

CO₂ absorption and microwave regeneration with high-concentration TETA nonaqueous absorbents

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Abstract: While nonaqueous organic-amine absorbents have great potential in reducing energy consumption of CO₂ capture, their absorption/desorption behaviors are still poorly understood when high-concentration polyamines are used. On the other hand, large scale CO₂ capture demands the use of high-concentration polyamines absorbents. Therefore, we investigated the absorption and microwave regeneration behavior of high-concentration triethylenetetramine (TETA) in three typical organic solvents, including polyethylene glycol 200 (PEG200), diethylene glycol (DEG), and ethylene glycol (EG). The results showed that high-concentration TETA nonaqueous absorbents demonstrate advantages in absorption rate and regeneration energy consumption. The average absorption rate of 2.0 and 5.0 mol/L TETA/EG was 2.84 and 4.70 times that of 0.6 mol/L, respectively. The energy consumption of TETA/EG and TETA/DEG decreased by 29.4 and 25.6% as the concentration increased from 0.6 to 5.0 mol/L. In addition, the high-concentration TETA/PEG200 absorbent demonstrated observable tolerance for water vapor, which usually exists in flue gas. Results also showed that microwave regeneration was superior to conventional conduction heating especially when high-concentration TETA/PEG200 absorbent were used. The energy consumption of microwave regeneration of the absorbent with a concentration of 0.6, 2.0, and 5.0 mol/L was reduced by 65.9, 81.2, and 86.0%, respectively when compared with conduction heating. © 2022 Society of Chemical Industry and John Wiley & Sons, Ltd.

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Keywords: CO₂ absorption; high concentration absorbent; microwave regeneration; TETA nonaqueous solutions; the flue gas impurities

Introduction

In the past 200 years, global warming, mainly caused by rapid growth of population, destruction of vegetation, and the use of fossil fuels, has become a new challenge that human beings must face.^{1–4} Carbon dioxide (CO₂) is responsible for 66% of the radiative climate forcing by all greenhouse gases, and the global average atmospheric concentration of CO₂ reached 412 ppm in 2020.^{5–7} Carbon capture, utilization, and storage (CCUS) is an effective way to reduce carbon emissions and deal with global warming.^{8,9}

Chemical absorption using 30 wt% monoethanolamine (MEA) aqueous solutions is considered as a performance benchmark technology in industry for CO₂ capture.^{10–12} However, the aqueous absorbent has a large amount of solvent loss during the desorption process when operating temperature exceeds 120°C, which causes high energy consumption. Studies show that more than 60% of the total energy consumption in the entire CO₂ capture process is consumed in the regeneration process.¹³ Meanwhile, this technology also suffers from severe amine degradation and volatilization, and equipment corrosion.¹⁴

Recently, nonaqueous and water-lean absorbents have attracted widespread attention for its great potential in reducing energy consumption because of lower sensible heat and latent heat compared with traditional aqueous solution.^{15,16} For example, Bougie et al.¹⁷ studied the nonaqueous MEA solutions (20–70 wt%) in a mixture of ethylene glycol and 1-propanol (EG/PrOH), diethylene glycol monoethyl ether (DEGMEE), and N-methylformamide (NMF), and the 20 wt% MEA/DEGMEE solutions resulted in good CO₂ cyclic capacities and the lowest energy consumption, which was 78% lower than the traditional 30 wt% MEA aqueous solution. Chen et al.¹⁸ and Tian et al.¹⁹ studied the performance of 20 wt% [DETAH]Br and 0.5–5.0 M MEA in PEG200, respectively, indicating that nonaqueous absorbent has lower regeneration temperature and excellent corrosion-resistance. Furthermore, many studies on

phase-change absorbents have been reported.

