

Energy-Efficient CO<sub>2</sub> Capture Using Nonaqueous Absorbents of Secondary Alkanolamines with a 2-Butoxyethanol Cosolvent

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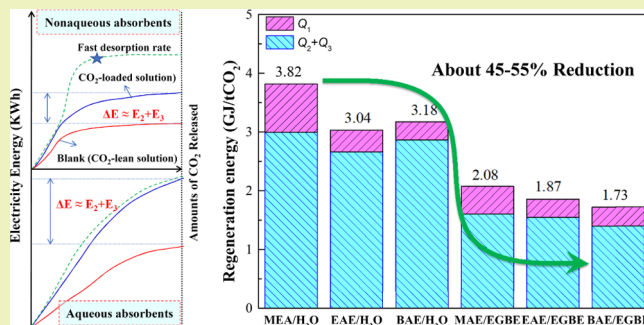
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Supporting Information

**ABSTRACT:** Nonaqueous amine-based absorbents by replacing water with organic solvents have potential advantages of low energy penalty and reduced amine degradation for CO<sub>2</sub> capture. An advanced nonaqueous system of 2-(butylamino)ethanol (BAE) with 2-butoxyethanol (EGBE) was proposed for low-energy consumption CO<sub>2</sub> capture. EGBE was selected as a green cosolvent because of its superior properties over the reported organics and water. A comprehensive study on CO<sub>2</sub> capture performance has been performed for secondary alkanolamine nonaqueous systems such as 2-(methylamino)ethanol (MAE), 2-(ethylamino)ethanol (EAE), and BAE and their aqueous counterparts. Product species in CO<sub>2</sub>-loaded solutions were identified by <sup>13</sup>C nuclear magnetic resonance and Fourier transform infrared spectroscopy. Regeneration energy consumption was also evaluated using a modified method and compared with that of conventional aqueous monoethanolamine (MEA). Results demonstrated that the aqueous 5.0 M secondary amine absorbents had higher absorption capacity and larger cyclic capacity than their nonaqueous counterparts. The desorption efficiency for both systems was in a descending order: BAE > EAE > MAE. Surprisingly, the cyclic capacity of aqueous and nonaqueous BAE systems was about 180 and 100% higher than that of aqueous MEA, respectively. The underlying reasons were also discussed. CO<sub>2</sub> can react with these amines, forming unstable carbamates and protonated amines in the EGBE solvent, whereas it forms bicarbonate species in addition to ionic couples in aqueous solutions. The regeneration heat duty of nonaqueous EGBE-based secondary amine absorbents was about 45–55% lower than that of aqueous MEA (3.82 MJ kg<sup>-1</sup> CO<sub>2</sub>). In addition, the feasibility of low-temperature desorption makes the BAE/EGBE absorbent a compelling solution for energy-saving CO<sub>2</sub> capture technology using low-grade industrial waste heat.

**KEYWORDS:** CO<sub>2</sub> capture, secondary alkanolamine, nonaqueous solvent, energy reduction, 2-(butylamino)ethanol, 2-butoxy ethanol



## INTRODUCTION

It is well accepted that anthropogenic carbon dioxide (CO<sub>2</sub>) emissions from industrial activities are the key contributors to global climate change, resulting in a significant environmental issue.<sup>1</sup> Carbon capture, utilization, and storage are one of the feasible pathways to mitigate CO<sub>2</sub> emissions.<sup>2,3</sup> Among the available capture methods such as absorption,<sup>4</sup> adsorption,<sup>5</sup> and membrane separations, solvent-based chemical absorption has attracted the most attention and may be the most close-to-market approach to be applied at an industrial scale in several industries such as flue gas treatment, biogas upgrading, and nature gas processing.<sup>6</sup> Aqueous 30 wt % monoethanolamine (MEA) is also considered to be a benchmark absorbent. However, severe amine degradation at high temperature and high energy consumption are the main hindrances preventing large-scale implementation of this technology.<sup>6,7</sup> Generally, solvent regeneration is a high-intensive energy process, which takes up about 60–80% of total energy consumption for CO<sub>2</sub> capture by aqueous amines.<sup>8</sup> During the regeneration step, the required heat energy consumption ( $Q$ ) is associated to three

key components: sensible heat ( $Q_1$ ) for heating up the solvent to the required desorption temperature; latent heat ( $Q_2$ ) of the water vapor leaving the desorber along with the desorbed CO<sub>2</sub> in the overhead gas stream; and desorption heat ( $Q_3$ ) for breaking the chemical bonds in CO<sub>2</sub>-loaded products.<sup>9</sup> It has been noted with concern that the use of water as a cosolvent is the weakest point in terms of regeneration energy consumption for these aqueous amine systems because of large specific heat capacity and enthalpy of vaporization of the water solvent and a high desorption temperature of 373–393 K.<sup>2,6</sup> Hence, substantial effort has been devoted to develop novel absorbents for an energy-efficient process, and the biggest challenge in this field is to maintain the comparative capture performance with

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aqueous amines yet avoiding, at least in part, the major disadvantage of high regeneration energy.

Some secondary alkanolamines with low heat of absorption have attracted special attention. Recently, extensive studies on the absorption behavior and performance,<sup>9–15</sup> physical properties,<sup>16–19</sup> and kinetics<sup>20–23</sup> have been performed on solvent-free and aqueous secondary alkanolamines for CO<sub>2</sub> capture. In these studies, single-component secondary amines presented high absorption efficiency and low regeneration temperature. However, the super high viscosity of the absorbents, especially after CO<sub>2</sub> absorption, was also highlighted, resulting in the poor mass transfer of CO<sub>2</sub> from the gas phase to liquid bulk.<sup>11,12</sup> For their aqueous systems, higher cyclic capacity and lower heat of reaction with CO<sub>2</sub> were observed in comparison with the conventional MEA. Moreover, aqueous 2-(ethylamino)ethanol (EAE) and 2-(methyamino)ethanol (MAE) were considered to have great prospect for industrial applications.<sup>15</sup>

Using organic solvents to replace water in the absorbents has proved to have significant advantages as for saving regeneration energy and potentially reducing corrosiveness and degradation. As a result, nonaqueous absorbents by blending secondary amines with organics have led to the advance development.<sup>6,24–35</sup> These reported organic solvents include volatile alcohols (e.g., methanol, ethanol, and butanol), low-volatile alcohols and glycols (e.g., benzyl alcohol and ethylene glycol) or their mixtures, glymes, dimethyl formamide (DMF), and ionic liquids. However, high-volatile alcohols (e.g., methanol and ethanol) as cosolvents can produce huge solvent loss when treating large-scale flue gas volume; thus, it seems to be impractical for potential industrial use. Although the glycols and ionic liquids have negligible vapor pressures under absorption conditions, the dramatic viscosity increase and the low diffusivity for mass transfer might result in poor CO<sub>2</sub> capture performance. The use of glycol diethers generally produces a liquid biphasic system, which could significantly reduce regeneration energy. Additional treatment of phase separation and deteriorating heat transfer for the CO<sub>2</sub>-lean and CO<sub>2</sub>-rich systems with superhigh viscosity are required for further consideration. The DMF solvent may also produce severe degradation under basic conditions, especially at elevated temperatures.

