

Alkoxy-Functionalized Amines as Single-Component Water-Lean CO₂ Absorbents with High Efficiency: The Benefit of Stabilized Carbamic Acid

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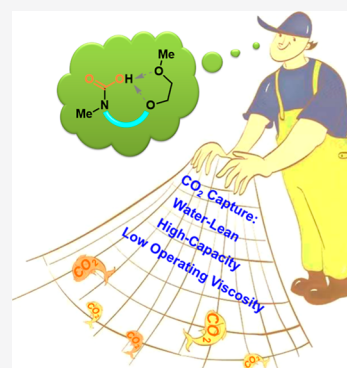


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ABSTRACT: Aqueous alkanolamine-based processes currently represent the most mature and widely employed CO₂ capture technology. However, extensive energy input and severe equipment corrosion constitute their major and inherent drawbacks due to the involvement of vast amounts of water as the diluent. Water-lean absorbents are proposed to deliver potential benefits, such as higher capacity and enhanced energy efficiency, by abandoning the aqueous solvent or replacing it with organic counterparts. Great efforts have been devoted to the development of CO₂ capture protocols under nonaqueous circumstance, but their industrial deployment is still challenged by the exponentially increasing viscosity during operation. In this work, a series of alkoxy-functionalized methylamines have been devised as single-component postcombustion CO₂ absorbents under water-lean condition. These nonaqueous amines are capable of reversibly capturing CO₂ with low viscosities (48–114 cP at 25 °C and 27–63 cP at 40 °C) at their maximal gravimetric capacities (15–21 wt % at 25 °C and 14–21 wt % at 40 °C). Comprehensive mechanistic studies by means of *in situ* Fourier transform infrared spectroscopy, density functional theory calculations, and control experiments revealed that the stabilization of sequestered CO₂ via intramolecular hydrogen bonding between *in situ* formed carbamic acid and the flexible alkoxy side chain of the designed amines would play the key role in enhancing both the capacity and flowability. Meanwhile, thermal desorption of the captured CO₂ could easily be carried out at a feasible temperature (75 °C) under ambient pressure, and the CO₂-saturated absorbents have remained intact at 80 °C for 2 days within a closed system. Furthermore, these novel amines would exhibit considerable physisorption by operating at high-pressure conditions (20 and 30 bar), thanks to the inherent CO₂-philicity of the alkoxy functionality. Hence, the integration of enhanced capacity, reduced operating viscosity, and mild regeneration makes such alkoxy-functionalized methylamine-type absorbent a compelling candidate for practical application.



1. INTRODUCTION

Excessive CO₂ emission from industrial related postcombustion streams currently contributes the majority of greenhouse gases that have been widely considered as the key factor for climate issues around the globe.^{1–3} The ever-increasing accumulation of anthropogenic CO₂ within the human environment triggers the alarm for its containment across the world; hence, the strategy of CO₂ capture, utilization, and storage (CCUS) is proposed to mitigate this serious environmental issue and, at the same time, provide value-added chemicals from such a nontoxic, easily available, and renewable resource of C1 building block.^{4,5} As a result, great efforts have been devoted to the establishment of efficient CO₂ capture technologies, which are fundamental for CCUS.⁶ Among them, aqueous alkanolamine blends-related processes represent the dominant protocols that have been applied at the industrial level in several scenarios, such as flue gas treatment, hydrogen production, and nature gas upgrading.^{7–9} Especially, aqueous monoethanolamine (MEA) at 30 wt % is considered as the industrial standard for CO₂ chemisorption because of its cheap price and prominent reactivity.^{10,11} In general, solvent

regeneration occupies approximately 70% of the total energy input during aqueous CO₂ scrubbing.¹² Hence, the large specific heat capacity and enthalpy of vaporization of water render it as the most vulnerable factor, according to the energy cost estimation.^{13–15} Not to mention that the high desorption heat of the sequestered CO₂ in aqueous environment requests a high temperature (usually around 120 °C) for stripping.^{16,17} Other drawbacks caused by the involvement of mass water as the diluent are low gravimetric capacity, serious equipment corrosion, and solvent evaporation during thermal regeneration.^{14,18} Consequently, the development of alternative protocols for energy-efficient and cost-effective CO₂ chemisorption under nonaqueous condition has become one of the main challenges in this area.

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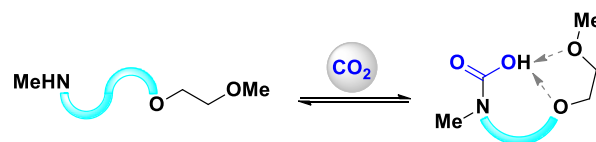
Water-lean absorbents have emerged in response to the calling for substantial improvement of the aqueous approaches, which could render a viable method to circumvent the high parasitic energy loading because of their relatively lower heat of absorption as well as reduced reversal temperature.^{19,20} Given the absence of the mass water diluent, equipment corrosion would also be relieved, along with enhancement of gravimetric capacity. To date, a variety of liquid absorbents that could operate under the nonaqueous condition have been devised and applied to CO₂ capture in the bench scale, examples of which are ionic liquids,^{21–24} deep eutectic solvents,^{25–28} siloxylated- and silylamines,^{29–32} alkanolguanidines,^{33–36} single-component amines,^{37–39} and their organic solutions.^{40–44} These absorbents would sustain in the liquid state before and after incorporation of CO₂ and could be thermally regenerated with fast kinetics at mild temperatures rather than at temperatures of 120 °C or above in the case of aqueous alkanolamines. Nevertheless, the industrial application of water-lean systems still has an intrinsic drawback to overcome, that is, the exponential increase of operating viscosity along with CO₂ uptake, which is usually several orders of magnitude larger than that of 30 wt % MEA solution and results in both inefficient internal mass transfer (deterioration of absorption and regeneration) and poor transportation in pipeline networks. Although such a limit could be eased by the introduction of low-viscosity organic diluents, the expense of gravimetric capacity is inevitable, and the solvent degradation issue will also be posed. Therefore, high-efficiency and industrializable approaches that not only avoid the addition of any diluents but also show persisting high flowability after CO₂ capture remain in urgent demand.

