AMINO ACID/AMINE HYBRID MATRIXES FOR ECO–FRIENDLY CO_2 CAPTURE AND FUNCTIONALIZATION

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Abstract

The continuous rise in atmospheric carbon dioxide CO_2 concentrations and the resulting greenhouse effect represent critical challenges for modern science. Adhering to the principles of green chemistry, this study investigates the efficiency of CO_2 capture in environmentally benign systems using aqueous solutions of various natural amino acid potassium salts, as well as hybrid mixtures comprising individual organic amines and inorganic bases. Methylamine (MA), diethylamine (DEA), ethylenediamine (EDA), and piperazine (PZ) were utilised both as pure single–component absorbents and as organic promoters in structural matrices, while potassium hydroxide (KOH) served as the inorganic base to modulate alkalinity. Dynamic monitoring of the absorption process, structural relationship determination, and quantitative calculation of the resulting chemical species (carbamates, bicarbonates/carbonates) in solution were performed using high–field quantitative 1H and ^{13}C NMR spectroscopy, pH–metry, and digital polarimetry.

A remarkable synergism was observed in the amino acid/piperazine and amino acid/ethylenediamine hybrid systems, with total carbon dioxide absorption efficiency exceeding 90%. Furthermore, the screening of individual pure amines and the evaluation of varying light conditions (complete darkness versus intense artificial illumination) on quaternized mono– and diamine systems illuminated the underlying

mechanisms of carbamate formation, opening new pathways for the development of photo-controlled carbon capture and utilising captured CO_2 as a functional C1 synthon for pharmaceutical development.

Keywords and phrases: Carbon dioxide, Amino acid salts, Organic amines, Hybrid matrices, NMR spectroscopy, Carbamates, Photo-controlled desorption.

ԱՄԻՆԱԹԹՎԱՅԻՆ/ԱՄԻՆԱՅԻՆ ՀԻԲՐԻԴԱՅԻՆ ՀԱՄԱԿԱՐԳԵՐԸ CO_2-Ի ԷԿՈԼՈԳԻԱՊԵՍ ԱՆՎՏԱՆԳ ՈՐՍՄԱՆ ԵՎ ՖՈՒՆԿՑԻՈՆԱԼԱՑՄԱՆ ԳՈՐԾԸՆԹԱՑՆԵՐՈՒՄ

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Համառոտագիր

Մթնոլորտում ածխածնի երկօքսիդի (CO_2) կոնցենտրացիայի շարունակական աճը և դրանով պայմանավորված ջերմոցային էֆեկտը ժամանակակից գիտության էական մարտահրավերներից են: Կանաչ քիմիայի սկզբունքներին համապատասխան, այս աշխատանքում ուսումնասիրվել է CO_2-ի կլանման արդյունավետությունը էկոլոգիապես անվտանգ համակարգերում՝ տարբեր բնական ամինաթթուների կալիումական աղերի ջրային լուծույթների, ինչպես նաև դրանց հիման վրա ձևավորված անհատական օրգանական ամինների ու անօրգանական հիմքերի հիբրիդային խառնուրդների կիրառմամբ: Մեթիլամինը (MA), դիէթիլամինը (DEA), էթիլենդիամինը (EDA) և պիպերազինը (PZ) օգտագործվել են ինչպես մաքուր միաբաղադրիչ կլանիչներ, այնպես էլ որպես օրգանական խթանիչներ կառուցվածքային մատրիցներում, իսկ կալիումի հիդրօքսիդը (KOH) հանդես է եկել որպես միջավայրի հիմնայնությունը կարգավորող անօրգանական հիմք:

^{1}H, ^{13}C ՄՄՌ սպեկտրոսկոպիայի, pH–մետրիայի և թվային պոլարիմետրիայի միջոցով իրականացվել է կլանման պրոցեսի դինամիկ մոնիտորինգ, կառուցվածքային օրինաչափությունների բացահայտում և լուծույթում ձևավորվող քիմիական ձևերի (կարբամատներ, բիկարբոնատներ/կարբոնատներ) քանակական հաշվարկ: Բացահայտվել է զգալի սիներգիզմ ամինաթթու/պիպերազին և ամինաթթու/էթիլենդիամին հիբրիդային համակարգերում, որտեղ ընդհանուր ածխածնի երկօքսիդի կլանման արդյունավետությունը գերազանցել է 90%–ը: Բացի այդ, անհատական մաքուր ամինների սկրինինգը և քվատերնիզացված մոնո– ու դիամինային համակարգերի վրա տարբեր լուսային պայմանների (լիակատար մթություն և ինտենսիվ արհեստական լուսավորություն) ազդեցության գնահատումը լուսաբանել են կարբամատների առաջացման հիմքում ընկած մեխանիզմները՝ նոր ուղիներ բացելով ֆոտոկառավարվող ածխածնի որսման համակարգերի մշակման և որսված CO_2–ը դեղագործական նպատակներով որպես ֆունկցիոնալ C1 սինթոն կիրառելու համար:

