as an indicator of the solubility of CO_2 in a solvent. Specifically, solvents with lower RED values are known to exhibit greater CO_2 solubility when evaluating the viability of potential carbon capture absorbents. The blue dashed line below represents the solvents with stronger solubility than MEA. From Figure 4B, we can see that most solvents in the primary, secondary, and tertiary amine groups have better solubility than MEA, and the solubility improves as the carbon chain grows and the structure becomes more complex. We studied several unqualified molecules (S14, S15, S16, S18, S26, S27) in the tertiary amine group and found that they have a common feature, that is, they all contain two or more hydroxyl groups. Therefore, we can roughly assume that one hydroxyl group of amine solvents is more favorable to dissolve carbon dioxide, while the increase in the number of hydroxyl groups plays an inhibitory role instead.

Liquid heat capacity affects tower plate efficiency and heat consumption, and low heat capacity solvents help reduce the sensible heat required for the desorption process, resulting in low-energy recycling. In Figure 5A, by analyzing the molecular structure and molecular weight, we find that the liquid heat capacity is basically positively correlated with the molecular weight, where an increase in the number of hydroxyl and amino groups significantly increases the heat capacity, which is important for screening solvents in industry. MEA excels in this comparison due to its low molecular weight and simple structure. Molecules such as S2, S10, and S17 also show excellent performance.

The molar density of the liquid should be as high as possible because it facilitates adequate contact with the solute and better mass and heat transfer. The molar density of a liquid is the reciprocal of the molar volume. From Figure 5B, most of the primary and tertiary amines do not perform as well as MEA, but they are still in line with the requirements.

During the solvent screening process, the first properties to consider are T_m and T_b, as they are critical in determining whether the solvent is suitable for tower operation. Following this, pKa and RED are evaluated to determine the absorption rate and capacity of the solvent for CO_2. Lastly, Cp, ρ, and Pvp are assessed to determine the mass transfer efficiency and volatility of the solvent.

In this study, a total of 31 amine solvents were involved in the screening, which were numbered S1–S31. By combining the multi-objective optimization method in Equation (1), the screening steps were as follows:

In the first stage, we require $T_m < T_A$ and $T_b > T_D$. At this time, S5, S7, S14, S26, S27, and S30 are excluded from the candidate solvents ($a_1 = 0$).

In the second stage, we require $pKa_{(solvents)} > pKa_{(MEA)}$. At this time, S8, S9, S15, S16, S17, S18, S19, S20, S23, and S29 are excluded from the candidate solvents ($a_2 = 0$).

In the third stage, we require $RED_{(solvents)} < RED_{(MEA)}$. At this time, S31 is excluded from the candidate solvents ($a_3 = 0$).

In the fourth stage, we require $Cp_{(solvents)} < Cp_{(MEA)}$. At this time, all solvents are excluded from the candidate solvents. However, in order to make the solution of the problem closer to reality, we specify ($a_4 = 11$) when S22 and S25 are excluded from the candidate solvents.

In the fifth stage, we require $\rho_{(solvents)} > \rho_{(MEA)}$. At this time, all solvents are excluded from the candidate solvents. However, in order to make the solution of the problem closer to reality, we specify ($a_5 = 8$) when S4, S24, and S28 are excluded from the candidate solvents.

In the sixth stage, we require that $Pvp_{(solvents)} < Pvp_{(MEA)}$. At this time, S10 is excluded from the candidate solvents. ($a_6 = 0$).

In the end, seven solvents that showed excellent performance were retained, except for S1 (MEA). They are S2, S3, S6, S11, S12, S13, and S21, and their comprehensive performance is shown in Figure 6.

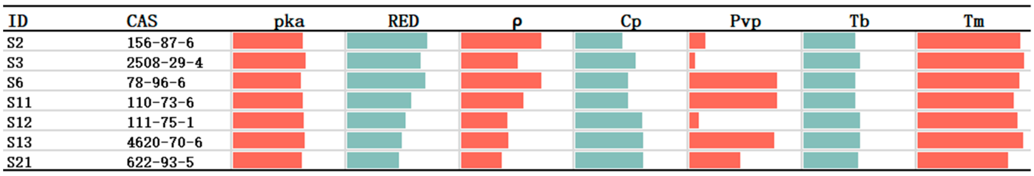


Figure 6. Potential solvents comprehensive performance chart.

4. Conclusions

In this study, a CAMD method based on group contribution was employed to conduct a multi-criteria screening of various organic ethanol amines for efficient CO_2 capture. A parametric analysis of 31 amine solvents was carried out using this method. Firstly, the predicted values obtained from the group contribution method are found to be in good agreement with the experimental values, with all parameters having an δ value within the acceptable range. The same method was then used to compute the performance parameters of the 31 amine solvents. The optimal solvent composition was found based on the reference solvent MEA, with an aqueous solvent preferred due to its advantages of fast absorption rate, high capacity, and low energy consumption.

This method enables the systematic evaluation of a large number of molecules and components, significantly streamlining the screening and design process and improving experimental efficiency. It has good prospects for CO_2 capture. However, the absorption mechanism, energy consumption magnitude, and environmental impact of most of the promising absorbents are not yet clear, thus, preventing industrial applications. Therefore, in order to achieve efficient capture of CO_2, the rapid screening of chemical absorbers for CO_2 capture is still an aspect for further research.

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