In our continuous efforts to develop new concepts as well as efficient strategies for CO₂ capture and further transformation,^{45–47} we envision that the viscosity of several traditional aliphatic amines at the CO₂-saturated state could be significantly reduced though careful alkoxy functionalization.^{48,49} The alkoxy arm embedded within the amine structure could create more free volume through its high conformational flexibility, thereby greatly enhance the flowability, and would ultimately intensify the interior mass transfer behavior to increase CO₂ capacity and thermoreversibility.^{50,51} Ether-functionalized ionic liquids has also been separately studied for CO₂/SO₂ capture through chemi- and/or physisorption.^{52–56} Meanwhile, carbamic acid is considered to be a feasible form of sequestered CO₂ in the amine scrubbing process due to the full utilization of the nitrogen moiety (1:1 stoichiometry between CO₂ and nitrogen) and its relatively easy reversal compared with that of ammonium carbamate.^{30,40,57} Furthermore, intramolecular hydrogen bonding is preferable if carbamic acid as an uncharged species dominates within the chemisorption system after CO₂ uptake, thus leading to lower operating viscosity than in the intermolecular hydrogen bonding scenarios.³⁸ Notably, the alkoxy chain has been proved by recent reports to be a viable hydrogen bond acceptor that could bind the acidic proton to form multiple complexation.^{58,59} We then propose a simple structural modification method for aliphatic primary amines that involves fixation of an appropriate alkoxy substituent to such a cheap and versatile industrial commodity, aiming to acquire reduced operating viscosity that enables smooth processing at the water-lean status under industrially relevant conditions and, in the meantime, increase capture capacity via

stabilization of the *in situ* formed carbamic acid through intramolecular hydrogen bonding.

Herein, we would like to disclose a series of alkoxy-functionalized methylamines that are not only economical with low-cost precursors as well as convenient and scalable synthesis but also able to reversibly capture CO₂ with enhanced capacity and mild operating viscosity in a single-component manner (Scheme 1). Although both aliphatic amines and ionic liquids

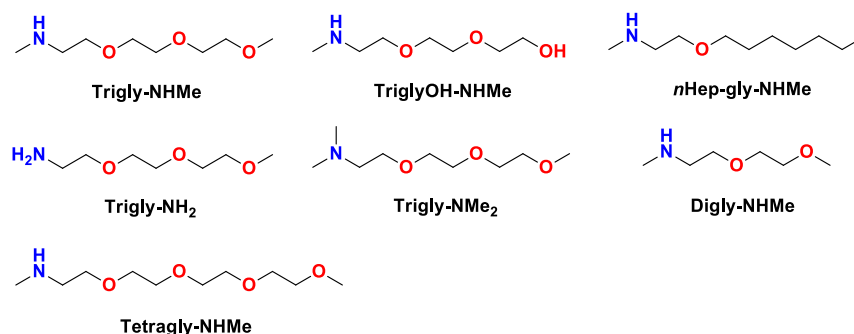
Scheme 1. Symbolic Structure of Alkoxy-Functionalized Methylamines and Their Incorporation with CO₂



modified with an ether attachment have been reported by us^{48,49} and others^{52–56} to achieve better flowability after CO₂ incorporation, this work constitute the first example of performance enhancement via the formation of carbamic acid species promoted by the introduction of an appropriate alkoxy functionality under the water-lean condition. The stabilization mechanism for *in situ* formed carbamic acid along with capture release thermodynamics of these newly devised absorbents were systematically interpreted using density functional theory (DFT) calculations, *in situ* Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC) measurements, vapor–liquid equilibrium (VLE) measurements, and designed control experiments, and their potential as competent candidates for industrial application was fully unveiled.