Բանալի բառեր և բառակապակցություններ՝ Ածխաթթու գազ, ամինաթթվային աղեր, օրգանական ամիններ, հիբրիդային մատրիցներ, ՄՄՌ սպեկտրոսկոպիա, կարբամատներ, ֆոտո–կառավարվող դեսորբցիա:

ГИБРИДНЫЕ МАТРИЦЫ НА ОСНОВЕ АМИНОКИСЛОТ И АМИНОВ ДЛЯ ЭКОЛОГИЧЕСКИ БЕЗОПАСНОГО УЛАВЛИВАНИЯ И ФУНКЦИОНАЛИЗАЦИИ CO_2

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Аннотация

Непрерывный рост концентрации углекислого газа (CO_2) в атмосфере и вызванный этим парниковый эффект представляют собой серьезные вызовы для современной науки. В соответствии с принципами «зеленой химии», в данной работе исследована эффективность улавливания CO_2 в экологически безопасных системах с использованием водных растворов калиевых солей различных природных аминокислот, а также гибридных смесей, сформулированных с участием индивидуальных органических аминов и неорганических оснований. Метиламин (MA), диэтиламин (DEA), этилендиамин (EDA) и пиперазин (PZ) использовались как в качестве чистых однокомпонентных поглотителей, так и в качестве органических промоторов в структурных матрицах, тогда как гидроксид калия (KOH) применялся в качестве неорганического основания для регулирования щелочности среды. Динамический мониторинг процесса абсорбции, установление структурных закономерностей и количественный расчет образующихся в растворе химических форм (карбаматов, бикарбонатов/карбонатов) осуществлялись методами ЯМР (^{1}H, ^{13}C) спектроскопии, pH-метрии и цифровой поляриметрии.

Обнаружен значительный синергизм в гибридных системах аминокислота/пиперазин и аминокислота/этилендиамин, где общая эффективность абсорбции диоксида углерода превысила 90%. Кроме того, скрининг индивидуальных чистых аминов и оценка влияния различных условий освещения (полная темнота по сравнению с интенсивным искусственным освещением) на кватернизованные моно- и диаминные системы позволили прояснить фундаментальные механизмы образования карбаматов. Это открывает новые пути для разработки фотоуправляемых систем улавливания углерода и

последующего использования уловленного CO_2 в качестве функционального C1-синтона для создания перспективных фармацевтических препаратов.

Ключевые слова и фразы: Углекислый газ, соли аминокислот, органические амины, гибридные матрицы, ЯМР спектроскопия, карбаматы, фотоуправляемая десорбция.

Introduction

Global Threats of the Greenhouse Effect and the Ecological Crisis

The unprecedented expansion of human consumption, rapid industrial development, and the massive processing of fossil hydrocarbon resources—namely coal, oil, and natural gas—have led to global and anomalous shifts in the Earth's atmospheric composition. Today, fossil fuels generate the vast majority of global electricity, resulting in the annual emission of billions of tons of greenhouse gases into the atmosphere. According to recent alarming reports from the World Meteorological Organisation (WMO) and the Intergovernmental Panel on Climate Change (IPCC), atmospheric carbon dioxide (CO_2) levels have exceeded 152% of the pre-industrial baseline, surpassing the critical threshold of 420 ppm. If emissions continue at the current rate, the concentration of CO_2 could reach up to 570 ppm by the year 2100. This trajectory will lead to a 1.9 °C rise in the global average temperature, a 3.8-meter increase in sea levels, the catastrophic melting of glaciers, and the widespread collapse of global ecosystems **[1–3].**

For centuries, photosynthesis served as nature's balanced mechanism for maintaining a closed carbon cycle on Earth. However, current anthropogenic emissions are so immense that natural ecosystems are no longer capable of capturing and neutralising this excess independently without technological intervention. Consequently, it is a primary task for modern science and humanity to develop and implement sustainable, energy-efficient Carbon Capture and Storage/Utilisation (CCS/CCU) technologies **[2–5].**

Figure 1. Conceptual illustration of green carbon capture technologies mitigating industrial CO_2 emissions into the atmosphere.

Armenia's Climatic Potential and Alternative Carbon Sources

This environmental challenge is exceptionally relevant for the Republic of Armenia. As a country with limited domestic fossil fuel reserves, Armenia is entirely dependent on imported energy resources. At the same time, the country possesses magnificent geographical and climatic conditions suitable for the advancement of

photochemical and solar technologies. Notably, the capital city of Yerevan receives approximately 2,630 hours of sunlight annually, which represents an exceptionally high solar index. Therefore, coupling solar energy with chemical CO_2 capture and photocatalytic conversion processes offers a strategic pathway to create alternative, renewable carbon sources. This paradigm is of paramount importance for the nation's scientific and economic independence, enabling the transformation of captured CO2 into industrial monomers and clean, eco-friendly fuels [1–3].