Phase-change absorbents can significantly reduce the energy consumption in the regeneration step since only CO₂-rich phases must be regenerated. For example, Zheng et al.²⁰ and Tao et al.^{21,22} proposed two excellent liquid-solid phase-changing absorbents of TETA/ethanol and TETA/PEG200 by screening several amine/organic solvent combinations, and studied their CO₂ absorption and phase-changing behavior at 0.2–1 M. Zhou et al.²³ developed a nonaqueous liquid–liquid phase-changing absorbent of 2-((2-aminoethyl)-amino)ethanol (AEEA)/dimethyl sulfoxide (DMSO)/pentamethyldiethylenetriamine (PMDETA), which had a CO₂ absorption capacity of 1.75 mol/mol AEEA at 1 M, and the rich phase contributed 96.8% of the CO₂ capacity.

In addition to the development of new absorbents, researchers also applied the microwave heating to the CO₂ regeneration process, which has advantages of noncontact and rapid heating, high selectivity, and good controllability.^{24,25} Zhang et al.²⁶ investigated the absorption–desorption cycles with 0.5 M DETA/NMP using microwave heating, and the results showed that the system had a relatively stable cycling performance. Ping et al.²⁷ reported that the regeneration energy consumption of nonaqueous 2-(butylamino)ethanol (BAE)/2-butoxyethanol (EGBE) was significantly reduced to about 1.73 MJ kg^{−1} CO₂, which is about 55% lower than that of aqueous MEA under the same operating conditions using microwave heating. Li et al.²⁸ investigated the characteristics of microwave regeneration for nine TETA nonaqueous solutions at 0.6 M, and the results showed that the heating rate of a solution in the microwave was primarily affected by its viscosity, dielectric constant, and heat capacity. The energy consumption using microwave regeneration for 30 wt% TETA/BDO decreased by 69% compared to a 30 wt% MEA aqueous solution regenerated by conductive heating.

Although many new nonaqueous absorbents have been developed, only a few studies have mentioned their industrial application prospects. Studies have shown that increasing the concentration of MEA

aqueous solution was expected to reduce the energy consumption of CO₂ capture.^{29,30} At present, the concentration of nonaqueous absorbents used in most studies is less than 1 mol/L, especially polyamine absorbents with high absorption capacity.^{18,20,21,23,31,32} This is relatively low compared with the concentration of MEA aqueous solution (5 mol/L) in practical industrial application, so the absorption–desorption behavior of non-aqueous organic amine absorbents at high concentration still need to be studied.

Furthermore, flue gas impurities such as SO_x, NO_x, and water vapor have been proven to deactivate adsorbents during CO₂ capture, but there is still a lack of understanding of the effects on new absorbents.^{33–35} The flue gas usually contains water vapor. For nonaqueous absorbents, accumulation of water vapor in the system will inevitably affect the absorption–desorption performance.

Based on the above problems existing in the research of nonaqueous absorbents, in this work, we studied the absorption behavior of high-concentration TETA in three typical organic solvent absorbents, including polyethylene glycol 200 (PEG200), diethylene glycol (DEG), and ethylene glycol (EG). TETA was used considering its high absorption capacity, relatively low vapor pressure than MEA, and high regeneration efficiency as demonstrated in the studies.^{21,28,36–38} And the performance of MEA aqueous solution was compared. In addition, the microwave heating was used to study the regeneration performance of TETA absorbents, and the properties of microwave heating regeneration with high concentration nonaqueous absorbents were explored. Finally, the effect of water vapor in flue gas on TETA nonaqueous absorbents with high concentration was studied.

Materials and methods

Chemicals

Triethylenetetramine (TETA, ≥99.5%), ethylene glycol (EG, ≥99.7%), polyethylene glycol 200 (PEG200, ≥99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Monoethanolamine (MEA, ≥99%) and diethylene glycol (DEG, ≥99.0%) were purchased from Aladdin Chemistry Co., Ltd. Compressed CO₂ (≥99.99 vol%), and compressed N₂ (≥99.99 vol%) were purchased from Jingong Specialty Gases Co., Ltd. All the chemicals in this study were used without further purification.