2. EXPERIMENTAL SECTION

2.1. Materials and Equipment. A quadrupole time-of-flight mass spectrometer with a Z-spray ionization source (Micromass, Wythenshawe, UK) and a Bruker AvanceII 400 M type spectrometer were employed to record the high-resolution mass spectra and nuclear magnetic resonance (NMR) spectra (¹H NMR: 400 MHz and ¹³C NMR: 100 MHz), respectively. A JF-5 type apparatus manufactured by Daqing Ri Shang Instrument Manufacturing Co., Ltd was used to measure the water content. A NTV-CAP1 viscometer provided by Shanghai Ni Run Intelligent Technology Co., Ltd was applied to determine the dynamic viscosities (as the average of three independent tests). The *in situ* FTIR spectrum collected at atmospheric pressure was recorded on a METTLER TOLEDO ReactIR 15 apparatus. For the *in situ* FTIR experiment performed at high pressure, a combination of METTLER TOLEDO ReactIR 45 m and a 100 mL stainless-steel Parr autoclave reactor modified with a ZnSeW AR window was employed. High-purity CO₂ (99.999%) and CO₂/N₂ mixed gas (15 vol % CO₂) were used as received without further purification. Related amines, alkoxyethyl alcohols, polyethylene glycol dimethyl ether (average molecular weight 250), pyridine, and thionyl chloride were obtained commercially from Energy Chemical. The formula of aMDEA [activated methyl diethanolamine (MDEA)] was made up of piperazine (5 wt %), MDEA (45 wt %), and H₂O (50 wt %). Alkoxyethyl chlorides were synthesized from corresponding alkoxyethyl alcohols on the basis of the reported method.⁶⁰ All

Table 1. Effect of Functionalization on Capacity and CO₂-Saturated Viscosity^a

entry	alkoxy-functionalized amine	CO ₂ uptake ^b		viscosity ^c (cP)
		(mol %)	(wt %)	
1	Trigly-NHMe	72	18	91
2	TriglyOH-NHMe	59	16	832
3	nHep-gly-NHMe	61	15	56
4	Trigly-NH ₂	68	18	503
5	Trigly-NMe ₂	5	1	7
6	Digly-NHMe	64	21	114
7	Tetragly-NHMe	74	15	48
8	30 wt % MEA	53	12	11

^aCO₂ absorption and viscosity measurement were performed at 25 °C. ^bEquilibrium CO₂ loading. ^cViscosity at the equilibrium CO₂ loading.

the other solvents and reagents were purchased as commodities and used directly without further purification.

2.2. Synthetic Procedure. Selected alkoxyethyl chloride (240 mmol) and the corresponding amine aqueous solution (30 wt %, 240 mL) were charged to a 300 mL pressure vessel equipped with a safety valve, which was heated at 60 °C for 12 h. After cooling to room temperature, the reaction mixture was transferred to a pre-cooled open flask, and NaOH (500 mmol) was added slowly with continuous stirring in 30 min (be careful for the evolution of gaseous amines). Subsequently, the basified resultant was poured into a separating funnel and extracted by CHCl₃ (100 mL) three times. Chloroform extracts were combined, dried over anhydrous sodium sulfate, and concentrated on a rotary evaporator. Target absorbents were obtained in nearly quantitative yields via fraction distillation under reduced pressure (water pump).

2.3. CO₂ Capture and Release. For CO₂ capture under atmospheric pressure, a 20 mL Schlenk tube was used to perform chemisorption. Typically, 3 mL of the indicated absorbent was charged into the tube at 25 or 40 °C. After gas replacement using CO₂ within the reactor, the terminal needle of a CO₂ transfer line was inserted into the bottom of the absorbent. The capture process was performed with a flow rate of 0.1 L CO₂/min, and the corresponding capacity was determined via the gravimetric method using an analytical balance (± 0.0001 g) every 5 min. Once the absorption equilibrium (usually no more than 30 min) was reached, the resulting CO₂-saturated absorbent would be transferred to an open flask (20 mL), in which CO₂ desorption was carried out at indicated stripping temperature under 300 r/min magnetic stirring within 60 min. The amount of released CO₂ was determined using gravimetry.

For CO₂ capture under high pressure, a 15 mL oven-dried autoclave equipped with a CO₂ inlet and a pressure gauge was used to perform chemi- and physisorption. Typically, 3 mL of the indicated absorbent was charged into the autoclave at 25 °C. After gas replacement, CO₂ was timely injected at 35 °C to

maintain a certain target pressure under continuous magnetic stirring. Finally, the amount of captured CO₂ was determined via the gravimetric method using an analytical balance (± 0.0001 g) with 90 min of saturation.

2.4. In Situ FTIR Analysis. For high-pressure *in situ* FTIR analysis, the combination of a METTLER TOLEDO ReactIR 45 m apparatus (fixed with a 30 bounce DiCOMP *in situ* probe and an MCT detector) and a Parr stainless-steel autoclave (100 mL, modified with a ZnSe/AR window) was introduced to collect the spectrum. In a typical experiment, the Parr autoclave was first vacuumed and warmed to certain target temperature, after which a single background spectrum of 256 scans was collected. Subsequently, 25 mL of the indicated absorbent was introduced using an attached injection port. CO₂ pressurization was then performed to reach a desired pressure within 8 h, while at the same time, FTIR scans were collected using the DiCOMP probe. The ReactIR 45 m spectrometer was programmed to record spectra every 30 s during 8 h. The emerging FTIR signals around 2330 cm⁻¹ (asymmetric carbonyl vibration of dissolved CO₂) and within the 1600–1700 cm⁻¹ region (asymmetric carbonyl vibration of incorporated CO₂) were used to describe physisorption and chemisorption, respectively. During spectrum processing, a pristine absorbent was used as the standard background and subtracted for clearness.