Screened Single Amines and Amino Acid Salts as a Green Chemistry Alternative

The alkanolamine-based scrubbing systems currently used in industry for carbon capture (such as monoethanolamine, MEA) exhibit severe structural drawbacks: they are toxic and volatile, cause equipment corrosion, and require substantial thermal energy during solvent regeneration. To meet the contemporary criteria of Green Chemistry, aqueous solutions of various natural amino acids and their hybrid blends with functional amines have become the centre of intensive research. Amino acids possess zero volatility, high biodegradability, negligible toxicity, and high stability against oxidative degradation [4–10].

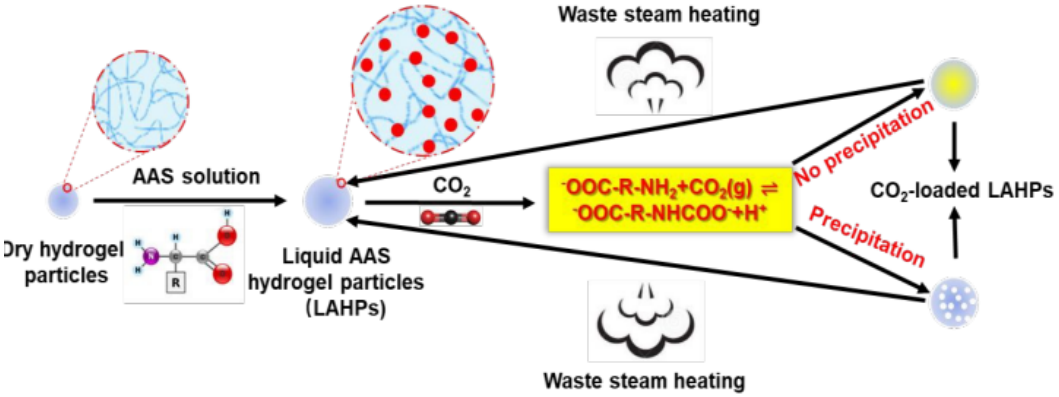

Figure 2. Application of hydrogels immobilised with amino acid salt solutions for carbon dioxide capture.

To systematically address these factors, this comprehensive study evaluates CO_2 absorption profiles across two distinct structural levels: first, by mapping the structural relationships, basicity, and interactions within pure individual organic mono- and diamines (MA, DEA, EDA, PZ); and second, by optimizing multi-component aqueous mixtures composed of different natural amino acid potassium salts (including L-threonine series) promoted by those functional organic amines or balanced with inorganic bases (KOH) **[11].**

Biological and Pharmaceutical Significance of Carbamates

A pivotal aspect of this research focuses on the targeted chemical transformation of the captured CO_2. Serving as a versatile, inexpensive, and readily available C1 building block (synthon), carbon dioxide can replace highly toxic and hazardous reagents traditionally used in organic synthesis, such as phosgene ($COCl_2$) and volatile isocyanates. The primary products of CO_2 capture in amine-containing systems are carbamates (urethanes), which constitute crucial structural motifs in numerous

biologically active substances and pharmaceutical formulations.

The carbamate group (–NH–COO–) ensures high bioavailability and plays an essential role in drug–receptor interactions due to its dual capacity to form hydrogen bonds as both a donor and an acceptor. Crucially, the chemical rearrangement of carbamates provides a direct synthetic pathway to cyclic carbamates, known as oxazolidinones. Compounds belonging to the oxazolidinone class currently serve as the structural backbone for some of the most potent antimicrobial and antibacterial agents in clinical medicine.

The first clinically approved antibiotic of this class, **Linezolid**, exhibits exceptional antimicrobial activity against multidrug–resistant Gram–positive pathogens, including methicillin–resistant *Staphylococcus aureus* (MRSA) and vancomycin–resistant *Enterococci* (VRE). Other highly promising representatives of this family, such as **Eperezolid**, **Radezolid**, **Tedizolid**, and **Posizolid**, similarly feature this chiral, cyclic carbamate core. Given the high demand for the stereoselective synthesis of chiral pharmaceutical building blocks, the strategic utilisation of natural chiral amino acid frameworks for CO2 fixation offers green synthetic routes to optically active, high–value pharmaceutical scaffolds **[12–18].**

Theoretical Background and Reaction Chemistry

Zwitterionic Equilibrium of Amino Acids and Activation Mechanisms

In an open aqueous environment, pristine natural amino acids dominantly exist in their zwitterionic intramolecular salt configurations, where the basic amino site is protonated into a non–nucleophilic ammonium form ($-NH_3^+$), while the carboxylic acid moiety is deprotonated into a carboxylate group ($-COO^-$). Under these baseline physiological pH levels, the lone pair of electrons on the amino nitrogen is entirely sequestered, eliminating its capacity to attack electrophilic carbon centres like that of gaseous carbon dioxide.

