

# Research Progress on Mixed Amines and Phase Change Systems

Xiankang Hong

<sup>\*1</sup>*School of Environment and Architecture, University of Shanghai for Science and Technology, Shanghai, China, 200093*

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## **Abstract**

With the annual increase in global carbon emissions, the resulting environmental issues are becoming increasingly severe. CCUS technology, as a crucial means of carbon capture and storage, has become the focus of extensive research by scholars. Currently, the most common method for CO<sub>2</sub> capture is the amine-based process, yet it still faces challenges such as high energy consumption and degradation rates. Therefore, there is still significant room for improvement in the development of CO<sub>2</sub> capture technology based on amine solutions. In this paper, we review the current research status of CO<sub>2</sub> capture using amine solutions both domestically and internationally in recent years. We systematically elaborate on the progress in absorbent research, providing insights for industrial-scale carbon capture and environmental protection.

**Keywords:** CO<sub>2</sub> absorption, Alkanolamine Solution, Reaction Mechanism, Phase change absorbent.

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## I. INTRODUCTION

Given the current social environment, the rapid development of human industrialization has resulted in the substantial emission of CO<sub>2</sub> into the atmosphere, leading to global warming [1]. Failure to promptly address the issue of CO<sub>2</sub> emissions is projected to cause a global surface temperature increase of 2.5 to 7.8°C by 2100 [2]. In response to this problem, Carbon Capture, Utilization, and Storage (CCUS) technology has emerged as a crucial means of carbon mitigation, garnering significant attention from scholars [3-5]. The initial phase of CCUS involves CO<sub>2</sub> capture, which is the process of separating CO<sub>2</sub> from industrial production, energy utilization, or the atmosphere [6]. This process is primarily categorized into pre-combustion capture, oxy-fuel combustion capture, and post-combustion capture [7].

Post-combustion capture is a technology that separates and purifies CO<sub>2</sub> from the flue gas tailings after dust removal and desulfurization following the combustion of fossil fuels. Generally, this technology is installed downstream of dust removal and desulfurization and denitrification units. Therefore, it can be integrated with boilers without altering existing boiler structures. It boasts high selectivity and capture rates. Currently, it is a mature technology. Mainstream absorbent liquids on the market include ammonia solution [8], potassium carbonate solution [9], ionic liquids [10], and alkanolamine solution [11]. Ammonia solution tends to evaporate easily, greatly hindering its development potential in carbon capture. Moreover, leakage of ammonia solution can cause secondary environmental pollution. Potassium carbonate solution has a low absorption rate and a greater corrosive effect on equipment. The production process of ionic liquids is complex and expensive, making them unsuitable for large-scale use in power plants. Therefore, alkanolamine solution is the most commonly used and suitable absorbent solution currently [12-14].

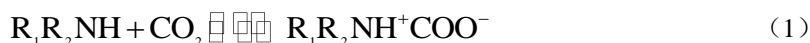
The amine absorption method, characterized by high absorption efficiency and large processing capacity, is the most suitable technology for large-scale carbon capture in various industries. However, this method suffers from high energy consumption and significant solvent loss. Therefore, improving the absorbent to achieve high absorption efficiency and designing a feasible process with low regeneration energy consumption is of significant importance for industrial carbon capture and environmental protection.

## II. Traditional alcohol amine method

### 2.1 Primary and Secondary Amines Absorption Mechanism

It is generally believed that different types of organic amines exhibit different mechanisms for CO<sub>2</sub> absorption, which mainly include zwitterion mechanism and alkaline catalysis mechanism. Primary and secondary amine molecules mainly refer to molecules with active hydrogen atoms around the nitrogen atom, and their reaction with CO<sub>2</sub> follows the "zwitterion mechanism." This reaction mechanism was proposed and improved by CAPLOW [15] and DANCKWERTS [16]. According to the zwitterion mechanism, the reaction between primary and secondary amines and carbon dioxide is completed through a two-step reaction: the first

step is the reaction of CO<sub>2</sub> with amine molecules to generate zwitterionic intermediates; the second step is the deprotonation of zwitterions to form ionic aminofornate and protonated amine. The reaction equations are as follows:



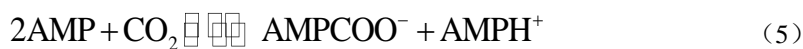
### 2.2 Tertiary Amines Absorption Mechanism

The alkaline catalytic hydration mechanism proposed by Donaldson et al. [17] is widely accepted. It is observed that tertiary amines lack hydrogen atoms on their amino groups, so they do not follow the zwitterion mechanism during CO<sub>2</sub> absorption; hence, tertiary amines do not directly react with CO<sub>2</sub> to form zwitterions. However, tertiary amines readily undergo protonation reactions with H<sub>2</sub>O, thereby facilitating the dissociation of H<sub>2</sub>O molecules to release OH<sup>-</sup>. The free OH<sup>-</sup> ions in solution react with dissolved CO<sub>2</sub> to form HCO<sub>3</sub><sup>-</sup>.