Compared with other organics, 2-butoxyethanol (ethylene glycol monobutyl ether, EGBE) has low volatility, low viscosity, and readily biodegradable features.<sup>36,37</sup> More importantly, EGBE has low specific heat capacity (EGBE: 2.38 kJ·kg<sup>−1</sup>·K<sup>−1</sup> and H<sub>2</sub>O: 4.19 kJ·kg<sup>−1</sup>·K<sup>−1</sup>) and relatively low viscosity compared with the reported low-volatile organics. It is also environmentally friendly and unlikely to cause adverse effects to human health and the environment, as a result of delisting from the hazardous air pollutants.<sup>38</sup> Secondary alkanolamines with different alkyl groups connected to an N atom have attracted special attention because of the comparative reaction kinetics, lower heat of absorption, larger CO<sub>2</sub> capacity, and enhanced stability in comparison to MEA. Blending of these secondary alkanolamines with EGBE has potential advantages over the reported absorbents for CO<sub>2</sub> capture. To the best of our knowledge, the study on capture performance for these proposed systems is insufficient in comparison with aqueous MEA for this purpose. Moreover, the impact of different steric hindrances on CO<sub>2</sub> absorption and desorption characteristics and the stability of resultant products for aqueous and nonaqueous secondary alkanol-

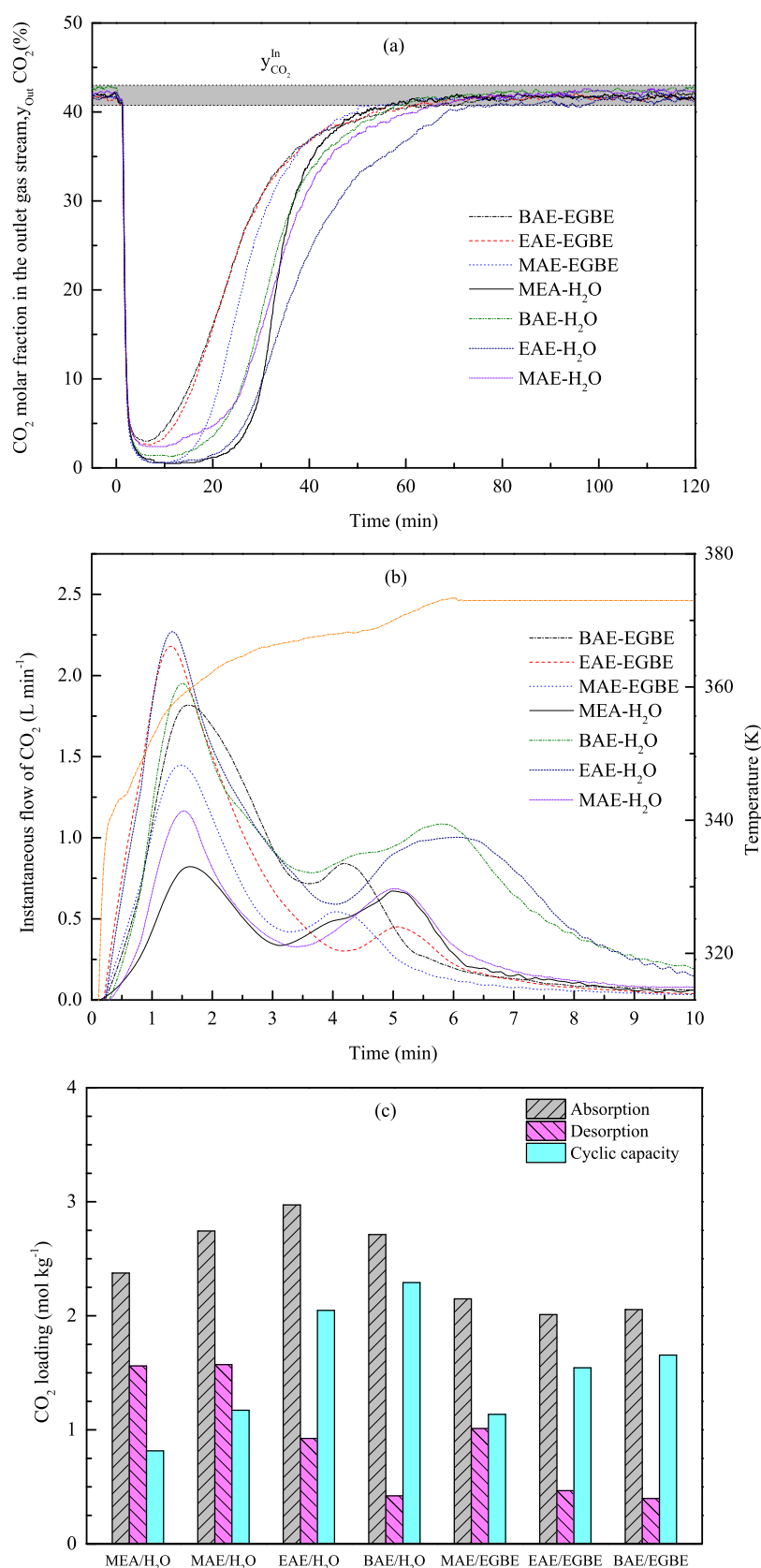
amines with an increasing length of alkyl groups on an amino atom need to be revealed in detail. Experimental comparison of regeneration energy consumption under the same conditions for these absorbent systems was also demanding for further practical consideration.

In this work, we have proposed nonaqueous alkanolamine-based systems using EGBE as a cosolvent to replace water for CO<sub>2</sub> capture. With the aim of changing steric hindrance by replacing one hydrogen from the nitrogen atom in the MEA molecule with methyl, ethyl, and butyl groups, three secondary alkanolamines, that is, MAE, EAE, and 2-(butylamino)ethanol (BAE), were used for the main compositions in the absorption systems. CO<sub>2</sub> absorption (313 K) and desorption (373 K) characteristics in the abovementioned systems were analyzed under ambient pressure and compared with those of aqueous counterparts and conventional aqueous 5.0 M MEA. Reaction mechanisms were explored by <sup>13</sup>C nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) analysis on CO<sub>2</sub>-free and CO<sub>2</sub>-loaded samples. The stability of the proposed absorbent was evaluated by several continuous cycles of absorption–desorption. Overall energy consumption for CO<sub>2</sub>-loaded solutions prepared under the same absorption conditions was experimentally measured at 373 K in an electrical heating apparatus and the relative energy consumption was evaluated using aqueous 5.0 M MEA as a baseline case. In our opinion, this experimental study may provide useful information to select suitable absorbents for an energy-efficient CO<sub>2</sub> capture process.

## EXPERIMENTAL SECTION

**Chemicals and Materials.** MEA (CAS no. 141-43-5, 99.12% GC purity), MAE (CAS no. 109-83-1, 99.25% GC purity), and EGBE (CAS no. 111-76-2, 99.82% GC purity) were purchased from Aladdin Reagent, China. EAE (CAS no. 110-73-6, 99.90% GC purity) and BAE (CAS no. 111-75-1, 99.70% GC purity) were purchased from Sigma-Aldrich. All chemicals were used as received without further purification. Water was produced from a Merck-Millipore Aquelix 5. The detailed information of these chemicals is listed in the [Supporting Information](#) Table S1.<sup>36,37</sup> Aqueous and nonaqueous solutions were prepared by dissolving amine into a solvent (water or EGBE) in a volumetric flask at 298 K. The total amine concentration in all solutions was fixed at overall 5.0 mol dm<sup>−3</sup> (M). Electronic analytical balances (OHAUS, CP214, Scout SE 1501F) were used for mass measurements. N<sub>2</sub> (99.99%, v/v), CO<sub>2</sub> (99.99%, v/v), and a standard gas (20.00 ± 0.02% CO<sub>2</sub> balanced with N<sub>2</sub>) were purchased from the Shijiazhuang Xisanjiao oxygen generation station and used for calibration of two nondispersive infrared CO<sub>2</sub> analyzers (GXH-3011N, 0–20%; SKS-BA-CO<sub>2</sub>, 0–100%; uncertainty 1.0% FS).<sup>39</sup>

**CO<sub>2</sub> Absorption and Desorption.** CO<sub>2</sub> absorption–desorption performance for different systems was evaluated by batch experiments at near atmospheric pressure. A schematic diagram of the experimental apparatus for screening absorption and microwave desorption is shown in [Figure S1](#). For CO<sub>2</sub> absorption, two kinds of gas mixtures (i.e., 12.6 and 42.0 vol % CO<sub>2</sub> balance with N<sub>2</sub>) were used in this work to simulate the different CO<sub>2</sub> sources. The detailed absorption procedure can be found in the [Supporting Information](#). Generally, the duration time was 2.0 and 3.5 h for 12.6 and 42.0 vol % CO<sub>2</sub> sources, respectively. Three samples were taken for the measurement of CO<sub>2</sub> loading ( $\alpha$ ) using a modified Chittick CO<sub>2</sub> apparatus ([Figure S1](#)) and physical properties. After absorption, the reactor with the CO<sub>2</sub>-rich solution was moved to a MCR-3 microwave reactor (Zhengzhou Kechuang Instrument Co., Ltd., China). The solution was programmatically heated to 373 K in 2 min and the desorption process lasted for 1.0 h. The released CO<sub>2</sub> was cooled using a Graham condenser, and the flow rate was recorded using a CO<sub>2</sub> mass flow meter (CS200A, Beijing Sevenstar Flow Co., Ltd.)