$$CO_2 + {}^{-}OOC\text{-}R\text{-}NH_2 \rightleftharpoons \left[{}^{-}OOC\text{-}R\text{-}NHCOO^{-}\right]\left[H_3N^{+}\text{-}R\text{-}COO^{-}\right] \quad (1)$$

To overcome this inherent thermodynamic barrier and unlock the nucleophilic potential of the amino framework, chemical activation is required. This is systematically accomplished through the introduction of stoichiometric amounts of strong inorganic bases, such as potassium hydroxide (KOH), which shift the chemical equilibrium by converting the zwitterion into a highly reactive potassium amino acid salt. Alternatively, strong organic mono– or diamines can be blended into the matrix to act as localised proton acceptors, deprotonating the –NH3+ groups in situ and generating a highly localised nucleophilic cascade [6–7].

Carbamate Formation Kinetics and Thermodynamic Boundaries

Following the widely accepted zwitterion mechanism or base–catalysed mechanism of CO_2 binding to primary and secondary amine groups, the reaction proceeds via a two–step sequence [9–11]. Initially, the nucleophilic nitrogen atom attacks the electrophilic carbon atom of CO_2, generating a transient, unstable

zwitterionic intermediate containing a positive charge on the nitrogen and a negative charge on the carboxylate group:

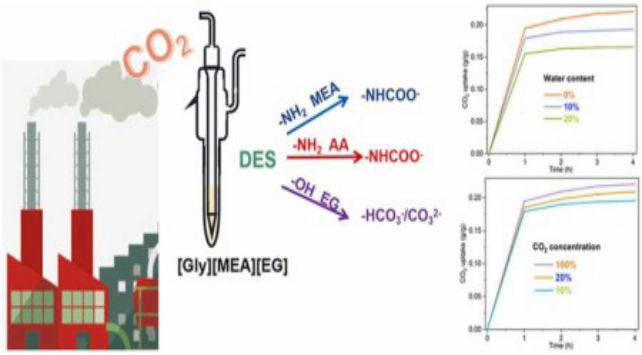

Figure 3. Schematic mechanism of CO_2 capture inside a hybrid glycine/monoethanolamine/ethylene glycol solvent system.

In the subsequent rate-determining step, a second equivalent of a basic molecule (either another free amine from the solution, an amino acid salt, or a hydroxyl ion) rapidly abstracts the proton from this intermediate to form a thermodynamically stable carbamate salt. Thus, under anhydrous or low-moisture constraints, the traditional reaction chemistry displays a strict 2:1 amine-to-CO_2 stoichiometry:

$$CO_2 + {}^-OOC\text{-}R\text{-}NH_2 \rightleftharpoons {}^-OOC\text{-}R\text{-}NH_2{}^+COO^- \quad (2)$$

By combining steps (1) and (2), the overall stoichiometric equation for carbamate formation can be represented as follows:

$$CO_2 + 2\,{}^-OOC\text{-}R\text{-}NH_2 \rightleftharpoons {}^-OOC\text{-}R\text{-}NHCOO^- + {}^-OOC\text{-}R\text{-}NH_3{}^+ \quad (3)$$

2.3. Hydrolytic Equilibria and Bicarbonate Pathways

When the capture matrix is deployed in a purely aqueous medium, the primary carbamate species undergo competitive, reversible hydrolysis. The extent of these competitive pathways is deeply governed by the specific stability constant of the carbamate structure and the localised pH of the solvent. The reaction can be formally expressed as follows:

$${}^-OOC\text{-}R\text{-}NHCOO^- + H_2O \rightleftharpoons {}^-OOC\text{-}R\text{-}NH_2 + HCO_3^- \quad (4)$$

Through this pathway, the captured carbon is transformed from an organic carbamate structure into inorganic bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) fractions. This chemical conversion effectively liberates the original amine molecule, allowing it to undergo subsequent cycles of gas capture [8–10]. Consequently, in highly alkaline aqueous matrices, the total carbon dioxide capture threshold can theoretically double, transitioning from the restrictive stoichiometry of 0.5 moles of CO_2 per mole of amine up to an advanced 1:1 capacity.

Mechanism of Amine–Promoted Synergism in Hybrid Matrices

In multi–component hybrid solutions containing both amino acid potassium salts and structurally flexible organic diamines (such as piperazine), a highly complex, cooperative kinetic phenomenon occurs. Piperazine features a cyclic, secondary diamine framework characterised by exceptionally high localised nucleophilicity and reduced steric constraints. During the initial moments of gas introduction, piperazine captures CO_2 at a rate significantly outperforming the bulk amino acid matrix, instantly converting into piperazine–carbamate and protonated piperazine intermediates.