### 2.3 Hindered Amines Absorption Mechanism

Sterically hindered amines refer to amines with amino groups located on the third carbon atom, or secondary amines with amino groups located on the second and third carbon atoms. Taking common AMP as an example, the reaction mechanism of sterically hindered amines is illustrated.



## III. PROGRESS IN THE RESEARCH OF ABSORBENTS

### 3.1 Mixed Amine Absorbents

The traditional amine absorption method commonly uses monoethanolamine (MEA) and piperazine (PZ) as chemical absorbents, which exhibit fast absorption rates but high desorption energy consumption. On the other hand, tertiary amine N-methyldiethanolamine (MDEA) has a high absorption capacity and low desorption reaction heat, albeit with slower absorption rates. Meanwhile, 2-amino-2-methyl-1-propanol (AMP), as a secondary amine, demonstrates intermediate absorption rates between primary and tertiary amines due to steric hindrance effects. Therefore, traditional amine solvents face challenges in simultaneously achieving high absorption capacity and low desorption energy consumption. To address this, researchers have explored the strategy of using blends of organic amines with complementary properties. These mixed amines combine the absorption performance of two types of amine solutions to meet the requirements of both high absorption capacity and low desorption energy consumption. Zhang[18] employed diethylenetriamine (DETA) as the primary absorbent and triethanolamine (TEA) as the auxiliary absorbent, with MEA as a reference standard. The resulting solvent achieved a saturated CO<sub>2</sub> absorption capacity of 3.71 mol/L, a maximum desorption rate of 1.94 mmol/(L·min), and a desorption energy of 160 kJ/mol. Compared to MEA, the saturated absorption capacity increased by 34.42%, the maximum desorption rate increased by 170%, and the energy consumption decreased by 21.2%. Chen[19] simulated the CO<sub>2</sub> absorption and desorption performance of MEA absorbent and a blend of MEA and spatially hindered amine AMP using Aspen Plus software. The results showed that the absorption and desorption performance of the mixed amine with a concentration of 30 wt% (molar ratio MEA:AMP = 1:1) outperformed that of the single MEA absorbent. Wang[20] investigated the enhancement of CO<sub>2</sub> capture capacity in MDEA solution by using triethylenetetramine (TETA) and aminoethylpiperazine (AEP). The results indicated that the CO<sub>2</sub> absorption capacity, average absorption rate, and desorption efficiency

of 26% MDEA + 2% TETA-2% AEP + 70% H<sub>2</sub>O were 3.08, 3.05, and 1.18 times higher than those of 30% MDEA solution, respectively. Lu [21] found that adding activators such as MEA, DEA, PZ, and AMP to MDEA base solution can enhance the saturation absorption capacity of the absorbent. Suleman[22] conducted experiments and modeling on carbon dioxide solubility in AMP/MDEA under high gas loading conditions at pressures (102.5-4110 kPa), temperatures (303.15-343.15K), and solvent concentrations (1+1 and 2+2 M). The results showed that adding AMP to MDEA increased the overall carbon dioxide loading, consistent with experimental values reported in the literature. However, due to the intrinsic properties of amines, their regeneration capability remains limited.

### 3.2 Phase Change Absorbents

Based on organic amine solutions, the chemical absorption method consumes a high amount of energy during the regeneration process [23], accounting for over 80% of the total energy consumption for CO<sub>2</sub> capture. Since the concept of phase-change absorbents was proposed by scholars at Hampton University in 2009, it has been demonstrated that restricting absorbent entry into the desorption unit can effectively reduce the energy required for regeneration [24]. In recent years, researchers have shifted their focus to physical solvent-based phase-change absorbents, which can significantly reduce the energy consumption for regeneration by minimizing the sensible and latent heats during desorption [25-26]. In phase-change absorption systems, CO<sub>2</sub> absorption leads to the formation of CO<sub>2</sub>-lean and CO<sub>2</sub>-rich phases, and by only thermally regenerating the CO<sub>2</sub>-rich phase, the regeneration energy consumption of the system is successfully reduced. Phase-change component systems are categorized into liquid-liquid phase change and liquid-solid phase change absorbents.