Apparatus and procedures

CO₂ absorption experiments were carried out with 100 mL fresh solution of a specific concentration (0.6, 2.0, 5.0 mol/L) in a 500-mL three-necked flask. The flask is immersed in a water bath to maintain at reaction temperature (60°C), and the magnetic stirring ensured intensive mixing of the gas and liquid. The flow rate of pure CO₂ and simulated flue gas (15 vol% CO₂:85 vol% N₂) was controlled at 100 mL/min by the mass flow meters under the atmospheric pressure. The outlet gas flow rate was measured by soap-film flowmeter, and the concentration was measured by gas chromatograph (TCD, GC9750, Fuli Analytical Instrument Company). The reaction equilibrium is considered to be reached when the flow rates and concentrations of outlet and inlet gas are equal.

CO₂ desorption experiments were carried out in the same three-necked flask. The flask with saturated CO₂ absorbent was placed in the heating equipment, and was first swept with N₂ for 10 min. After the generated gas was condensed by the serpentine condenser tube, it was passed into a gas-washing bottle filled with concentrated sulfuric acid to remove the residual water vapor. Finally, the regeneration rate was measured by soap-film flowmeter. The loaded absorbents were regenerated by microwave heating using adjustable lab-microwave oven (MKX-H1C1B, Qingdao Microwave Creative Technology Co., Ltd). The maximum input power of the oven was 800 W. The oven is equipped with infrared temperature measurement and electromagnetic stirring, and its control panel can automatically record the input power and temperature at different time. There are two heating modes used in the experiments: (a) constant-power heating, heating power and time should be set, with no temperature control, only temperature monitoring. (b) Constant-temperature and pulse heating, heat-preservation temperature and power should be set, with the oven automatically controlling microwave start-stop. For conductive heating, the heating belt was wound around the outer surface of the flask. Heating temperature was automatically controlled by the heating belt, and input power was adjustable. Heating time was recorded. For the above two regeneration methods, the input power of equipment was used to calculate the energy consumption.

The viscosity of solutions was measured by a digital viscometer (NDJ-5S, Shanghai Bangxi Instrument

Technology Co., Ltd.). First, the viscosity of the solution to be measured was estimated and the corresponding test rotor was selected. Then 30 mL solution to be tested in the test cylinder was placed in a thermostatic water bath at 60°C. Later the solution and rotor were kept at 60°C, and the viscosimeter was turned on to measure and read the data.

Calculation and analysis methods

Assuming that N₂ was not absorbed by absorbents, the absorption rate of CO₂ of simulated flue gas was calculated using Equation (1):

$$r_{\text{abs}} = \frac{L \cdot (C_0 - C_1)}{1 - C_1} \quad (1)$$

where r_{abs} is the absorption rate of CO₂ (mL/min), L is the gas flow rate before absorption (100 mL/min in this work), C_0 and C_1 are the CO₂ molar fraction of the inlet and outlet gas respectively.

According to the ideal gas law, the absorption rate of pure CO₂ was determined by Equation (2):

$$r_{\text{abs}} = \frac{P \Delta V_{\text{CO}_2}}{RT} \quad (2)$$

where r_{abs} is the absorption rate of CO₂ (mol/min), P is ambient pressure (Pa), ΔV_{CO_2} is the volumetric flow difference value of inlet and outlet CO₂ (mL/min), R is the ideal gas constant, and T is absorption temperature (K).

The total absorption quantity N_1 was obtained by integrating r_{abs} with time, and N_2 was obtained by weighing the quality difference of absorbent before and after reaction. When the difference between N_1 and N_2 was less than 5%, the data were considered reliable. In this premise, the final absorption quantity N_{ab} was N_2 .

The solutions after regeneration experiments were titrated with hydrochloric acid, and the residual CO₂ was collected by drainage method. The total CO₂ regeneration quantity could be obtained by the difference between absorption quantity and the residual CO₂. After a complete absorption-desorption cycle, we could calculate the CO₂ recovery rate: $\text{RE} = N_{\text{de}}/N_{\text{ab}}$. The total energy consumption E (kJ) of the whole regeneration process was obtained by integrating heating power with time. The energy consumption per unit mass of CO₂ was determined as follows: $\text{EC} (\text{kJ/g}) = E/m$, where m is the regeneration mass of CO₂. It should be noted that because of the vast differences in microwave equipment and solution container used by different researchers, the measured regeneration

energy consumption is specific to the setup used in this work and therefore cannot be directly compared to values in other literature. But the energy consumption data in this study can be used to compare different TETA solutions as all experiments were performed under the same conditions.