Once formed, these protonated diamine species act as dynamic, long–range proton shuttles within the solution. They rapidly transfer protons away from the newly attacking amino acid nitrogen atoms to the bulk medium, significantly accelerating the activation of the remaining amino acid fractions. This cooperative interaction effectively bypasses the conventional kinetic bottlenecks associated with amino acid viscosity and mass–transfer limitations, resulting in a profound synergetic enhancement of both capture capacity and overall fixation kinetics.

Photochemical Modulation of Quaternized Systems

To achieve an intelligent, low–energy carbon management system, structural modification can be performed by targeting the amines via alkylation to produce quaternized ammonium salt derivatives. These quaternary centres introduce permanent, localised positive charges into the molecular architecture, inducing strong local electrostatic fields. When these configurations are exposed to high–intensity artificial or natural illumination, the electronic density across the neighbouring carbamate and ammonium linkages undergoes a profound transition. The photon energy selectively destabilises the coordinate covalent networks within the ammonium–carbamate complexes, driving the reversible equilibrium toward the formation of loosely bound bicarbonate structures. This light–induced behaviour opens the possibility of replacing conventional, energy–intensive thermal regeneration methods with targeted, photo–controlled desorption processes **[9, 13].**

Experimental Section

Reagents, Substrates, and Matrix Preparation

All chemical reagents, including natural amino acids (L–threonine, L–alanine, glycine, L–valine), organic monoamines (methylamine, 40 wt.% in water; diethylamine, ≥99.5%), organic diamines (ethylenediamine, ≥99.5%; piperazine, anhydrous ≥99%), and potassium hydroxide flakes (≥85%), were purchased from Sigma–Aldrich and Merck and utilized without further chemical purification. Deionised water with a specific conductivity of ≤0.055 $\mu S/cm$ was employed as the universal solvent across all configurations.

Aqueous solution series of pure individual organic amines (MA, DEA, EDA, PZ) were prepared at controlled molar concentrations matching the reference metrics. For the amino acid series, standard stock solution profiles were systematically formulated (e.g., L–threonine matrices were precisely adjusted to 13.4 wt.%). Activation of the zwitterionic frameworks was carried out by adding crystalline potassium hydroxide at precisely controlled molar ratios of 1:1, 1:2, 1:3, and 1:4 relative to the amino acid concentration. Hybrid absorbents were assembled by

blending the activated amino acid potassium salts with equivalent molar portions of the respective organic promoters.

Synthesis and Quaternization of Amine Models

The quaternization reactions targeting the monoamines and diamines were performed to successfully isolate structural quaternary ammonium salt derivatives for specific photochemical evaluations. In a typical procedure, a solution of the corresponding amine (such as methylamine or piperazine) in anhydrous ethanol was treated dropwise with stoichiometric amounts of iodomethane under a nitrogen atmosphere at 0 °C. The reaction mixture was stirred continuously for 12 hours while slowly warming to room temperature. The resulting white crystalline precipitates of quaternized ammonium salts were isolated via filtration, washed thoroughly with chilled diethyl ether, and dried under high vacuum for 24 hours. The purity and structural configuration of the isolated salts were meticulously verified using ^{1}H and ^{13}C NMR spectroscopy prior to gas absorption runs.

CO_2 Absorption and Experimental Setup

The gas–capture protocols were performed in a custom–engineered, jacketed glass bubble column reactor with an internal volume of 50 mL. The operational temperature was held constant at 25.0±0.1 °C utilising a circulating water bath, and the baseline pressure was maintained at 1 atm. Highly pure carbon dioxide gas (≥ 99.999) was introduced into the bottom of the liquid absorbent matrix through a calibrated porous gas sparger (pore size 10–16 μm) at a stable, regulated flow rate of 50 mL/min.

To comprehensively explore the influence of photochemical modulation, experiments were systematically split into two distinct testing environments:

• **Dark Conditions:** The entire reactor configuration, lines, and sampling ports were completely insulated with thick layers of reflective aluminium foil and light–blocking materials to ensure total exclusion of external photons.

• **Illuminated Conditions:** The reactor core was subjected to continuous, multidirectional irradiation from an array of high–intensity artificial cold–white LED lamps delivering a stable photon flux across the visible spectrum.

Samples (0.5 mL) were carefully extracted from the reactor at predefined time intervals using airtight syringes to prevent ambient gas exchange and immediately transferred to chilled NMR tubes for prompt spectroscopic analysis.

Analytical Apparatus and Measurement Protocols

• **pH–Metry:** The continuous shifts in the liquid–phase hydrogen ion activity were recorded using a high–precision Benchtop pH Meter calibrated before each run with standard buffer solutions (pH 4.01, 7.00, and 10.01) at 25 °C.

• **Digital Polarimetry:** Conformational transformations and modifications within the chiral environments of the amino acid backbones were monitored using an *Insmark Digi Polarimeter* equipped with a sodium lamp (– = 589 nm) operating with a precision path length cell.

