Support Information (SI) Appendix

Rapid Screening of CO₂ Capture Fluids

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Section 1: Automated image processing procedure

To facilitate the high-throughput analysis of the absorption and desorption characteristics of captured fluids in microchannels, a Python script is developed to process the experiment video files autonomously. The script extracts individual frames from the video and segments them into 11 distinct rows, each representing a microfluidic channel (see Fig.S1). The automated image processing focuses on detecting the gas-liquid interface within each channel segment, utilizing the Sobel edge detection method to identify sharp intensity changes in the image, corresponding to the interface between gas and liquid phases. After detecting these interfaces, the script outputs them for user validation to ensure the accuracy of the detection.



Fig.S1 Automated image analysis and performance parameters calculation

The script then tracks the position of these interfaces in each channel over time, converting the pixel displacement into physical distances based on the known microfluidic channel width. A key feature of the script is its capability to account only for unidirectional interface movement, thereby minimizing false detections from reflections or bubbles that might be misconstrued as interface movement. The data detailing the interface displacement across each channel is compiled into a data

frame, which aids in the analysis by calculating interface displacement/velocity and incorporating the gas state equation. This code allows for high-throughput analysis of microfluidic experiments, enhancing the screening efficiency of CO_2 capture fluids.

The code of the image processing can be found at the following link:

https://colab.research.google.com/drive/12wxMmjb1ZWu0t8VFwMjMJClnOABELWc7#scrollTo= Y3Hwag3mBeHy

Section 2: Information of the amines used in the experiment

Classification	Amines	Molar mass (g/mol)	CAS
Primary amines	Monoethanolamine (MEA)	61.08	141-43-5
Primary amines	Pentylamine (PA)	87.16	110-58-7
Secondary amines	Diethylamine (DA)	73.14	109-89-7
Secondary amines	Diethanolamine (DEA)	105.14	111-42-2
Tertiary amines	N-Methyldiethanolamine (MDEA)	119.16	105-59-9
Tertiary amines	Triethanolamine (TEA)	149.19	102-71-6

Table S1 Information of the amines used in the experiment

Section 3: Temperature control in CO₂ desorption test

In CO₂ desorption tests, the resistive heating plate is preheated to ~95°C and secured on a Z-axis slide. When the gas-liquid interface reaches the appropriate position, the resistive heating plate is elevated to make contact with the microchip, heating the target area. The microchip can be raised to 70°C within 5-6 seconds and further heated to 80°C ~16 seconds later, as illustrated in Fig.S2(a). Additionally, we introduce a thermally conductive pad between the microchip and heating plate to ensure a stable and uniform temperature distribution in the target region, as depicted in Fig.S2 (b).



Fig.S2 Temperature control in CO₂ desorption tests: (a) Temperature ramping curve: microchip can be heated to \sim 70°C within 6s, and further elevated to 80°C around 16s; (b) Temperature distribution on the chip.

Section 4: Simulation of the diffusion process of the reaction products

Compared to the dynamic gas-liquid slug flow, the quasi-static design adopted in this study exhibits relatively lower mass transfer efficiency. The mass transfer of reaction products and amine molecules within the microchannel is primarily influenced by molecular diffusion. Typically, the amine solution post-reaction contains various complex substances, including dissolved CO₂, amine molecules, carbamate, carbonate, bicarbonate, or other ions. To roughly evaluate the diffusion process of reaction products at the experimental time scale, we simulated the diffusion process of individual substances and calculate the concentration distributions in the microchannel. The diffusion process is characterized by Fick's law:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \nabla c_i) = 0 \tag{1}$$

where *D* represents the diffusion coefficient, m²/s; *c* is the concentration mol/m³. It is worth noting that diffusion coefficients of various substances in aqueous solutions differ, and their interactions become more intricate in the presence of multiple substances. The diffusion coefficients of amines in aqueous solutions range from 10^{-9} m²/s -10^{-10} m²/s [1]. For simplicity, we have selected the upper limit of 10^{-9} as the diffusion coefficient for the reaction products. Additionally, we assume that the reaction between amine molecules and CO₂ occurs instantaneously at the interface, implying that the concentration of reaction products at the interface is equal to the concentration of amines, i.e., 3 mol/L.