Results and discussion

Absorption performance

Saturated absorption capacity and viscosity

As shown in Table 1 and Table 2, five absorbents with 0.6, 2.0, 5.0 mol/L were investigated in this study. The physical absorption capacity of three organic solvents is significantly higher than that of water, which is related to the molecular structure. The ether bonds in EG, DEG, and PEG200 molecules can promote absorption of CO₂.³⁹ There is no direct correlation between the chemical absorption of absorbents and physical absorption of corresponding solvents.

It can be seen from the results that water as a solvent has a significant advantage in terms of absorption capacity. The absorption capacity of MEA and TETA aqueous solutions can reach more than 95% of the theoretical maximum capacity. The concentrations hardly affect the absorption capacity of aqueous absorbents. For nonaqueous absorbent, when the concentrations of absorbents increase, the viscosity of absorbents increases significantly with the increase of concentration. But the effect of concentration on absorption capacity is not obvious. The most affected absorbent is TETA/PEG200, and its absorption capacity decreases by only 8% when concentration increases from 0.6 to 5.0 M. While absorption capacity of TETA/EG and TETA/DEG decreases by 2% and 4%, respectively.

Absorption rate

The CO₂ absorption rate and capacity of TETA nonaqueous solutions were measured at different concentrations and 60°C. The TETA and MEA aqueous solutions were also examined as a comparison. Results in Figure 1 show that for all five organic amine absorbents, the absorption rates first remain high for a certain time and then begin to decrease. When the concentration is higher, the high-rate absorption is maintained for a longer time. For the three nonaqueous absorbents, the maximum absorption rate of 0.6 M absorbents can only be maintained for about 10 min under the experimental conditions, while the 2.0 and

Table 1. Absorption capacity and phase change of five absorbents at different concentrations and 60°C.

Absorbents	Absorption capacity of organic solvents (g/kg)	Absorption capacity (mol CO ₂ /mol Amine)			Physical state after absorption
		0.6 mol/L	2.0 mol/L	5.0 mol/L	
MEA/H ₂ O	2.73	0.47	0.47	0.46	clear
TETA/ H ₂ O	2.73	1.91	1.90	1.90	clear
TETA/EG	4.01	1.74	1.72	1.72	clear
TETA/DEG	4.14	1.72	1.70	1.65	powder
TETA/PEG200	4.87	1.86	1.79	1.72	powder

Table 2. Viscosity of the five absorbents before and after absorption at different concentrations.

Absorbents	Liquid viscosity (mPa·s, 60°C)					
	0.6 mol/L		2.0 mol/L		5.0 mol/L	
	before	after	before	after	before	after
MEA/H ₂ O	1.3	4.7	2.5	6.4	2.7	9.2
TETA/ H ₂ O	1.4	6.5	3.5	8.4	4.4	10.3
TETA/EG	14.2	54.7	13.4	245	13.1	638
TETA/DEG	18.5	70.2	17.4	338	16.8	>1000
TETA/PEG200	23.4	26.8	21.5	>2000	20.1	>2000

5.0 M absorbents can maintain the maximum absorption rate for about 30 and 60 min. The absorbent at high concentration has an obvious advantage in absorption rate. Taking TETA/EG as an example, the average absorption rate of 2.0 and 5.0 M solution within 120 min is 2.84 times and 4.70 times that of 0.6 M, respectively. Because the higher concentration solutions contain more amine groups, and their total absorbed dose is larger under same conditions (Figure 2).

The absorption load of nonaqueous absorbents at high concentrations is significantly reduced (Figure 2), which may be attributed to the higher viscosity that increases the mass transfer resistance. However, this adverse effect will gradually weaken as the absorption time increases. For example, the absorption load of 5.0 M TETA/PEG200 at 20, 60, and 120 min is 16.2, 31.4, and 49.7% of 0.6 M TETA/PEG200, respectively. Therefore, when researching or using high-concentration absorbents, the absorption time can be appropriately extended under the premise of ensuring a certain absorption rate.