• **Nuclear Magnetic Resonance Spectroscopy:** High–field quantitative Nuclear Magnetic Resonance (qNMR) measurements were executed on a *Bruker Avance Neo 400* spectrometer operating at a proton resonance frequency of 400.13 MHz and a carbon resonance frequency of 100.61 MHz. All spectra were recorded at

a regulated probe temperature of 298 K.

To guarantee highly accurate, quantifiable integration profiles for all reacting components and intermediates, the 1D ^{13}C spectra were acquired using an inverse–gated proton–decoupling sequence (zipper decoupling) with a precisely evaluated relaxation delay (d1) set to ≥10 s to completely prevent T1–relaxation saturation errors. Deuterated water (D_2O) enclosed in a coaxial inner insert tube was used as the universal external lock and reference standard.

Data Availability Statement: The chemical and spectroscopic data supporting the findings of this study are available from the corresponding author upon reasonable request.

4. RESULTS AND DISCUSSION

Chemophysical Profiles: pH–Metric Dynamics and Chiral Conformation Reconfiguration

The introduction of gaseous carbon dioxide into both the pure organic amine liquids and the newly developed potassium amino acid salt series immediately altered the overall chemophysical parameters of the liquid phases. In all monitored configurations, a rapid, steep decline in baseline pH values was observed during the first 15–20 minutes of gas injection, followed by a steady plateau as the systems reached chemical saturation.

This uniform decline in alkalinity serves as an indirect macro–indicator of the continuous depletion of the highly basic, free nucleophilic amine groups (-NH_2 or -NH-) inside the solution as they coordinate with the incoming CO_2 molecules to yield weakly acidic carbamate or bicarbonate products.

Simultaneously, digital polarimetric screening of the optically active amino acid salt configurations revealed deep shifts in the specific optical rotation angle (α). For instance, within the L–threonine matrix, the original specific rotation values underwent a controlled structural inversion as carbon capture advanced. Because the asymmetric chiral centre of L–threonine is positioned directly adjacent (—–position) to the reactive amino nitrogen site, any major alteration in the localised electronic density, steric configuration, or intermolecular hydrogen bonding network surrounding this nitrogen atom directly alters the optical activity profile of the molecule. The observed polarimetric variations provide direct evidence of the formation of an ordered chiral carbamate network within the solution.

Quantitative qNMR Analysis of Carbonate and Carbamate Speciation

High–resolution quantitative ^{13}C qNMR spectroscopy provided detailed structural data, enabling the direct identification and precise quantification of the chemical species coexisting in the liquid matrix without disturbing the chemical equilibrium. Upon the introduction of CO_2, the spectra of all reactive matrices developed two major groups of carbon resonances positioned downfield from the solvent background, corresponding to newly isolated chemical environments:

1. **Organic Carbamate Species (-$NHCOO^-$):** These carbons generated distinct, well–resolved resonance peaks clustered within the chemical shift window of δ = 161.5 – 163.0 ppm. The precise position of these signals was highly dependent on the identity of the parent amine, reflecting differences in structural shieldings.
2. **Inorganic Carbon Fractions (HCO_3^-/CO_3^{2-}):** These species generated

a combined singular resonance signal oscillating between α = 160.0 – 160.8 ppm. Due to rapid proton exchange kinetics occurring between the bicarbonate and carbonate ions in water, these two states merge into a single time–averaged peak, whose exact chemical shift correlates with the final equilibrium pH of the matrix.

Through integration of these peaks against reference standards using a long relaxation delay ($d1$ = 10 s), the precise molar allocation of the captured carbon was mapped over time. Looking closely at the activated L–threonine/KOH matrix series, the initial 1:1 molar configuration favoured the accumulation of stable threonine–carbamate complexes. However, when the inorganic base fraction was raised to 1:2 and 1:4, the high concentration of hydroxyl ions (OH^-) maintained a strongly alkaline environment throughout the run. This alkalinity promotes the hydrolytic breakdown of the primary carbamates, driving the carbon partition toward inorganic bicarbonates. This shift releases free amino acid sites to capture additional gas, leading to a substantial enhancement in the total CO_2 absorption capacity.

Structural Relationships and Kinetic Profiles of Screened Pure Amines

The baseline evaluation of individual pure organic amines revealed that their intrinsic carbon capture performance is strictly governed by structural characteristics, spatial parameters, and basicity. Methylamine (MA), a primary monoamine, demonstrated rapid initial capture rates, but its ultimate capacity was mathematically bound by the 2:1 stoichiometric limit due to the high stability of its resulting acyclic carbamate salt. Diethylamine (DEA), a secondary monoamine, exhibited low capture kinetics and an extended saturation timeline. This depressed performance stems from the steric hindrance exerted by the two flexible ethyl arms flanking the nitrogen atom, which limits the access of CO_2 to the nucleophilic centre.