**Figure 1.** CO<sub>2</sub> capture performance of aqueous and nonaqueous secondary amine systems compared with that of aqueous MEA. (a) Absorption profiles at 313 K. The CO<sub>2</sub> concentration in the gas mixture was  $42.0 \pm 0.5\%$ ; (b) CO<sub>2</sub> desorption profiles by microwave desorption at 373 K; and (c) comparison of absorption and cyclic capacity.

under standard conditions. Samples were taken at 373 K and cooled down to room temperature to analyze the CO<sub>2</sub> loading of the CO<sub>2</sub>-

lean solution. The CO<sub>2</sub> cyclic capacity ( $\Delta\alpha$ ) is defined by the difference of CO<sub>2</sub>-rich loading after absorption and CO<sub>2</sub>-lean loading

Table 1. CO<sub>2</sub> Absorption and Desorption Performance of Aqueous and Nonaqueous 5.0 M Amine Solutions<sup>a</sup>

amine-based absorbent			absorption (313 K)					desorption (373 K)			
5.0 M	$\rho$ (kg·m <sup>-3</sup> )	$\eta$ (mPa·s)	CO <sub>2</sub> % <sup>b</sup>	$\alpha$ (mol·kg <sup>-1</sup> )	$\rho$ (kg·m <sup>-3</sup> )	$\eta$ (mPa·s)	$r_{\text{CO}_2} \times 10^5$ (mol·kg <sup>-1</sup> ·s <sup>-1</sup> )	$\alpha$ (mol·kg <sup>-1</sup> )	$r_{\text{CO}_2} \times 10^5$ (mol·kg <sup>-1</sup> ·s <sup>-1</sup> )	$\Delta\alpha$ (mol·kg <sup>-1</sup> )	RE, %
MEA/H <sub>2</sub> O	1003.5	1.618	A	2.375	1106.7	2.242	103	1.560	16.98	0.815	34.3
			B	2.301			29.5	1.627	13.68	0.674	29.3
MAE/H <sub>2</sub> O	990.0	2.719	A	2.744	1106.9	8.643	105	1.572	19.76	1.172	42.7
			B	2.523			32.2	1.546	15.07	0.977	38.7
EAE/H <sub>2</sub> O	976.9	3.868	A	2.972	1103.5	8.544	101	0.925	41.85	2.047	68.1
			B	2.591			29.6	1.008	31.31	1.583	61.1
BAE/H <sub>2</sub> O	934.3	6.242	A	2.712	1050.3	25.06	109	0.421	41.25	2.291	84.5
			B	2.343			33.1	0.471	37.07	1.872	79.9
MAE/EGBE	902.0	3.566	A	2.148	995.1	24.34	109	1.012	20.72	1.136	52.9
			B	1.911			32.2	1.054	13.52	0.857	44.8
EAE/EGBE	897.1	3.993	A	2.010	980.5	27.97	87.8	0.466	28.59	1.544	76.8
			B	1.841			30.7	0.491	23.36	1.350	73.3
BAE/EGBE	881.4	5.342	A	2.054	966.4	50.13	88.3	0.398	29.23	1.656	80.6
			B	1.764			29.4	0.428	22.07	1.333	75.6

<sup>a</sup>CO<sub>2</sub> absorption at 313 K and desorption at 373 K.  $\alpha$  is defined as the moles of CO<sub>2</sub> per kg of CO<sub>2</sub>-free solution after CO<sub>2</sub> absorption or desorption, and the combined uncertainties  $u$  are  $u_c(\alpha) = 0.035 \text{ mol}\cdot\text{kg}^{-1}$  and  $u_c(10^5R) = 0.5 \text{ mol}\cdot\text{kg}^{-1}\cdot\text{s}^{-1}$ .  $r_{\text{CO}_2}$  is the average absorption rate of CO<sub>2</sub> in the first 30 min and the average desorption rate of CO<sub>2</sub> in the first 10 min. Cyclic capacity ( $\Delta\alpha$ ) is defined as the CO<sub>2</sub> loading difference between the CO<sub>2</sub>-rich and CO<sub>2</sub>-lean solutions. Regeneration efficiency is expressed as the percentage of desorbed CO<sub>2</sub> with respect to the total CO<sub>2</sub> captured in the solution. Physical property data were obtained at 313 K. <sup>b</sup>Two CO<sub>2</sub>/N<sub>2</sub> gas mixture sources were used at a flowrate of 30 L/h in this work: (A) 42.0 ± 0.5% CO<sub>2</sub> and (B) 12.6 ± 0.5% CO<sub>2</sub>.

after desorption, with units in moles of CO<sub>2</sub> per kg of CO<sub>2</sub>-free absorbent solution. The average rate of CO<sub>2</sub> absorption in the first 30 min was also calculated based on the recorded data (see the Supporting Information).

The stability of the proposed absorbents was also investigated by means of several continuous cycles of absorption (313 K)–desorption (373 K) tests in order to give assessments of the long-term solvent behavior and CO<sub>2</sub> working capacity ( $\Delta\alpha$ ). In this case, after the 1st desorption run, the CO<sub>2</sub>-lean solution was used for the next absorption–desorption cycle instead of the fresh absorbent.

**Evaluation of Regeneration Energy Consumption.** The experimental apparatus for measuring the overall electrical energy ( $E_T$ ) required during solvent regeneration is shown in Figure S2. A similar apparatus and operating procedure were reported in our previous work.<sup>39,40</sup> A modified method for calculating the regeneration heat requirement was applied in this work.<sup>39</sup> Therefore, in the resultant CO<sub>2</sub>-lean solution after desorption, referred as the blank counterpart systems, the same desorption procedure was performed again to obtain the energy required without CO<sub>2</sub> desorption ( $E_0$ ) for each system. Aqueous 30% (5 M) MEA was used as a baseline case.

Electricity energy  $\Delta E$  (i.e.,  $E_T - E_0$ ) is referred as the difference between the measured electricity energy for the CO<sub>2</sub>-loaded and blank counterpart solution in the first 1 h under the same conditions, which is related to the combined electrical energy ( $\Delta Q$ ) for solvent vaporization and desorption heat. Therefore, the regeneration energy consumption, the unit in GJ t<sup>-1</sup> CO<sub>2</sub> or MJ kg<sup>-1</sup> CO<sub>2</sub> released, can be estimated by the sum of sensible heat  $Q_{\text{sen}}$ , reaction heat  $Q_{\text{reac}}$ , and latent heat of vaporization of the solvent  $Q_{\text{vap}}$  during CO<sub>2</sub> desorption, as below

$$Q_{\text{reg}} = Q_{\text{sen}} + Q_{\text{reac}} + Q_{\text{vap}} = (Q_1 + \Delta Q)/m_{\text{CO}_2} \quad (1)$$

$$Q_1 = m_s \times C_{p,s} \times \Delta T \quad (2)$$

$$\Delta Q = Q_2 + Q_3 = (E_T - E_0) \times \omega \times 3.6 \times 10^6 \quad (3)$$

$$\text{RE, \%} = Q_{\text{reg,i}}/Q_{\text{reg,baseline}} \times 100\% \quad (4)$$

where  $Q_1$ ,  $Q_2$ , and  $Q_3$  are the heat required for heating the solution, decomposition of CO<sub>2</sub>-loaded products, and vaporization of the solvent, respectively, in units of kJ.  $m_{\text{CO}_2}$  is the mass of the CO<sub>2</sub>

released.  $m_s$  is the mass of the solutions used, and  $C_{p,s}$  is the estimated specific heat capacity of the solutions from the pure components.<sup>36,41,42</sup>  $\Delta T$  was set to be 10 K for desorption at 373 K.  $E_T$  and  $E_0$  are the heat requirement for the CO<sub>2</sub>-loaded and corresponding blank solutions in the first 60 min during the regeneration process, respectively.  $\omega$  is the conversion factor of electricity to effective heat, and the value of 0.75 was assumed in this work. The relative energy consumption was used for evaluating regeneration energy consumption, which is defined as the  $Q_{\text{reg,i}}$  for a specific system divided by  $Q_{\text{reg,baseline}}$  for the aqueous 30% MEA system in the first 60 min during CO<sub>2</sub> desorption.