2.5. DSC Measurement. A NETZSCH DSC 206 thermal analyzer was used to carry out DSC measurements. The experimental temperature range was set to be from 0 to 300 °C with a heating rate of 5 °C/min. A ca. 4 mg sample of the indicated CO₂-saturated absorbent was loaded and sealed in an aluminum crucible for calorimetry. In a typical DSC curve, regeneration enthalpy was calculated via integration of the peak area of the corresponding CO₂ desorption event, and the reversal/evaporation temperature was obtained by reading the vertex value of the corresponding desorption/volatilization event. Graphic illustrations can be found in the [Supporting Information](#).

2.6. DFT Calculation. All calculations were performed using Gaussian 16⁶¹ suite of the programs. The DFT method of M06-2X was used for single-point energy calculations, geometry optimizations, and frequency analyses. The SMD-GIL⁶² solvent model was applied to the environment simulation of the pristine alkoxy-functionalized methylamine and the corresponding ammonium carbamate/carbamic acid derived from it and CO₂. The all-electron basis set of def2svp was introduced for every atom. Identification of the geometrically optimized stationary points as minima (no imaginary frequency) was performed via frequency calculations, while thermodynamic data could also be attained using the same method. The def2tzvp basis set was employed to improve the energy accuracy by calculating the corresponding single-point energies of all atoms of every optimized structure. The combination of single-point energy was used to figure out the relative free energy with the help of Gibbs free energy correction.

2.7. VLE Curve. For the VLE test under pressure, a 15 mL oven-dried autoclave equipped with a CO₂ inlet and an electronic pressure gauge with an accuracy of ± 0.01 kPa was used to perform the absorption. Typically, 3 mL of the indicated absorbent was charged into the autoclave at 25 °C. After gas replacement, a certain amount of CO₂ was introduced into the reactor at the target temperature under continuous magnetic stirring. The corresponding CO₂ capacity was determined via the gravimetric method using an analytical balance (± 0.0001 g) when a constant pressure was observed.

3. RESULTS AND DISCUSSION

3.1. Effect of Alkoxy Functionalization. Alkoxy-functionalized amines were obtained by stirring the mixture of the corresponding aqueous amine solution with the selected alkoxyethyl chloride at 60 °C for 12 h. These reactions proceeded quantitatively without any catalyst or the standard Schlenk technique. Water contents of the products were determined to be all below 1 wt %. Preliminary investigations were carried out at ambient temperature under water-lean condition, and the effect of projected structural functionalization on capacity and viscosity at CO₂-saturated state is depicted in Table 1. As predesigned, **Trigly-NHMe** was verified to be a viable candidate for single-component CO₂ chemisorption with a molar capacity far exceeding the typical 50 mol % (entry 1). Notably, the compelling gravimetric CO₂ uptake of 18 wt % along with an industrially feasible operating viscosity (91 cP) was also presented. The exponential viscosity increase that is encountered in traditional nonaqueous and solvent-free protocols was circumvented without the compromise of absorption capacity. The significance of the alkoxy pendant group with multiple oxygens as potential coordination sites for hydrogen bonding could be reassured by the inferior outcome of either **TriglyOH-NHMe** (without methyl terminal blocking, turned into a hydrogen bond donor) or **nHep-gly-NHMe** (partially replacing oxygen atoms with carbons, lack of coordination sites) as well (entries 2 and 3). Meanwhile, methylation on nitrogen was also proved to be vital as the operating viscosity of **Trigly-NH₂** was observed to be more than 5 times that of **Trigly-NHMe** (entry 4). Physisorption by the backbone of the designed absorbent was revealed to be negligible compared with its chemisorption (entry 5 vs 1). Furthermore, cutting the ethoxy unit from the side chain of the absorbent would cause a viscosity increment in CO₂-loaded state, accompanied by a lowered molar capacity (entry 6),

whereas its increase would suffer a loss of the gravimetric CO₂ uptake in exchange for better flowability (entry 7). Capture performance by 30 wt % MEA under current condition is also provided for comparison, and it could be obviously observed that the viscosity superiority due to water dilution could be matched to a great extent through elaborate functionalization of these nonaqueous absorbents (entries 1, 6, or 7 vs 8). These results on the structure–property relationship could sufficiently demonstrate the crucial role of alkoxy group as both hydrogen bond acceptor and conformational flexibility supplier under water-lean condition, rendering significant enhancement in absorption capacity as well as operating viscosity.

3.2. Formation of Carbamic Acid. The outstanding performance obtained by **Trigly-NHMe** could support the proposition that the majority of sequestered CO₂ should be stabilized in the carbamic acid form and the alkoxy functionality would act as hydrogen bond acceptor for complexation. Hence, further tests were performed for better elucidation of the intramolecular hydrogen bonding between *in situ* formed carbamic acid and the alkoxy side chain (Table 2).

Table 2. Control Experiments with Trigly-NHMe^a

entry	diluent	molar ratio of the absorbent to diluent	CO ₂ uptake ^b (mol %)
1	neat		72
2	DMF	1:2	83
3	DMF	1:4	86
4	DMF	1:8	104
5	DMSO	1:8	101
6	EtOH	1:8	63
7	MeOH	1:8	53

^aCO₂ absorption was performed at 25 °C, and the background physisorption of each selected diluent is negligible compared with the chemisorption of **Trigly-NHMe** at ambient pressure. ^bEquilibrium CO₂ loading.