In contrast, ethylenediamine (EDA) and piperazine (PZ) demonstrated vastly superior capture profiles. As a linear primary diamine, EDA provides two unhindered reactive sites per molecule, allowing for a dense network of carbamate linkages. Piperazine, a cyclic secondary diamine, delivered the highest initial capture kinetics. The rigid, pre–organised heterocyclic ring of piperazine minimises steric hindrance while maintaining high local electron density on the secondary nitrogen sites, leading to rapid coordination with electrophilic carbon centres.

Cooperative Synergism in Hybrid Multi–Component Systems

When these individual organic promoters were integrated with natural amino acid potassium salts to form hybrid, multi–component absorption matrices, a powerful cooperative synergy was observed. The highest overall carbon dioxide capture efficiencies—consistently exceeding **90%** of the total theoretical threshold—were achieved in the hybrid matrices pairing amino acid salts with either piperazine (PZ) or ethylenediamine (EDA).

Dynamic tracking via qNMR highlighted the steps of this cooperative mechanism:

• **Phase I (Kinetic Capture):** Due to its high nucleophilicity and lower mass–transfer resistance, the unhindered cyclic diamine (PZ) reacts preferentially with the incoming gas, forming piperazine–monocarbamate and protonated piperazine ions.

Phase II (Proton Transfer Cascade): The newly formed protonated piperazine

species act as highly efficient proton–acceptor shuttles. They abstract protons from the zwitterionic or weakly unprotonated amino acid fractions, rapidly generating highly reactive, free nucleophilic amino acid sites.

• **Phase III (Amino Acid Fixation):** The newly activated amino acid sites capture CO_2, leading to a highly stable mixture of mixed carbamate networks. This cooperative catalytic pathway bypasses the typical viscosity–related mass–transfer limitations of pure amino acid solutions, achieving high capture capacities along with fast reaction rates.

Photochemical Modulation and Reversible Desorption Dynamics

The evaluation of gas capture under different light profiles revealed a unique phenomenon within the matrices containing quaternized mono– and diamines. When these systems were tested in the dark, they followed standard exothermic carbon–capture pathways, accumulating stable ammonium carbamate salts with minimal baseline degradation.

However, when identical quaternized matrices were exposed to high–intensity artificial illumination, a distinct shift in the equilibrium profiles was observed. The permanent positive charges on the quaternized nitrogen centres induce strong localised electrostatic fields that polarise the adjacent carbamate linkages. Under intense visible–light illumination, these structures absorb photon energy, destabilising the coordinate–covalent carbon–nitrogen bonds within the carbamate fractions. This photo–excitation drives the chemical equilibrium away from organic carbamates toward loosely bound inorganic bicarbonates.

Because bicarbonate species require significantly less thermal energy to undergo complete decomposition than highly stable organic carbonates, this light–induced restructuring provides an elegant strategy for carbon management. It demonstrates a pathway in which the energy–intensive thermal stripping processes traditionally used in carbon capture can be supplemented or replaced with targeted, photo–controlled desorption methods.

Conclusions

1. Comprehensive, environmentally benign carbon capture matrices were successfully engineered by combining various natural amino acid potassium salts, independent organic mono– and diamines, and structurally modified quaternized ammonium derivatives.
2. High–field quantitative ^{13}C qNMR spectroscopy, operating with a specialised inverse–gated decoupling sequence ($d1 \geq 10$ s), enabled the direct structural identification and precise quantitative mapping of organic carbamate and inorganic bicarbonate/carbonate species coexisting within the liquid absorbent phase.
3. Structural screening demonstrated that steric hindrance within secondary monoamines like diethylamine significantly restricts capture kinetics, whereas the rigid, pre–organised heterocyclic structure of piperazine maximises capture rates.
4. A powerful cooperative synergism was discovered in hybrid matrices combining amino acid salts with piperazine or ethylenediamine. This interaction delivers carbon dioxide capture efficiencies exceeding 90% by utilising organic diamines as high–speed proton–transfer shuttles that

accelerate activation of amino acid sites.

5. Photochemical evaluation demonstrated that high–intensity illumination destabilises carbamate linkages within quaternized amine configurations, shifting the equilibrium toward low–energy bicarbonate forms. This behaviour offers a promising foundation for the development of energy–efficient, photo–controlled carbon desorption systems. Furthermore, using natural chiral amino acid frameworks as carbon sinks yields stable carbamate matrices that can serve as non–toxic, sustainable C1 building blocks for the synthesis of high–value pharmaceutical targets, such as the oxazolidinone antibiotics Linezolid and Eperezolid.