**Analytical Methods.** CO<sub>2</sub> loading of samples can be measured by acid titration using a modified Chittick CO<sub>2</sub> apparatus, shown in Figure S1c. <sup>13</sup>C NMR spectra and FTIR spectra were recorded using a Bruker Avance 500 spectrometer and a PerkinElmer Frontier FTIR spectrometer, respectively. The detailed methods can be found in the Supporting Information. It should be pointed out that deuterated dimethyl sulfoxide (DMSO-*d*<sub>6</sub>) was used as a deuterium lock solvent for nonaqueous samples in order to avoid the possible hydrolysis of carbamate.

## RESULTS AND DISCUSSION

**Comparison of Capture Performance of Aqueous and Nonaqueous Amines.** CO<sub>2</sub> absorption (313 K)–desorption (373 K) performance for aqueous and nonaqueous secondary amines with a constant molar concentration (i.e., 5.0 mol L<sup>-1</sup> at 298 K) was investigated under the same operating conditions at near atmospheric pressure. Two gas mixtures (i.e., 12.6 and 42.0 vol % CO<sub>2</sub>, balanced with N<sub>2</sub>) were used as the feed gas to simulate different CO<sub>2</sub> sources in this work. It should be noted that no purge gas was used during microwave desorption for CO<sub>2</sub>-loaded solutions. Aqueous 30 mass % MEA was used as a baseline case to compare and evaluate the effect of solvents on capture performance of the absorbents studied. Preliminary investigation showed that the MEA/EGBE system produced liquid–solid phase change after CO<sub>2</sub> absorption. A more detailed comparison cannot be carried out because of the different process procedures employed. Thus, this system was not considered in the present work. The



representative curves are shown in Figure 1 and the Supporting Information Figure S3. Results are summarized in Table 1.

It can be observed from Figure 1a that during CO<sub>2</sub> absorption for the 42.0% CO<sub>2</sub> feed gas, aqueous and nonaqueous amine systems showed excellent absorption efficiency (>90%) in the first 25 and 10 min, respectively. After that, the absorption efficiency decreased sharply down to about 15–20% at 40 min. In general, aqueous 5.0 M amine systems maintained the higher absorption efficiency than the corresponding amine/EGBE systems during the absorption process, which can probably be ascribed to different reaction products and the effect of viscosity of CO<sub>2</sub>-loaded systems on the gas–liquid mass transfer process. It was noted that the viscosity was increased for all systems after CO<sub>2</sub> absorption, but the viscosity of the nonaqueous systems increased much higher than that of aqueous systems, especially under high CO<sub>2</sub>-loading conditions, as presented in Table 1. It was also found that the loading capacity of aqueous secondary amine systems was about 2.7–3.0 mol/kg (i.e., 0.53–0.57 mol/mol amine), which was about 15% higher than that (about 2.4 mol/kg) for the 5 M MEA. Among these systems, aqueous EAE showed the best absorption capacity. However, all the nonaqueous secondary systems had a relatively low absorption capacity of about 2.0–2.2 mol/kg (i.e., 0.37–0.40 mol/mol amine). The absorption capacity of 5 M amine systems in a descending order at 313 K is EAE/H<sub>2</sub>O > MAE/H<sub>2</sub>O ≈ BAE/H<sub>2</sub>O > MEA/H<sub>2</sub>O > MAE/EGBE > EAE/EGBE ≈ BAE/EGBE. It is worth noting that the absorption capacity does not differ significantly with changing the alkyl chain length in the secondary alkanolamine structure. As for the 12.6% CO<sub>2</sub> feed gas, very similar trends are found in Figure S3. However, significant reduction in absorption rate was observed for all systems, in addition to small drops in absorption loading.

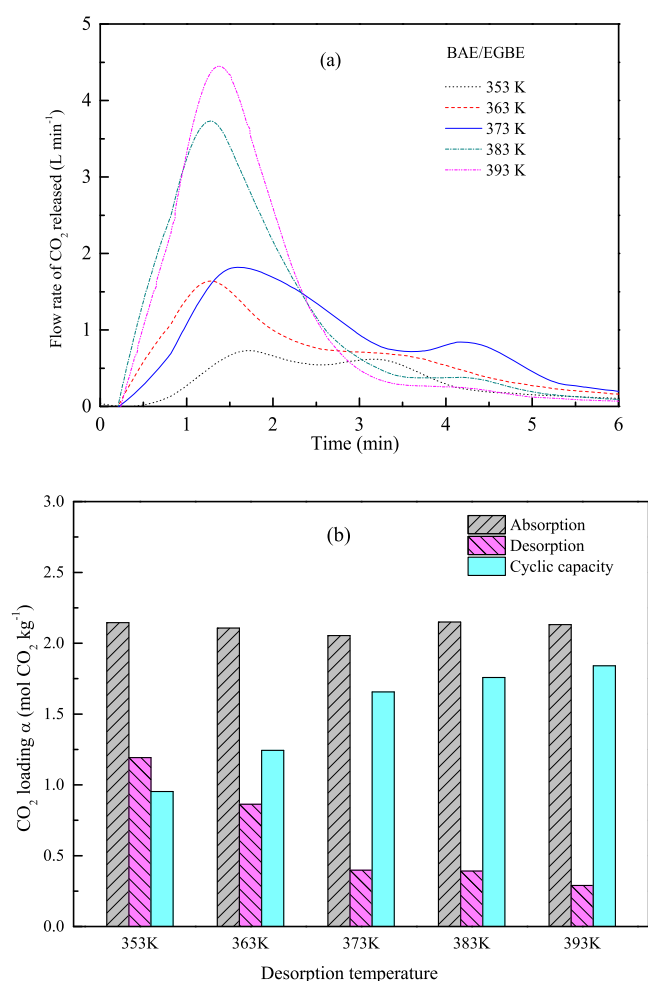
Figure 1b shows the profiles of instantaneous CO<sub>2</sub> flow of CO<sub>2</sub>-loaded absorbents under the same desorption conditions. Microwave heating is an effective way to heat the solution to 373 K from the starting point (about 343 K). The whole desorption process was generally completed in 10 min. It should be pointed out that the fluctuation of the desorption curve with two peaks at 1–2 and 4–6 min was probably due to the changing heating power when approaching the desorption temperature. The representative temperature profile was also shown along with the desorption rate. It was worth noting that the maximum values of the desorption rate were observed for all the systems in the first 3 min when the solution temperature was not higher than 365 K. The desorption rates are roughly in the order: EAE-based > BAE-based > MAE-based > MEA-based system. The observed sequence is quite similar to the results for the average desorption rate in the first 10 min. Compared with the nonaqueous systems, all the aqueous amine systems had much higher desorption rates in the last 5 min, which probably benefited from the gas flow effect of the water vapor for the solution at relatively low CO<sub>2</sub> loading.

Comparison of cyclic capacity is shown in Figure 1c. In this work, the calculated cyclic capacity for the 5 M MEA absorbent was about 0.8 mol CO<sub>2</sub>/kg solution. It was found that all the secondary amine systems presented much higher cyclic capacity (1.1–2.3 mol CO<sub>2</sub>/kg) in comparison with the primary amine system. It was noted that the carbon chain length of these secondary amines does affect their cyclic capacity, irrespective of the aqueous system or nonaqueous system. With increasing alkyl carbon on the amino atom of secondary alkanolamines, a clear increase in cyclic capacity was

observed, which was mainly ascribed to the increasing desorption efficiency because of the effect of steric hindrance on the product stability. The cyclic capacity for the studied absorbent in a descending order is as follows: BAE/H<sub>2</sub>O > EAE/H<sub>2</sub>O > BAE/EGBE > EAE/EGBE > MAE/H<sub>2</sub>O ≈ MAE/EGBE > MEA/H<sub>2</sub>O. Surprisingly, about 75–85% of regeneration efficiency was obtained for the BAE-based systems, as presented in Table 1 and Figure S4. However, aqueous 5 M MEA showed very low regeneration efficiency (about 30%) under the same operating conditions. As it is well known, the sensible heat required is related to the heat capacity and the cyclic capacity of the system used. High CO<sub>2</sub> cyclic capacity is favorable for reducing the regeneration energy. Taking advantages of EGBE with significantly low solvent vapor pressure under desorption conditions, BAE/EGBE and EAE/EGBE systems can also decrease the contribution of heat of evaporation of solvents to the overall regeneration energy consumption.