The progressive dilution of **Trigly-NHMe** by the polar aprotic solvent dimethylformamide (DMF) showed significant improvement of the CO₂ molar uptake until exceeding 100 mol % for a total carbamic acid predominance (entries 2–4 vs 1). These results could provide the experimental evidence for the proposed mechanism as dilution is a common method for the enhancement of intramolecular interactions. A similar result was attained when dimethyl sulfoxide (DMSO) was introduced to the absorption system at an 8:1 M ratio (entry 5). However, in the case of polar protic diluents, such as EtOH and MeOH, CO₂ molar capacity of **Trigly-NHMe** would be obviously reduced due to the hydrogen bond donor nature of the alcoholic solvent for competitive coordination (entries 6 and 7). Therefore, CO₂-saturated **Trigly-NHMe** (72 mol % uptake) as a mixture of carbamic acid (44 mol %) and ammonium carbamate (28 mol %) that falls short of the theoretical 100 mol % capacity could possibly be attributed to its undiluted neat state, in which the intermolecular proton transfer is unfavorable, yet inevitable.

Subsequently, the *in situ* FTIR technique was employed to gain spectroscopic proof for the formation of carbamic acid. As shown in Figure 1a, neat **Trigly-NHMe** revealed two characteristic (C=O) vibrations at 1689^{30,57,63} and 1658 cm⁻¹, corresponding to the carbamic acid and ammonium carbonate derived from 1:1 and 2:1 (mole of amine vs mole of CO₂) incorporation of CO₂, respectively. Meanwhile, the

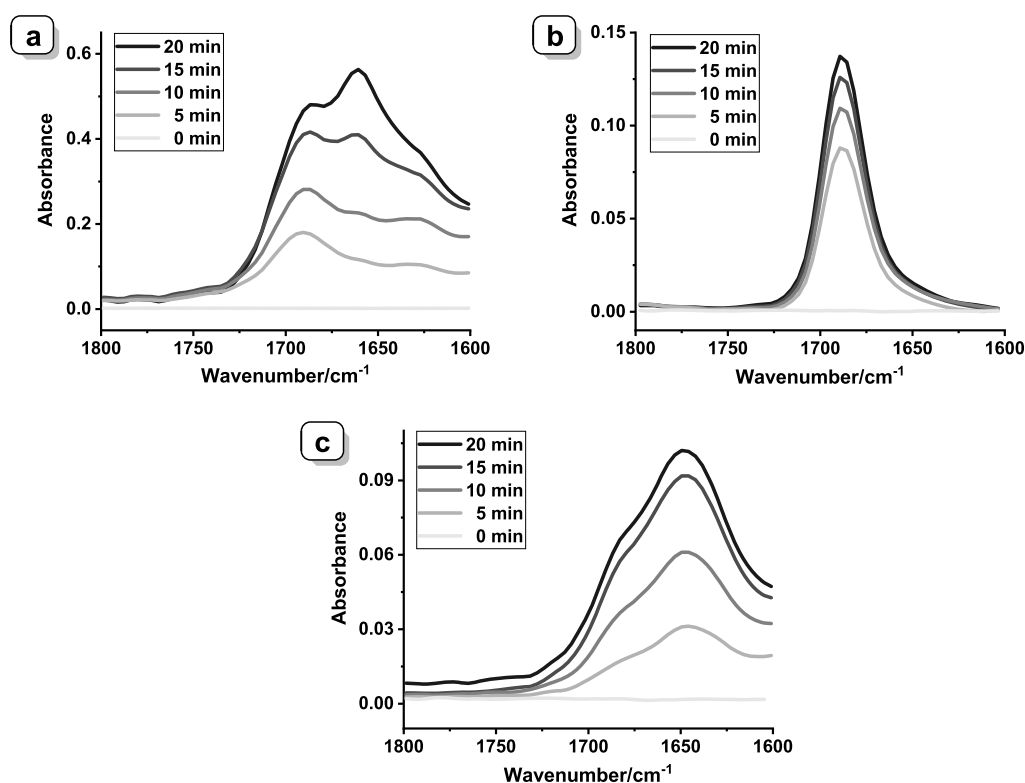


Figure 1. FTIR asymmetric stretching of carbonyl from chemisorbed CO₂ by neat Trigly-NHMe (a), DMSO-diluted Trigly-NHMe in an 8:1 M ratio (b), and EtOH-diluted Trigly-NHMe in an 8:1 M ratio (c) at 25 °C.

signal of *in situ* formed carbamic acid (1689 cm⁻¹) prevailed when the polar aprotic diluent DMSO was introduced in a massive amount (Figure 1b). On the contrary, the EtOH-diluted Trigly-NHMe solution displayed indistinctive carbonyl stretching in the carbamic acid region, while the ammonium carbonate was disclosed to be the main product as a result of CO₂ chemisorption (Figure 1c). These spectroscopic observations correlated well with the aforementioned control experiments (Table 2) and provided clear evidence for the equilibrium of carbamic acid and ammonium carbamate within a neat system. In addition, full FTIR spectra of neat Trigly-NHMe before and after the CO₂ uptake are depicted in Figure S1, and signal enhancing of CO₂-loaded Trigly-NHMe in the range of 3000–3400 cm⁻¹ was possibly caused by O–H stretching of carbamic acid as well as N–H vibration of ammonium carbamate.