The non-permeable boundary condition is imposed on the microchannel wall:

$$(-D\nabla c) \cdot \mathbf{n} = 0 \tag{2}$$

where **n** represents the unit normal to the solid surface. The mathematical model is solved using COMSOL Multiphysics software based on the finite element method. Fig.S3 displays the concentration distribution of reaction products in the microchannel at 50s, 100s, and 150s, with the origin of the abscissa set at the gas-liquid interface. Notably, the diffusion distance is consistently below 1mm within the experimental timeframe (<100s). This observation implies that chemical reactions during CO₂ absorption and desorption tests predominantly take place in close proximity to the gas-liquid interface. Although the amine solution in the test channel is interconnected with the main channel and upstream/downstream pipelines during the tests, the relatively short test duration results in the formation of a quasi-closed system. In the CO₂ desorption rate tests, the decomposition of carbamate (bicarbonate or carbonate) generating CO₂ primarily occurs near the phase interface, and the released CO₂ predominantly enters the CO₂ gas slug on the left side.



Fig.S3 Concentration distribution of reaction products of CO_2 and amine solution within the microchannel (horizontal axis originating at the gas-liquid interface). The inset figure illustrates the concentration distribution at 100s.

References:

[1] Snijder E D, te Riele M J M, Versteeg G F, et al. Diffusion coefficients of several aqueous alkanolamine solutions[J]. Journal of Chemical and Engineering data, 1993, 38(3): 475-480.

Section 5: The influence of vapor pressure on gas slug expansion during CO₂ desorption

In desorption tests, the capture fluids are 3 mol/L aqueous amine solutions, with amine molar fractions below 0.1. According to Raoult's law, the vapor pressure of the capture solution is the sum of the vapor pressures of its components multiplied by their respective molar fractions. Consequently, it is reasonable to assume that the vapor pressure of the capture fluid is primarily governed by water. For various capture fluids, the influence of vapor pressure on gas slug expansion during desorption is largely similar, rendering the effect of vapor pressure negligible. However, this assumption does not apply to DA. Antoine equation estimates the vapor pressure of DA at 80°C to be approximately 200 KPa [1]. At this temperature, the partial pressure of DA (with a mole fraction of 0.073) is approximately 16 KPa, while water's partial pressure (with a mole fraction of 0.927) is approximately 44 KPa [2]. In this scenario, the vapor pressure of the amine will significantly affect the movement of the liquid slug.

Table S2 The	proportion	of amine's par	tial pressure	to the total vanc	or pressure of the	solution at 80°C
Table 52 The	proportion	of annue s par	that pressure	to the total vape	f pressure of the	solution at 60 C

Solution	Amine's partial	Amine's partial Water's partial	
	pressure	pressure	Froportion
DA	16.0 KPa	43.9 KPa	26.7%
PA	3.4 KPa	43.8 KPa	7.2%
MEA	0.14 KPa	44.4 KPa	0.3%
MDEA	<0.1 Kpa	43.8 KPa	<0.3%
DEA	<0.1 Kpa	44.0 KPa	<0.3%
TEA	<0.1 Kpa	43.5KPa	<0.3%

References:

[1] Yin X, Du C, Du Z, et al. Measurement, modelling and molecular dynamics analysis for isobaric vapour-liquid equilibria of binary or ternary system (diethylamine, ethyl acetate, triethylamine). The Journal of Chemical Thermodynamics, 2020, 151: 106251.

[2] Wexler A. Vapor pressure formulation for water in range 0 to 100 °C. A revision. Journal of research of the National Bureau of Standards. Section A, Physics and chemistry, 1976, 80(5-6): 775.

Section 6: CO₂ absorption capacity of different amines in literatures

Table S3 Comparison of CO₂ absorption capacity measured in our study with literature data

Amines	CO ₂ partial	Concentration	Literature	Measured	Difference (%)
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	pressure		absorption capacity	absorption capacity	
DEA	2.65 bar	1 mol/L	1.027 [1]	1.086	5.44%
MDEA	2.65 bar	1 mol/L	1.055 [2]	1.101	4.15%
MEA	2.65 bar	1 mol/L	0.985 [3]	1.020	3.44%
MEA	1.5 bar	1 mol/L	0.907 [3]	0.955	5.05%
MEA	1 bar	1 mol/L	0.873 [3]	0.891	2.07%
MEA	0.5 bar	1 mol/L	0.788 [3]	0.819	3.79%

*Some absorption capacity data in the literature are obtained through linear interpolation

References:

[1] Lee J I, Otto F D, Mather A E. Solubility of carbon dioxide in aqueous diethanolamine solutions at high pressures. Journal of Chemical and Engineering Data, 1972, 17(4): 465-468.

[2] Bhairi A M. Experimental equilibrium between acid gases and ethanolamine solutions. Oklahoma State University, 1984.

[3] Lee J I, Otto F D, Mather A E. Equilibrium between carbon dioxide and aqueous monoethanolamine solutions. Journal of Applied Chemistry and Biotechnology, 1976, 26(1): 541-549.