In order to verify the effect of desorption temperature on regeneration efficiency, additional experiments were performed for the nonaqueous BAE/EGBE system at increasing regeneration temperature from 353 to 393 K. Desorption experiments were carried out after CO<sub>2</sub> absorption under the same conditions for each fresh solution. A comparison of the desorption rate and the corresponding working capacity is shown in Figure 2. As expected, increasing the desorption temperature can increase significantly the desorption rate and the total amount of CO<sub>2</sub> released. Generally, the maximum desorption rate can be enhanced by a factor of 50% with 10 K increase in the investigated range. It was also noted that the desorption efficiency and cyclic capacity did not change a lot when the temperature was greater than 373 K, although the higher desorption temperature can shorten the effective desorption time. It can be seen that the increase in desorption temperature from 373 to 393 K caused a slight improvement in cyclic capacity, about 0.20 mol CO<sub>2</sub>/kg, but about 40% reduction in desorption time.

**Quantitative Analysis of Regeneration Energy Consumption.** It was noted that the regeneration energies measured in the literature varied a lot in different apparatus, even for the most commonly used 30% MEA. Although the finding is basically true that an absorbent consuming more regeneration energy in the lab-scale device will similarly require more energy industrially, the reported methods overestimate the real energy consumption to desorb the CO<sub>2</sub> because, in large part, of some unnecessary energies taking up a relatively large proportion in the total energy. These energies for heating the equipment, heat dissipation, and unnecessary solvent evaporation at relatively low CO<sub>2</sub> loading were generally lumped into the overall thermal energy consumption in the reported data, and their values fluctuated greatly in different devices. In this work, the cumulative overall electrical energies for heating the CO<sub>2</sub>-rich and CO<sub>2</sub>-lean (as a blank case) solutions were recorded, and their difference ( $\Delta E$ ) along the desorption time can be represented as the electrical energy required for desorption heat ( $Q_2$ ) and latent heat of solvent evaporation ( $Q_3$ ) during the regeneration step. This method can also minimize the effect of the heat dissipation at relatively high desorption temperature. A graphic representation is shown in Figure 3a. The sensible heat  $Q_1$  can be estimated from the reported specific heat capacity of the components and the reasonable temperature difference between the top and bottom of the desorption column. Thus, the regeneration

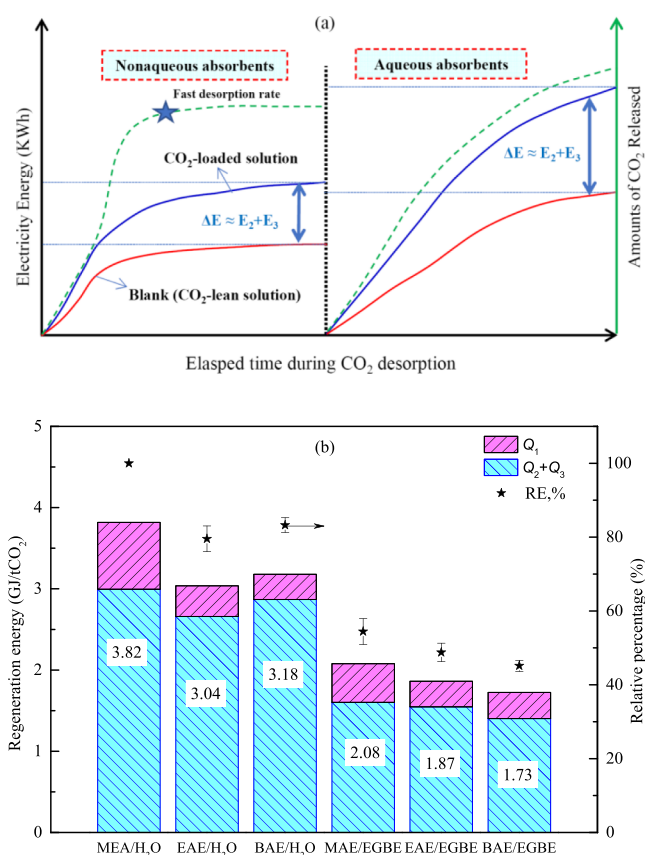


**Figure 2.** Effect of temperature on CO<sub>2</sub> desorption performance of the nonaqueous BAE/EGBE system: (a) desorption rate of CO<sub>2</sub> and (b) comparison of working capacities at various temperatures.

energy consumption  $Q$  (see eq 1) can be used here to compare the regeneration performances of different absorbents in a more reasonable approach.

Profiles of the cumulative amounts of CO<sub>2</sub> released, the accumulative electricity energy for the CO<sub>2</sub>-rich and blank solution, and the energy difference for each system are presented in the Supporting Information Figure S5, along with a baseline case of aqueous 5 M MEA for comparison. As can be seen, the cumulative amounts of CO<sub>2</sub> desorbed showed a negligible change for aqueous systems after 60 min and nonaqueous systems after 30 min. It is also worth noting that the slopes of the accumulative electricity energy curves of aqueous systems after 60 min are much higher than those of nonaqueous systems, which is possibly due to the higher evaporation rate of water than that of EGBE at 373 K. In order to compare on the same basis, the recorded data in the first 60 min were used for evaluation of their desorption performances. Comparison of regeneration energy consumption for aqueous and nonaqueous carbonated amine solutions is summarized in Table 2. All parameters required for estimation of the sensible heat  $Q_1$  are listed in the Supporting Information Table S2.

According to the results presented in Table 2, the regeneration heat for the aqueous 5 M MEA system was 3.82 MJ kg<sup>-1</sup> CO<sub>2</sub>, which was consistent with reported values of 3.7–4.3 MJ kg<sup>-1</sup> CO<sub>2</sub> without optimizing process



**Figure 3.** Regeneration energy consumption for CO<sub>2</sub>-saturated aqueous and nonaqueous systems at 373 K for 60 min. Absorption under the CO<sub>2</sub> partial pressure about 45.0 kPa at 313 K. (a) Graphic representation for calculation of the electricity energy required ( $\Delta E$ ) for vaporization of the solvent ( $Q_2$ ) and the energy required for the CO<sub>2</sub> desorption reaction ( $Q_3$ ). Note: The conversion factor of electricity to effective heat energy is assumed to be 75%. (b) Total regeneration energy of various absorbents in comparison with that of the baseline case (aqueous MEA).

configurations.<sup>43–45</sup> Clearly, there is a significant influence of the nonaqueous solvent instead of water on the total regeneration energy consumption ( $Q_{\text{reg}}$  in MJ kg<sup>-1</sup> CO<sub>2</sub>). The nonaqueous absorbents including MAE/EGBE (2.08 MJ kg<sup>-1</sup> CO<sub>2</sub>), EAE/EGBE (1.87 MJ kg<sup>-1</sup> CO<sub>2</sub>), and BAE/EGBE (1.73 MJ kg<sup>-1</sup> CO<sub>2</sub>) exhibited a significantly lower energy requirement for solvent regeneration, as shown in Figure 3b. The results also suggest that regeneration heat requirement is affected by sterically hindered secondary alkanolamines with different alkyl chain lengths. Additionally, the regeneration heat for all studied systems was also calculated using  $\omega = 100\%$ , as presented in the Supporting Information Table S3. The relative energy indicated that the EGBE-based absorbents can significantly reduce the regeneration heat requirement by 45.4–54.7% compared with aqueous 5 M MEA.