In a DMF or DMSO solution of Trigly-NHMe, protonation of the amino group of another absorbent molecule is prohibited by intramolecular hydrogen bonding, thus rendering a 100 mol % capacity. However, in the neat system, which really matters as a candidate for further application, proton transfer from *in situ* formed carbamic acid still occurred as mentioned above, resulting in a considerable amount of intermolecular ammonium carbamate, which would in turn deteriorate CO₂ capacity. To have a deeper understanding of the nature of reaction tendency between intermolecular and intramolecular samples, which determines the reaction stoichiometry, DFT calculations were conducted for the interaction of Trigly-NHMe with CO₂ in neat condition. As shown in Figure 2, the calculated Gibbs free energy of formation for ammonium carbamate ($\Delta G_a = -2.4$ kcal/mol) is only slightly higher than that of carbamic acid ($\Delta G_b = -2.5$ kcal/mol). This result suggests that although the formation of



Figure 2. Optimized structures of CO₂-loaded Trigly-NHMe. (a) Intermolecular ammonium carbamate, $\Delta G_a = -2.4$ kcal/mol. (b) Intramolecular carbamic acid, $\Delta G_b = -2.5$ kcal/mol. H: white, C: gray, N: blue, and O: red.

carbamic acid is preferred in the case of neat Trigly-NHMe (44 vs 28 mol %), its coexistence with ammonium carbamate could not be avoided due to the inadequate Gibbs free energy gap. Consequently, the realistic CO₂ molar uptakes for current alkoxy-functionalized methylamines would stand as an intermediate value between 50 and 100 mol %.

3.3. Absorption and Desorption Behavior. In the following study, alkoxy-functionalized methylamines were exposed to CO₂ (bubbling) at 40 °C (the supposed working temperature within the absorber for CO₂ removal from flue gas) for practical evaluation. As seen in Table 3, gravimetric CO₂ uptakes (14–21 wt %) of all three absorbents enlisted showed no significant temperature dependence when compared with those obtained at 25 °C (Table 1), whereas their flowability at the CO₂-loaded state was greatly enhanced. Notably, the absorption by any of these amines could reach equilibrium in no more than 10 min, rendering strong kinetic performance at 40 °C (Figure S3). Absorption performance under CO₂/N₂ mixed gas (15 vol % CO₂) was then investigated, and corresponding equilibrium capacities went downward by 2–3 wt % due to the decrease of CO₂ stream concentration. Viscosities at an approximately 25 mol % CO₂

Table 3. Operating Characteristics of Alkoxy-Functionalized Methylamines^a

entry	absorbent	CO ₂ uptake ^b (wt %)	viscosity ^c (cP)	T _{rev} ^d (°C)	ΔH _{regen} ^e (kJ/mol _{CO2})	T _{evap} ^f (°C)
1	Digly-NHMe	21 (18) ^g	63	59	56	121
2	Trigly-NHMe	17 (15) ^g	41	63	62	189
3	Tetragly-NHMe	14 (11) ^g	27	72	74	250

^aCO₂ absorption and viscosity measurement were performed at 40 °C. ^bEquilibrium CO₂ loading. ^cViscosity at the equilibrium CO₂ loading. ^dReversal temperature for the absorbent with CO₂ loading. ^eRegeneration enthalpy for the absorbent with CO₂ loading. ^fEvaporation temperature for the unreacted absorbent. ^gEquilibrium CO₂ loading using CO₂/N₂ mixed gas (15 vol % CO₂).

loading at 40 °C are listed in Table S1 as these results (no more than 12 cP) would better reflect the realistic flowability under the industrial condition. Other than capacity and viscosity, reversibility is also recognized to be a vital property to estimate the feasibility of a devised approach since the main barrier to implement industrial CO₂ capture is the high-energy input during solvent regeneration. For this consideration, reversal properties of these functionalized methylamines were illustrated by DSC measurement in terms of three indicators, that is, reversal and evaporation temperature as well as enthalpy of regeneration. Apparently, both T_{rev} and T_{evap} along with ΔH_{regen} increased by fixing an additional ethoxy unit to the alkoxy side chain, possibly due to the gradual strengthening of intra/intermolecular interaction as well as the growth of molecular weight. DSC results of other nonaqueous absorbents that have been reported capable of reversibly capturing CO₂ are enlisted in Figure S4 for comparison. In general, Tetragly-NHMe is regarded as a capable contender for postcombustion CO₂ capture because of its mild desorption temperature, viable enthalpy of regeneration,⁶⁴ and sufficient temperature gap between reversal and evaporation, while Digly-NHMe and Trigly-NHMe could be economically feasible for the precombustion scenario due to their lower enthalpies.