Microwave regeneration performance

Regeneration rate

The regeneration behavior of the absorption product was investigated by microwave constant-power heating mode under 160 W and 15 min. The desorption rate–time curves of the five absorbents at different concentrations and the total regeneration CO₂ volume within 15 min are shown in Figure 3. For the five CO₂-loaded absorbents, microwave heating at 160 W for 15 min is still not enough to regenerate completely. During the heating time of 15 min, the regeneration rate of the five absorbents in the first 8 min was relatively low, and increased significantly after 8 min. This is because at the beginning of heating, the temperature of solutions is relatively low and the viscosity is relatively high. After the temperature rises to the temperature at which the product can decompose, the carbamate begins to decompose and a large amount of CO₂ gas is released.

The maximum regeneration rate of TETA/PEG200 at three different concentrations is about 120 mL/min.

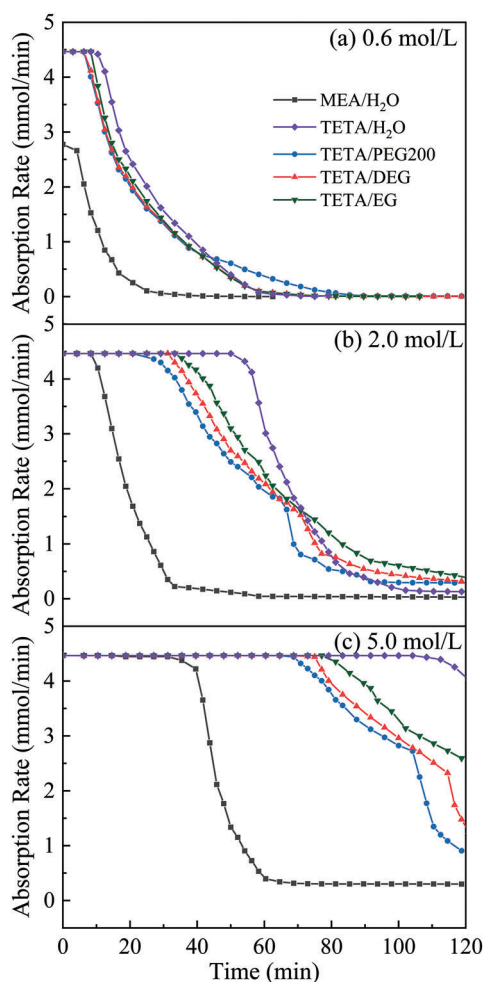


Figure 1. Absorption rates-time curves of five absorbents at concentrations of (a) 0.6 mol/L; (b) 2.0 mol/L; (c) 5.0 mol/L and 60°C.

This indicates that when the microwave power is determined, the maximum regeneration rate is not affected by the concentration of absorbent. Nonaqueous absorbents exhibit much higher regeneration rate than aqueous absorbent at all concentrations, with the best performance being that of TETA/PEG200 absorbent. The total regeneration CO₂ volume of TETA/PEG200 at 0.6, 2.0, and 5.0 M is 9.13, 7.20, and 7.10 times that of TETA/H₂O, respectively.

Regeneration energy consumption and cyclic performance

The nonaqueous CO₂-loaded absorbents at different concentrations were completely regenerated by microwave pulse heating under 400 W and 120°C, and the result is shown in Figure 4(A). Among the three

absorbents, TETA/PEG200 has the best regeneration performance. The dielectric constant can be used to measure the ability of a medium to absorb microwave energy. In general, the dielectric constant of liquid rises with the increase in temperature. In the temperature range we studied, the differences in the dielectric constant due to temperature changes was slight relative to those for different organic solvents. So, we directly quoted the dielectric constant measured at 20°C from the literature.^{28,40} It can also be seen from Figure 4(B) that the excellent regeneration performance of TETA/PEG200 can be explained by the extremely low dielectric constant of PEG200. Due to high dielectric constant and heat capacity of H₂O, the energy consumption of the aqueous solution is much greater than that of nonaqueous absorbents, so aqueous absorbents are not suitable for microwave regeneration. In our previous work, it was found that the regeneration energy consumption of amine-organic solvent absorbent is positively correlated with the dielectric constant of the solvent,²⁸ which is consistent with this work.