Although the BAE/H<sub>2</sub>O and EAE/H<sub>2</sub>O systems showed excellent absorption capacity and high cyclic capacity in the previous section, only 16.5–20% reduction in regeneration energy was achieved. It can be seen from Table 2 that the calculated difference ( $\Delta E$ ) of the overall electricity energy between the CO<sub>2</sub>-rich and CO<sub>2</sub>-lean solutions for aqueous systems is much higher than that for nonaqueous systems, especially for the BAE/H<sub>2</sub>O and EAE/H<sub>2</sub>O systems. The electrical energy required for decomposing the carbamate

Table 2. Comparison of Regeneration Energy Consumption for Aqueous and Nonaqueous Carbonated Amine Solutions

absorbent 5.0 M amine	run no.	CO <sub>2</sub> loading $\alpha$ (mol·kg <sup>-1</sup> )	CO <sub>2</sub> desorbed (mol)	electricity energy $\Delta E^a$ (kW h)	$Q_2 + Q_3^a$ (kJ)	$Q_1^b$ (kJ)	total thermal energy (kJ)	energy consumption ( $Q_{reg}$ ) (MJ/kg CO <sub>2</sub> )	relative energy <sup>c</sup> (%)
MEA/H <sub>2</sub> O	1	2.434	1.400	0.067	180.9	50.6	231.5	3.81	100
	2	2.384	1.427	0.071	191.7		242.3		
EAE/H <sub>2</sub> O	1	2.919	2.846	0.128	345.6	47.1	392.7	3.04	79.7
	2	2.972	2.877	0.120	324.0		371.1		
BAE/H <sub>2</sub> O	1	2.682	3.014	0.144	388.8	41.1	429.9	3.18	83.5
	2	2.678	2.953	0.135	364.5		405.6		
MAE/EGBE	1	2.132	1.437	0.035	94.5	30.0	124.5	2.08	54.5
	2	2.179	1.435	0.040	108.0		138.0		
EAE/EGBE	1	2.097	2.195	0.054	145.8	30.4	176.2	1.87	49.0
	2	2.079	2.128	0.055	148.5		178.9		
BAE/EGBE	1	2.075	2.121	0.048	129.6	29.9	159.5	1.73	45.3
	2	2.083	2.079	0.048	129.6		159.5		

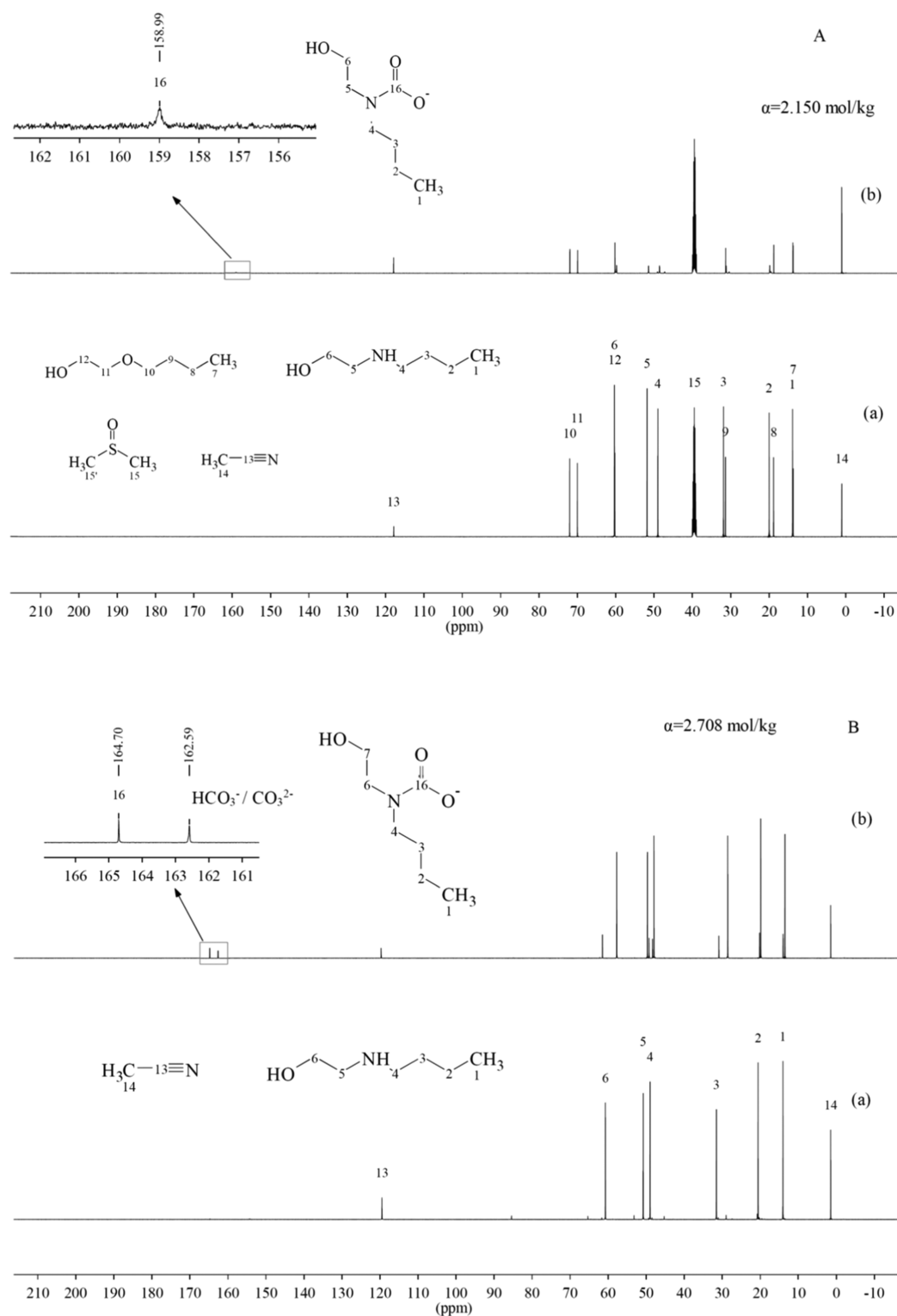
<sup>a</sup>Electricity energy  $\Delta E$  is referred as the difference between the measured electricity energy for the CO<sub>2</sub>-loaded and CO<sub>2</sub>-free solution in the first 1 h under the same conditions, which is related to the combined heat energy (i.e., vaporization heat  $Q_2$  and desorption heat  $Q_3$ ). The conversion factor of electricity to effective heat energy is assumed to be 75%. <sup>b</sup>Sensible heat ( $Q_1$ ) was estimated by the equation:  $Q_1 = m_s C_{p,s} \Delta T$ .  $\Delta T$  is generally the temperature difference between the bottom and top of the desorber column.  $m$  and  $C_p$  are the mass and the specific heat capacity of the solution for regeneration, respectively. Here,  $\Delta T$  was set to be 10 K. <sup>c</sup>Relative energy consumption (%) is defined as the required energy consumption for a specific system divided by the energy consumption for aqueous 5.0 M MEA as the baseline case (100%).

products and additionally evaporating the solvent along with CO<sub>2</sub> flowing for the studied absorbent had the following order: BAE/H<sub>2</sub>O > EAE/H<sub>2</sub>O > MEA/H<sub>2</sub>O > EAE/EGBE > BAE/EGBE > MAE/EGBE. However, the regeneration energy consumption is also strongly related to the quantity of CO<sub>2</sub> released at the same time. A descending order of CO<sub>2</sub> released in the first 60 min was observed as follows: BAE/H<sub>2</sub>O > EAE/H<sub>2</sub>O > BAE/EGBE ≈ EAE/EGBE > MAE/EGBE ≈ MEA/H<sub>2</sub>O. The results indicate that the substitution of hydrogen on the nitrogen in MEA by an alkyl group (i.e., methyl, ethyl, or butyl group) will lead to a significant decrease in stability of the carbamate product. The increasing steric hindrance by alkyl groups makes an unstable carbamate, resulting in the increasing desorption amount of CO<sub>2</sub>. In general, a low  $\Delta E$  and high quantity of CO<sub>2</sub> released will benefit for reducing the total regeneration energy consumption. Taking the BAE/H<sub>2</sub>O system as an example, the highest quantity of CO<sub>2</sub> released along with the highest  $\Delta E$  resulted in the combined energy ( $Q_2 + Q_3$ , in kJ kg<sup>-1</sup> CO<sub>2</sub>) at the similar level with aqueous MEA, as presented in the Supporting Information Table S4. Using the  $\Delta E$  method in this work, we also obtained the combined energy for the MEA/2-methoxyethanol (EGME) absorbent reported in our previous work.<sup>6</sup> A little higher  $\Delta E$  for MEA/EGME was observed than for all EGBE-based secondary amine systems. In general, all nonaqueous secondary amine systems performed with significantly low combined energy in comparison with aqueous primary amine, thanks in large part to the low desorption heat and the negligible vaporization of EGBE at the desorption temperature. Very similar results (Table S4) were also observed when desorption time was extended to 2.0 h.