Thermostability of Trigly-NHMe was investigated by heating the CO₂-loaded absorbent at 80 °C within a closed vessel for 48 h. After the vessel was vented, the remaining absorbent was removed, and ¹³C NMR spectroscopy was applied to determine its integrity. As illustrated in Figure 3a, the ¹³C NMR spectrum of the regenerated Trigly-NHMe (down) displayed nearly the same pattern as the pristine one (up), and no sign of thermal degradation was detected. Oxidation resistance of Trigly-NHMe was proved by its tolerance at 80 °C under O₂ (2 bar) for 48 h (Figure S5). Subsequently, the easy reversibility of Trigly-NHMe was demonstrated by means of *in situ* FTIR spectroscopy in a more intuitionistic way through the monitoring of the entire process of its CO₂ uptake and release (Figure 3b). Particularly, the characteristic peaks at 1689 and 1658 cm⁻¹, assigned to the asymmetric stretching of carbonyls from carbamic acid and ammonium carbamate, respectively, grew quickly upon the introduction of CO₂ and reached the equilibrium state in a short time. The rapid disappearance of both these carbonyl vibrations after the temperature increase revealed a complete and energy-saving regeneration step. The ¹³C NMR analysis together with *in situ* FTIR tracking of the CO₂ capture and release processes could give solid spectroscopic evidence for the preferable durability of the present research. Moreover, ten CO₂ absorption–desorption cycles by Trigly-NHMe were also implemented, resulting in a smooth efficiency without a significant decrease of capacity (Figure S6). These data indicate that given the large gap between reversal and evaporation temperatures, the mass losses of Trigly-NHMe during desorption by either evaporation or degradation is

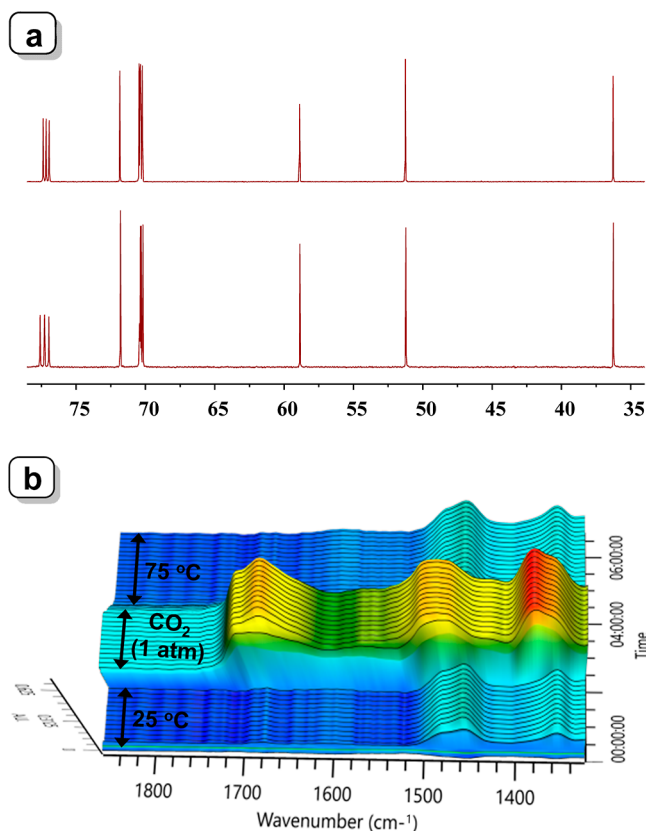


Figure 3. Reversibility of Trigly-NHMe. (a) ¹³C NMR spectra of Trigly-NHMe before (up) and after (down) heating at 80 °C in CO₂-loaded state for 48 h. (b) *In situ* FTIR spectroscopy of CO₂ capture and release by Trigly-NHMe.

insignificant, and the absorbent should hold its effective manner over many more cycles.

To gain more insights for practical utilization, Trigly-NHMe was then subjected to VLE testing. As depicted in Figure 4, its

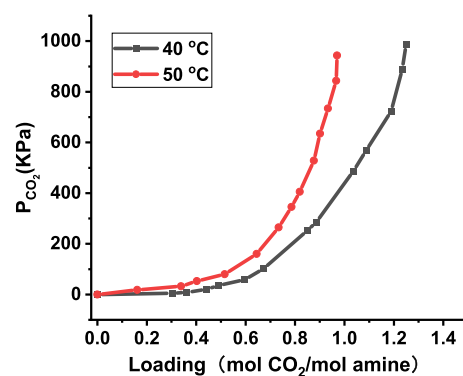


Figure 4. VLE curves for Trigly-NHMe.

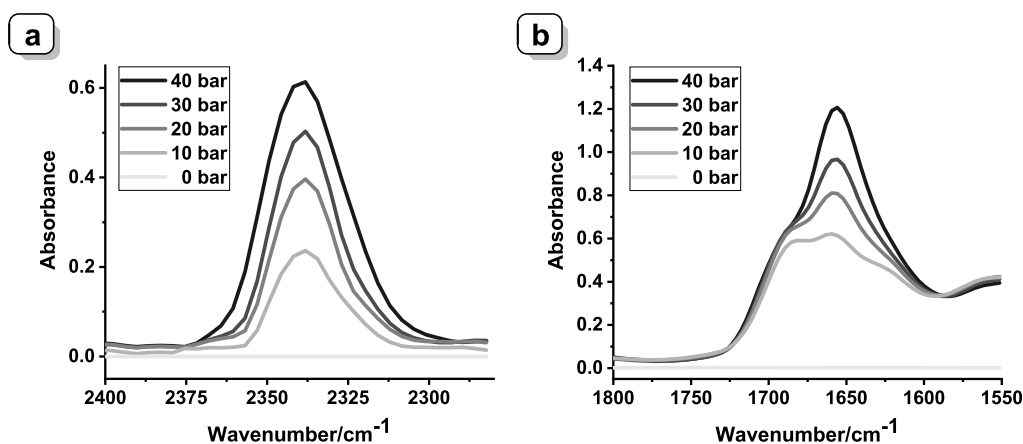


Figure 5. FTIR asymmetric stretching of carbonyl from physically dissolved CO₂ (a) and chemically bonded CO₂ (b) by Trigly-NHMe at 35 °C under high pressure.