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References

1. World Meteorological Organisation (2023). Greenhouse gases. [online] World Meteorological Organisation. Available at: https://wmo.int/topics/greenhouse–gases
2. World Meteorological Organisation. (2026). State of the Global Climate 2025 report. [online] Available at: https://wmo.int/media/announcement/state–of–global–climate–2025–report
3. World Meteorological Organisation. (2026). WMO confirms 2025 was one of the warmest years on record. [online] Available at: https://wmo.int/media/news/wmo–confirms–2025–was–one–of–warmest–years–record
4. Han Z., Yang R., Li R., Sun D., Zhang, B. and Kong, L. Integrated CO_2 Capture and Conversion Induced by Amines for Effective Electrocatalytic N–Methylation. Angewandte Chemie International Edition, 2026. doi:https://doi.org/10.1002/anie.2285211
5. Lim H., Kim K., Kim J., Park H.S., Kang J.H., Park J. and Song H. Experimental study of hollow fibre membrane contactor process using aqueous amino acid salt–based absorbents for efficient CO2 capture, Journal of Environmental Chemical Engineering, 12(5), 2024, p.113338. doi:https://doi.org/10.1016/j.jece.2024.113338
6. Lim H., Kim K., Park H.S., Kang J.H., Park J. and Song H. Continuous CO2 capture using a hollow fibre membrane contactor with stripper regeneration: Bench–scale validation with amino acid salt–piperazine absorbents. Carbon Capture Science & Technology, [online] 18, 2026, p. 100573. doi:https://doi.org/10.1016/j.ccst.2026.100573
7. Nisolle M., Pétaud G., Lécolier E., Lebaz N., Gagnière E., Agusti G. and Tayakout–Fayolle M. Precipitating Absorbents for Postcombustion CO_2 Capture: A Comprehensive Review. Industrial & Engineering Chemistry Research, 65(17), 2026, pp. 8594–8624. doi:https://doi.org/10.1021/acs.iecr.5c05272
8. Ghiasi M. and Hanane Sadat Eghtedari. Green CO2–capture cluster model using bioengineering of carbonic anhydrase enzyme: QM and QM/QM– approach. *Scientific Reports*, [online] 16(1), 2025, pp. 2806–2806. doi:https://doi.org/10.1038/s41598–025–32638–y.
9. Murakami R., Shiota K., Uchida A. and Inagaki F. Light–swing CO_2 capture: photoirradiation–based chemical CO_2 release based on photoisomerisation of azobenzene–amine/guanidine derivatives. Green Chemistry, 26(12), 2024, pp.7406–7413. doi:https://doi.org/10.1039/d4gc00736k.
10. Ni H., Zhao K., Liu S., Dai X., Liu C., Gao X., Zhang J., Liu H., Huang K.–W., Cui X. and Shi F. In situ capture and value–added utilisation of CO2 from flue gas using an ionic liquid polymer–supported Zn catalyst. Green Chemistry, [online] 27(29), 2025, pp. 8867–8874. doi:https://doi.org/10.1039/d5gc02324f.
11. Rana A. and Andino J.M. A Review of Materials for Carbon Dioxide Capture. Catalysts, [online] 15(3), 2025, pp. 273–273. doi:https://doi.org/10.3390/catal15030273.
12. Foti C., Piperno A., Scala A. and Giuffrè O. Oxazolidinone Antibiotics: Chemical, Biological and Analytical Aspects. Molecules, [online] 26(14), 2021, p. 4280. doi:https://doi.org/10.3390/molecules26144280.

13. Linthwaite V.L., Janus J.M., Brown A.P., Wong–Pascua D., O'Donoghue A.C., Porter A., Treumann A., Hodgson D.R.W. and Cann M.J. The identification of carbon dioxide–mediated protein post–translational modifications. *Nature Communications*, [online] 9(1), 2018, p. 3092. doi:https://doi.org/10.1038/s41467–018–05475–z.

14. Niemi T. and Repo T. Antibiotics from Carbon Dioxide: Sustainable Pathways to Pharmaceutically Relevant Cyclic Carbamates. European Journal of Organic Chemistry, 2019(6), pp.1180–1188. doi:https://doi.org/10.1002/ejoc.201801598.

15. Sarkar A., Bhattacharyya S., Dey S.K., Karmakar S. and Mukherjee A. Structure and properties of metal complexes of a pyridine–based oxazolidinone synthesised by atmospheric CO_2fixation. New J. Chem., 38(2), 2014, pp.817–826. doi:https://doi.org/10.1039/c3nj00990d.

16. Zappia G., Menéndez P., Giuliano Delle Monache, Misiti D., Nevola L. and Botta B. The Contribution of Oxazolidinone Frame to The Biological Activity of Pharmaceutical Drugs and Natural Products. 7(4), 2007, pp.389–409. doi:https://doi.org/10.2174/138955707780363783.

17. Zhang Q. and Jin X. Recent Advances in the Fixation of CO_2 to Form N–Containing Heterocyclic Compounds. Chemistry – A European Journal, 31(33), 2025. doi:https://doi.org/10.1002/chem.202500933.

18. Zhang Z., Ye J.–H., Wu D., Zhou Y. and Yu D.–G. Synthesis of Oxazolidin–2–ones from Unsaturated Amines with CO_2 by Using Homogeneous Catalysis. 13(17), 2018, pp. 2292–2306. doi:https://doi.org/10.1002/asia.201800672.