As it is known, the sensible heat also plays an important role in the energy required for solvent regeneration. As shown from eqs 1 and 2, the sensible heat  $Q_{sen}$  is associated with the cyclic capacity and the heat capacity of the solution used. As can be seen from Table S2, the sensible heat requirement (in kJ) for aqueous systems is 36–65% higher than nonaqueous systems, mainly because of the larger specific heat capacity of water (about 4.183 kJ kg<sup>-1</sup> K<sup>-1</sup>) than that of EGBE (about 2.380 kJ kg<sup>-1</sup> K<sup>-1</sup>). It was noted that the BAE/H<sub>2</sub>O system had the

lowest sensible heat  $Q_{sen}$  among these absorbents, which is ascribed to its maximum quantity of CO<sub>2</sub> desorbed from the solution. The sensible heat for the MEA/H<sub>2</sub>O system was calculated to be 0.82 MJ kg<sup>-1</sup> CO<sub>2</sub>, which was consistent with reported values of 0.63–0.90 MJ kg<sup>-1</sup> CO<sub>2</sub>.<sup>26,44,45</sup> The calculated sensible heat  $Q_{sen}$  had the following order: MEA/H<sub>2</sub>O >> MAE/EGBE > EAE/H<sub>2</sub>O > BAE/EGBE ≈ EAE/EGBE ≈ BAE/H<sub>2</sub>O. As a surprising result, the sensible and combined heat requirement for the BAE/EGBE system was found to be about 0.32 and 1.40 MJ kg<sup>-1</sup> CO<sub>2</sub>, respectively, which was significantly reduced in comparison with that of the baseline case (the benchmark 5 M MEA solution). About 55% energy reduction reflects that the 5 M BAE/EGBE solvent has great potential for energy-efficient CO<sub>2</sub> capture in a large-scale application.

Additionally, comparison of BAE-based nonaqueous blends was performed. Ethanol and ethylene glycol were selected as two representative nonaqueous solvents. CO<sub>2</sub> absorption and desorption were operated under the same conditions for comparison. It should be pointed out that the regeneration for the carbonated BAE/ethanol was carried out at 353 K because of its low boiling temperature, while that of the BAE/EG solution was performed at 373 K for solvent regeneration. The representative desorption profiles are also shown in the Supporting Information Figure S5 and the results are summarized in the Supporting Information Table S5. Compared with the BAE/EG solvent, the BAE/EGBE system shows low viscosity and large CO<sub>2</sub> cyclic capacity. The dramatic high viscosity of carbonated BAE/EG blends would deteriorate the mass transfer in the absorption column and heat transfer in the heat exchanger. The regeneration energy consumption for these two nonaqueous systems was found to be at the same level. For the ethanol-based system, a significant evaporation amount of the solvent (about 50 mL of ethanol) was observed, resulting in huge latent heat during the regeneration step. Therefore, the BAE/ethanol system had a larger combined heat energy  $\Delta E$  (i.e., vaporization heat  $Q_2$  and desorption heat  $Q_3$ ) in comparison with the EGBE/BAE system under the same operating conditions. As a result, the



**Figure 4.**  $^{13}\text{C}$  NMR spectra of aqueous and nonaqueous BAE solutions. (A) CO<sub>2</sub>-free (a) and carbonated (b) BAE/EGBE samples in DMSO- $d_6$ . (B) CO<sub>2</sub>-free (a) and carbonated (b) aqueous BAE samples in D<sub>2</sub>O.

regeneration energy consumption of BAE/ethanol (about 2.27 MJ kg<sup>-1</sup> CO<sub>2</sub>) was about 25% higher than that of EGBE/BAE.

**Analysis of Product Species in Aqueous and Nonaqueous Solvents.** As already confirmed in the previous section, aqueous secondary amine solvents can achieve higher absorption capacity in mol/mol amine than the nonaqueous counterparts under the same absorption conditions. In order to

understand their different absorption behaviors by the replacement of water with the organic solvent EGBE,  $^{13}\text{C}$  NMR and FTIR characterizations were performed to verify the product species in nonaqueous and aqueous amine solvents during CO<sub>2</sub> absorption. Peak assignment was performed according to literature data.<sup>6,16,24,29,30,46–51</sup> In our previous work,<sup>6</sup> it was pointed out that misleading carbon signals could



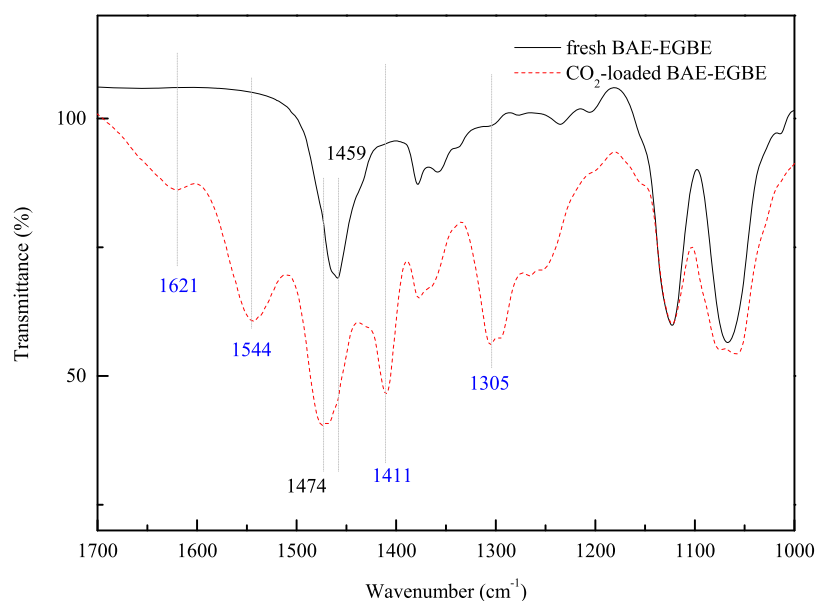


Figure 5. FTIR spectra of CO<sub>2</sub>-free and CO<sub>2</sub>-loaded BAE/EGBE solutions.

be found for the nonaqueous samples using D<sub>2</sub>O as an NMR solvent. DMSO-*d*<sub>6</sub> was used as a solvent instead of D<sub>2</sub>O for all the nonaqueous samples in order to prevent the carbamate hydrolysis. The representative <sup>13</sup>C NMR spectra of the BAE-based systems are shown in Figure 4 and those of other systems are shown in the Supporting Information Figures S6–S8. The CO<sub>2</sub>-free (a) and fully carbonated (b) samples at 30–50 kPa CO<sub>2</sub> partial pressure were prepared for nonaqueous (A) and aqueous (B) systems in these figures.