VLE behavior was measured at 40 and 50 °C (both are industrially relevant temperatures), respectively, and the resulting curves revealed a similar tendency for the dependence of capacity on pressure in either condition. Both VLE curves started out flat, implying that chemical interactions should proceed with high efficiency in low-pressure region, and almost all injected CO₂ was sequestered by chemisorption. After the chemical saturation was achieved, internal pressure of the testing autoclave began to increase drastically along with the increment of physisorption loading. The CO₂ uptakes by Trigly-NHMe at 50 °C were lower than those obtained at 40 °C, which could be ascribed to the negative effect of temperature on physisorption. Hence, these figures follow a general trend that the CO₂ uptake in nonaqueous Trigly-NHMe increases with CO₂ pressurization and decreases with temperature increase.

3.4. High-Pressure Performance. Alkoxy-functionalized methylamines devised in the present study represent compelling candidates for practical CO₂ scrubbing under postcombustion circumstance. Meanwhile, there are also other application scenarios that should be performed under high pressures, such as natural gas upgrading and CO₂ removal from the crude hydrogen stream generated by the water–gas shift.^{65,66} In these cases, chemisorption would be limited by a substantial reaction stoichiometry, while the ability of massive physisorption should play the key role regarding a condensed gas feed. For instance, traditional alkanolamine-type aqueous absorbents operate only in terms of chemical incorporation for flue gas treatment, and their capacity would barely increase once the equilibrium of chemisorption is reached, no matter how much the pressure grows. We anticipate that due to the installation of the alkoxy group with CO₂-philic nature,⁶⁷ these newly identified absorbents constructed using low-cost materials as well as a simple synthetic procedure would be competent for additional CO₂ physisorption in high-pressure operations. Therefore, Digly-NHMe and Trigly-NHMe were introduced to CO₂-loading experiments performed at 35 °C to simulate a high-pressure situation. Mole capacities of Digly-NHMe were measured as 129 mol % at 20 bar and 152 mol % at 30 bar, while those of Trigly-NHMe were 134 and 160 mol %, respectively, which are superior to those of the industrialized aMDEA and Selexol under identical absorption conditions (Table S2). These additional CO₂ loadings under high pressure were acquired as

the benefit of physisorption, and the superior performance by Trigly-NHMe should possibly be attributed to its additional ethoxy group, which could create more free volume for molecular flexibility through disruption of intermolecular packing, thus inducing significant enhancement in the physical solubility of CO₂. In order to understand the synergistic effect of chemisorption and physisorption, Trigly-NHMe was subjected to *in situ* FTIR analysis at 35 °C with a CO₂ pressure ramp from 0 to 40 bar. As illustrated in Figure 5a, the intensity of characteristic (C=O) stretching neighboring at 2335 cm⁻¹, which corresponds to the physical dissolved CO₂, gradually enhanced along with the pressure build-up. At the same time, two asymmetric (C=O) vibrations at 1689 and 1658 cm⁻¹, assigned to the intramolecular carbamic acid and intermolecular ammonium carbamate, respectively, surfaced, increased, and finally merged into one intense signal at approximately 1655 cm⁻¹ in the course of pressurization, indicating that the ammonium carbamate form of CO₂ capture prevailed as the dominated species under high pressure (Figure 5b). These results clearly demonstrate that besides the advantages acquired by deploying alkoxy functionalization onto the methylamine skeleton for the enhancement of capacity and flowability under ambient pressure, absorbents such as Trigly-NHMe that have several repeating ethoxy units are also feasible for high-pressure applications due to additional physisorption.

4. CONCLUSIONS

In summary, functionalized methylamines with an alkoxy pendant group covalently bonded to the nitrogen have been developed and applied for reversible CO₂ capture as single-component water-lean absorbents. Gravimetric capacities up to 21 wt % at either 25 or 40 °C have been achieved with low operating viscosities (48–114 cP at 25 °C and 27–63 cP at 40 °C) at the fully loaded status. It is shown that such a competitive performance could be attributed to the successful installation of the alkoxy group with high rotational freedom, which could both enhance system flowability by reducing operating viscosity and improve absorption capacity via stabilization of the *in situ* formed carbamic acid after CO₂ incorporation through intramolecular hydrogen bonding. Notably, the CO₂-loaded absorbents are tolerant to elevated temperatures and could remain intact for at least 48 h at 80 °C within a closed system. Additional CO₂ physisorption under

high operating pressures has also been attained due to the CO₂-philic nature of the alkoxy pendant group. Moreover, comprehensive studies by means of *in situ* FTIR, DSC measurement, and recycle tests were carried out to demonstrate the feasible reversibility of the present water-lean system. Consequently, these alkoxy-functionalized amines disclosed herein would provide an alternative direction for absorbent design to pursue advanced capacity and relieved energy penalty from the nonaqueous condition while retaining high reactivity and low operating viscosity as aqueous alkanolamine blends, thus contributing a solid step toward the application of single-component water-lean protocols for industrial CO₂ capture.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.2c01361>.

DSC curves, absorption–desorption cycles, characterizations for functionalized amines, and their NMR charts (PDF)

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Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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