The results in Figure 4(A) show that the concentration has a significant impact on the regeneration performance of the organic-amine nonaqueous absorbents. The CO₂ recovery decreases slightly with the increase of amine concentration. The CO₂ recovery of three nonaqueous absorbents only dropped by less than 5% as the concentration increased from 0.6 to 5.0 M. Although it has a slight adverse effect on the CO₂ recovery, increasing the absorbent concentration can significantly reduce the regeneration energy consumption. The microwave energy absorbed is primarily used as sensible heat to raise the temperature of a solution rather than to dissociate CO₂.^{24,28} As the concentration increases, total energy consumption does not increase much in same absorbent but more CO₂ can release from solutions. For TETA/DEG and TETA/EG, the regeneration energy consumption is reduced by 25.6 and 29.4% as the concentration increased from 0.6 to 5.0 M. For TETA/PEG200, the energy consumption is reduced by 21.7% as the concentration increased from 0.6 to 2.0 M. When the concentration is further increased to 5.0 M, the regeneration energy consumption increases instead, which may be attributed to the high viscosity of 5.0 M solution. When the absorption load is 0.5 mol CO₂/mol amine, the viscosity of 5.0 mol/L TETA/PEG200 is 1355 cp at 60°C, which is much higher than that of 2.0 mol/L TETA/PEG200 as 102 cp.

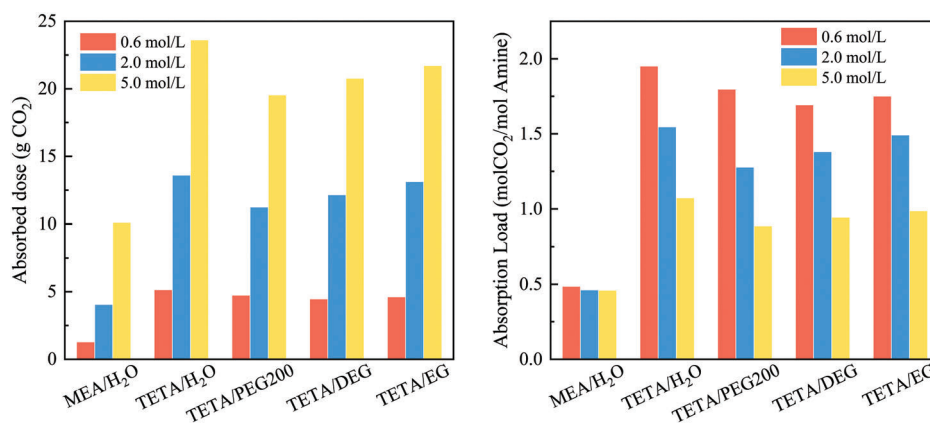


Figure 2. Absorbed dose (left) and Absorption load (right) of five absorbents at 0.6 mol/L, 2.0 mol/L, 5.0 mol/L concentrations and 60°C in 120 min