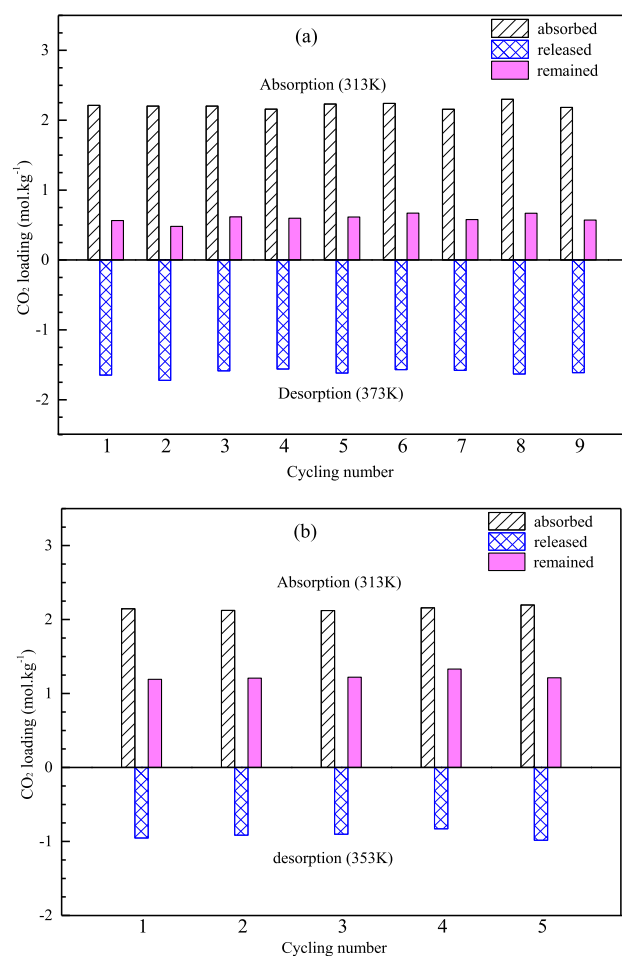
As can be seen in CO<sub>2</sub>-loaded aqueous primary and secondary amine samples, two new carbon signals appeared in sequence at about 164.5 and 162.5 ppm, which were assigned to the carbamate and HCO<sub>3</sub><sup>−</sup>/CO<sub>3</sub><sup>2−</sup> species, respectively. Because of carbamate hydrolysis to bicarbonate at relatively high CO<sub>2</sub> loading, comparable amounts of these species were found. In addition, a third <sup>13</sup>C peak was detected at 158.9 ppm in the spectrum of the EAE/H<sub>2</sub>O/CO<sub>2</sub> sample, which can be possibly assigned to the carbon of the alkyl carbonate species<sup>16</sup> or the hydrated CO<sub>2</sub> (H<sub>2</sub>CO<sub>3</sub>).<sup>47</sup> However, this new species was not found in other aqueous systems under the experimental conditions. With respect to nonaqueous samples, only one new carbon signal at 158.9–160.4 ppm was observed in the spectra at the CO<sub>2</sub> loading investigated. Other peaks near to the signals of pure secondary amines were observed because of the formation of carbamates. In the absence of water, CO<sub>2</sub> can react with secondary amines, only forming carbamates or carbamic acids or their mixtures.<sup>48</sup> These carbamate species under anhydrous conditions might not be much thermally stable than MEA carbamate in aqueous solution from three aspects. One is that the weak polar organics such as EGBE and DMSO might not stabilize well the ionic couples (amine carbamate and protonated amine), resulting in a greater equilibrium constant of the reaction. Thus, the system can easily recover the CO<sub>2</sub> and free amine. The other is due to the increasing steric hindrance of the alkyl chain length (*n* = 0, 1, 2, and 4) in the alkanolamine structures, H(CH<sub>2</sub>)<sub>*n*</sub>NH(CH<sub>2</sub>)<sub>2</sub>OH, which can enhance carbamate instability. Moreover, the reduced basic strength of amines in the low-dielectric constant solvent may decrease the activation

energy of CO<sub>2</sub> desorption.<sup>52</sup> It was also noted that the alkyl carbonate derivatives could not be detected in this work.

FTIR spectra before and after CO<sub>2</sub> uptake by nonaqueous secondary amine solutions are shown in Figure 5. Compared with the CO<sub>2</sub>-unloaded samples, three new characteristic peaks at approximately 1305, 1411, and 1544 cm<sup>−1</sup> were observed in the CO<sub>2</sub>-loaded BAE/EGBE, which were assigned to the C–N stretching of –NCOO<sup>−</sup>, the asymmetric ν<sub>C–N</sub> frequency of –NCOO<sup>−</sup> stretching, and asymmetric carbonyl (–COO<sup>−</sup>) stretching frequency, respectively.<sup>49–51</sup> These characteristic peaks implied the formation of the carbamate product in the solution. The weak shoulder peak at 1610–1645 cm<sup>−1</sup> could be attributed to NH<sub>2</sub><sup>+</sup> deformation of protonated amine or the alkyl carbonate species through a hydroxyl group.<sup>50</sup> Similar phenomena were also observed in the spectra of the CO<sub>2</sub>-loaded MAE/EGBE and EAE/EGBE solutions, as shown in the Supporting Information Figure S9.

**Solvent Stability.** Regenerability and long-term stability of the absorbents were initially investigated by solvent reuse in several absorption (313 K)–desorption (373 K) cycles. The representative cycling results for BAE/EGBE are shown in Figure 6. As can be seen, the absorption and desorption performance is relatively stable for the reused solvents in nine cycles, giving an average cyclic capacity of about 1.60 mol CO<sub>2</sub>/kg, which is also comparable with the result for the fresh solution in Table 1. This value is about 60% higher than that for the commonly used aqueous 5.0 M MEA. A high CO<sub>2</sub> working capacity is also beneficial for reducing the solvent circulation rate and lowering sensible heat requirement. A relatively stable change of conductivity was also observed for the solution before and after absorption, as presented in the Supporting Information Figure S10. The conductivity of the CO<sub>2</sub>-rich solution was about three times higher than that of the CO<sub>2</sub>-lean solution, which is indicative of the significant increase in ionic strength in the mixture. BAE carbamate can recover to free BAE and CO<sub>2</sub> during solvent regeneration, resulting in the decrease in electrical conductivity.

A low-temperature CO<sub>2</sub> capture technology could be a more effective use of waste heat or low-quality steam.<sup>53–55</sup> Thus, additional capture cycles were performed in order to verify the



**Figure 6.** CO<sub>2</sub> absorption–desorption cycling runs of 5.0 M BAE/EGBE solutions. CO<sub>2</sub> absorption at 313 K using a gas mixture containing 42% CO<sub>2</sub> and (a) thermal desorption at 373 K and (b) thermal desorption at 353 K.

feasibility of low-temperature desorption from the aspect of energy supply sources. As can be seen in Figure 6b, the regeneration at 353 K possessed a loading difference of about 0.92 mol CO<sub>2</sub>/kg, which is approximately equivalent to that of conventional aqueous MEA [under the conditions of absorption (313 K)–desorption (393 K)]. Using low-grade waste heat to desorb CO<sub>2</sub> from the nonaqueous absorbent instead of high-pressure steam is theoretically possible, in addition, preserving comparable desorption efficiency in comparison with aqueous MEA. It should be also noted that the proposed nonaqueous absorbent has a major drawback of greater cost of the EGBE cosolvent with respect to water. However, the cosolvent has negligible loss because of the low operating temperature and can be completely recycled. Low-temperature desorption can also offer several potential advantages in reducing amine thermal degradation, solvent evaporation, and equipment corrosion.<sup>54</sup> On the basis of preliminary experimental results, the proposed EGBE-based secondary amine absorbents demonstrated significant reduction in regeneration energy consumption or desorption temperature over the conventional aqueous MEA. Further investigation on CO<sub>2</sub> capture performance of these absorbents in packed columns is underway in our lab.

## CONCLUSIONS

In this study, nonaqueous amine absorbents containing secondary alkanolamines and the EGBE solvent were proposed for an energy-efficient CO<sub>2</sub> capture process. Aqueous secondary amines showed higher absorption capacity than nonaqueous systems, which is mainly due to the formation of bicarbonate species in addition to the ionic couples (i.e., protonated amine and carbamate) identified in nonaqueous solutions. Aqueous BAE had the highest desorption efficiency, resulting in the largest cyclic capacity in the studied systems. Nonaqueous EAE and BAE systems had about 20–25% reduction in absorption capacity and cyclic capacity but showed considerable decreases in regeneration heat compared to their aqueous counterparts. Taking advantages of the EGBE-based solution with low heat capacity, carbamate instability, and low volatility at desorption temperature, the regeneration energy consumption of nonaqueous EGBE/BAE was significantly reduced to about 1.73 MJ kg<sup>-1</sup> CO<sub>2</sub>, which is about 55% lower than that of aqueous MEA under the same operating conditions. Comparable capture efficiency with conventional amine scrubbing also makes the BAE/EGBE absorbent possible for low-temperature desorption as a compelling solution.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.0c06345>.

Estimation of the rate of CO<sub>2</sub> absorption, measurement of CO<sub>2</sub> loading, physicochemical property data of pure solvents, estimation of sensible heat requirement for various amine solutions during regeneration, comparison of regeneration energy consumption for various amine solutions at 373 K for 1 and 2 h, schematic diagram of the absorption–desorption and regeneration energy consumption apparatus, CO<sub>2</sub> absorption and desorption profiles for the gas mixture with 12.6% CO<sub>2</sub>, comparison of regeneration efficiency for aqueous and nonaqueous secondary amine systems, detailed profiles of solvent regeneration for CO<sub>2</sub>-rich and CO<sub>2</sub>-lean solutions at 373 K, <sup>13</sup>C NMR and FTIR spectra of CO<sub>2</sub>-free and CO<sub>2</sub>-loaded aqueous and nonaqueous amine systems, and variation in conductivity in nine cycling runs (PDF)

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## Notes

The authors declare no competing financial interest.

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