#### 3.2.1 Liquid-liquid phase change absorbent

Phase change absorbents generally consist of three substances: amines, alcohols, and water. Wang [27] used a mixture of DETA and cyclohexylamine to capture CO<sub>2</sub> from simulated flue gas, finding that the upper layer was CO<sub>2</sub>-rich and mainly composed of DETA and DETA carbamate, while the lower layer was CO<sub>2</sub>-lean, with cyclohexylamine present alone. Papadopoulos [28] designed a novel phase change solvent, S1N/DMCA (N-cyclohexyl-1,3-propanediamine and N,N-dimethylcyclohexylamine). The cyclic capacity was 1.19 mol/kg, and the regeneration energy consumption was 2.3 GJ/t. Hu [29], based on the Hansen solubility parameter theory, screened a novel phase change absorbent, MDEA/polyethylene glycol dimethyl ether (NHD)/H<sub>2</sub>O, using MDEA as the main absorbent, organic solvent as phase separation promoter, and water as the solvent. The results showed that the MDEA/NHD/H<sub>2</sub>O phase change absorbent had the highest thermal stability compared to the 30wt% MEA absorbent. The MDEA/NHD/H<sub>2</sub>O phase change absorbent with a mass ratio of 3:5:2 had the highest CO<sub>2</sub> absorption capacity of 1.1061 molCO<sub>2</sub>/L and reduced the volume of desorption liquid sent to the desorption unit by 42%. At a desorption temperature of 90°C, the CO<sub>2</sub> desorption efficiency reached 98.96%. Lu [30] studied a "amino-imidazole bifunctional ionic liquid-ethanol-water" phase change system for CO<sub>2</sub> capture, which exhibited good stability and recyclability, with an absorption rate of up to 1.548 mol/mol. Chen [31], using tertiary amine 3-methylamino-1-propanol (MAP) as the main absorbent, dimethyl sulfoxide (DMSO) as the organic diluent, and pentamethyldiethylenetriamine (PMDETA) as the auxiliary absorbent, prepared a novel MAP-DMSO-PMDETA ternary phase change absorbent. Experimental results showed that at a mass ratio of MAP, DMSO, and PMDETA of 3:6:11, liquid-liquid phase separation occurred after absorption saturation. The absorbent loading was 0.79 mol/kg, the absorption load was 0.47 mol/mol (based on MAP), the volume fraction of rich phase was 45.1%, and 95.1% of CO<sub>2</sub> was enriched. This ternary phase change absorbent exhibited excellent desorption performance and good cyclic stability. After 5 absorption-desorption cycles, the desorption load stabilized at around 0.34 mol/mol (based on MAP), and the desorption efficiency reached 69.4%.

#### 3.2.2 Solid-liquid phase change absorbent

Most liquid-solid phase change absorbents are water-poor or non-aqueous, and precipitate in solid form during absorption, which significantly reduces energy consumption and can reduce equipment corrosion. After CO<sub>2</sub> desorption, the solid phase can convert to the liquid phase, which can be mixed with the previously separated CO<sub>2</sub> lean solution and re-enter the absorption tower for recycling. The process flow of solid-liquid phase change absorbents for CO<sub>2</sub> capture is shown in Figure 1.8. Malhotra et al. [32] reported a novel amine-pyridine solvent with the potential to capture CO<sub>2</sub> from coal-fired power plants. The solvent rapidly forms crystalline solids with CO<sub>2</sub>, exhibiting a high CO<sub>2</sub> capture capacity (11% to 20%) and can be regenerated within the temperature range of 120 to 150°C. PERRY [33] developed a 1,3-bis(3-aminopropyl)tetramethyldisiloxane as a liquid-solid phase change absorbent, notable for its thermal stability, low energy consumption, and high CO<sub>2</sub> cycling capacity. Long Qinghai et al. [34] constructed an isophorone diamine (IPDA) - water binary solid-liquid phase change absorption system. The study showed that a 1.00 mol·L<sup>-1</sup> IPDA aqueous solution had a saturation absorption load of 0.85 mol CO<sub>2</sub>·mol·L<sup>-1</sup> at 313.15 K, with the absorption product being white

crystalline powder and enriched in the lower layer of the solution. The enriched liquid volume accounted for 43.60% of the total solution volume, while the CO<sub>2</sub> enrichment rate reached 93.98%. ZHENG [35] introduced a TETA+ethanol liquid-solid phase change adsorbent, which increased CO<sub>2</sub> solubility, achieving a CO<sub>2</sub> removal rate of up to 81.8%. Ren Enze [36] designed a liquid-solid phase change adsorbent composed of MDEA+PZ+N-methylpyrrolidone (NMP)+H<sub>2</sub>O. The results showed that when the mass fractions of NMP and PZ in the adsorbent reached 50% and 3% or more, respectively, the absorption of CO<sub>2</sub> produced PZ-aminoformate ester, reaching saturation and precipitating into solid phase, which initially increased with the increase of CO<sub>2</sub> solubility and later decreased with the generation of PZ-diaminoformate ester, which is more soluble in water, leading to a decrease in the solid phase. In conclusion, phase change adsorbents have significant energy-saving potential, but further research is needed on issues such as formulation, phase change mechanism, and phase change solution viscosity based on these adsorbents.

#### IV. CONCLUSION

The development history and research progress of the traditional alcohol amine method are systematically discussed. The primary challenge in the development of the alcohol amine absorption method remains the issue of regeneration energy consumption. Additionally, the regeneration performance of mixed amine methods is limited due to the nature of alcohol amines. The concept of phase change adsorbents has been proposed to address the regeneration energy consumption, offering significant insights and methods. Leveraging the phase separation properties of adsorbents reduces the regeneration volume and effectively lowers the regeneration energy consumption. In future studies, environmentally friendly adsorbents should be selected to construct phase change systems. However, phase change systems still face issues such as high viscosity. Therefore, novel adsorbents with high CO<sub>2</sub> absorption capacity, low regeneration consumption, low losses, and suitability for large-scale industrial production should be developed by integrating the properties of alcohol amine solutions. These efforts will provide crucial support for mitigating global greenhouse gas emissions.

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