Section 7: Vapor pressure and boiling point of different amines

Table S4 Vapor pressure and boiling point data of different capture fluids

Amines	Vanar Braggura (25°C)	Boiling point	Measured evaporation rate	
	vapor riessure (25 C)	(760 mm Hg)	(mm/min)	
DA	237 mm Hg	~55 °C	2.514 (35°C)	
PA	91.0 mm Hg	~104 °C	0.400 (35°C)	
MEA	0.404 mm Hg	~170 °C	0.071 (35°C)	
MDEA	2×10 ⁻⁴ mm Hg	~245 °C	0.027 (80°C)	
DEA	2.8×10 ⁻⁴ mm Hg	~269°C	0.022 (80°C)	
TEA	3.59×10 ⁻⁶ mm Hg	~335 °C	0.008 (80°C)	

*The data is taken from PubChem (National Library of Medicine, USA)

Section 8: DFT simulation support

In this work, six amine species, namely, 2-pentylamine (PA), N-methylethanolamine (MEA), diethylamine (DA), diethanolamine (DEA), N-methyldiethanolamine (MDEA), and triethanolamine (TEA) are investigated. Their structures are shown in Fig.S4. In an amine solution, CO₂ can be

absorbed in two ways: one is direct binding with amine and forming carbamates [1, 2], and the other is reacting with OH- and forming bicarbonate. For primary and secondary amines, the direct binding mechanism is kinetically favored [3], while the basic adsorption may dominate for tertiary amines due to steric hindrance. Thus, in the theoretical investigation, we focus mainly on the direct binding process. As is demonstrated in Fig.S5, the process involves two crucial states of the amine-CO₂ system: the adsorption state in which the CO₂ molecule is adsorbed near the amine nitrogen, and the zwitterionic state in which a chemical bond is formed between the amine N atom and the C atom in CO₂. The two intermediates are connected by a transition state featuring the formation of the C-N bond between the CO₂ molecule and the amine group.

All the calculations discussed herein are conducted with the ORCA 5.0.2 software package [4]. The initial guess of the structures of the three states is generated from chemical intuition. Geometry optimization and frequency calculation are performed under ωB97X-D3/aug-cc-pvTz level of theory with the polarizable continuum model for water (CPCM (water)) to account for the solvent effect. Transition states are optimized via the nudged elastic band (NEB) method. The optimization convergence criteria for individual structures are adjusted to ensure the expected imaginary modes are obtained (i.e. no imaginary mode for minima and one imaginary mode showing the formation of C-N bond for transition states). The Gibbs free energy of the systems is simulated at 308.15K. Single point energy calculations under DLPNO-CCSD(T)/aug-cc-pvtz/CPCM(water) level are performed on the optimized minima and transition states to correct the DFT electronic energy.



diethanolamine (DEA)

Fig.S4 Structure and abbreviation of the amines



Fig.S5 The CO₂-amine direct binding mechanism

	Relative Gibbs Free Energy (kJ/mol)						
	ωB97X-D3			DLPNO-CCSD(T)			
Amine	ADS	TS	ZW	ADS	TS	ZW	
MEA	0.00	21.18	12.00	0.00	24.26	15.84	
DA	0.00	19.89	4.70	0.00	19.96	2.89	
DEA	0.00	25.02	19.51	0.00	24.97	17.74	
MDEA	0.00	25.19	22.32	0.00	20.71	14.34	
PA	0.00	20.69	8.81	0.00	24.01	12.78	
TEA	0.00	45.69	44.54	0.00	37.07	33.20	

Table S5 Free Energy Profile of the Direct Binding Process

References:

[1] Lv B, Guo B, Zhou Z, et al. Mechanisms of CO_2 capture into monoethanolamine solution with different CO_2 loading during the absorption/desorption processes. Environmental science & technology, 2015, 49(17): 10728-10735.

[2] Hwang G S, Stowe H M, Paek E, et al. Reaction mechanisms of aqueous monoethanolamine with carbon dioxide: a combined quantum chemical and molecular dynamics study. Physical Chemistry Chemical Physics, 2015, 17(2): 831-839.

[3] Kortunov P V, Siskin M, Baugh L S, et al. In situ nuclear magnetic resonance mechanistic studies of carbon dioxide reactions with liquid amines in aqueous systems: New insights on carbon capture reaction pathways. Energy & Fuels, 2015, 29(9): 5919-5939.

[4] Neese F. Software update: the ORCA program system, version 4.0. Wiley Interdisciplinary Reviews: Computational Molecular Science, 2018, 8(1): e1327.