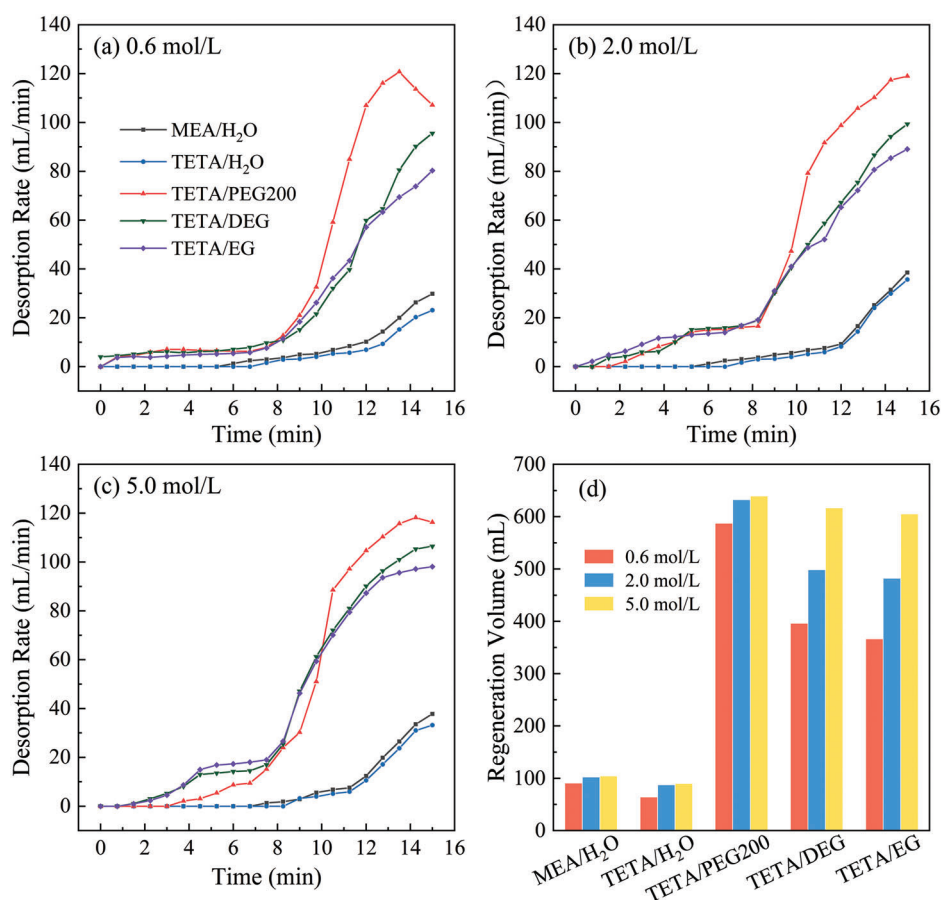


Figure 3. CO₂ Regeneration curves of different concentrations at 160 W microwave: (a) 0.6 mol/L; (b) 2.0 mol/L; (c) 5.0 mol/L; (d) Total regeneration CO₂ volume of absorbents in 15 min.

Studies have shown that in high-viscosity media, the corresponding speed of molecules to high-frequency oscillating electromagnetic fields such as microwaves will be slower.^{41,42}

Four absorption–desorption cycles for TETA nonaqueous solution with different concentration were conducted to evaluate the cyclic regeneration performance by microwave regeneration. The results in

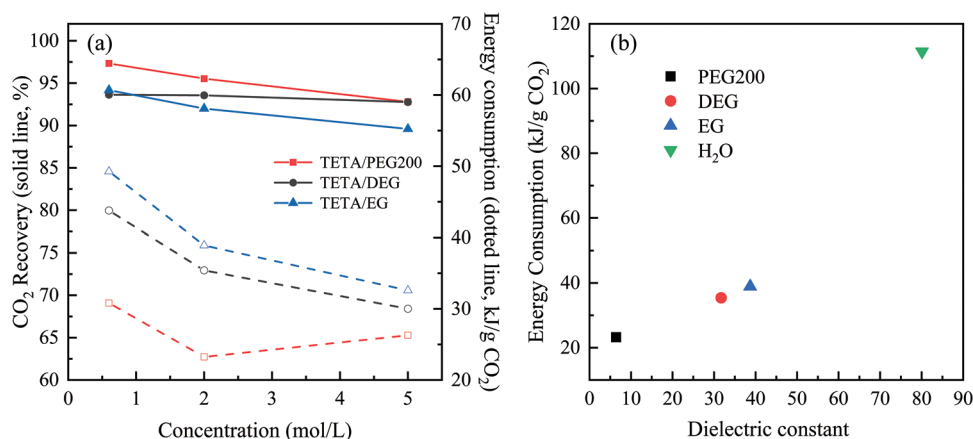


Figure 4. (a) Energy consumption and CO₂ recovery of different concentrations of absorbent under 400 W microwave; (b) Relationship between energy consumption and solvent dielectric constant (20°C, 2.45 GHz) for 2.0 mol/L TETA solutions.

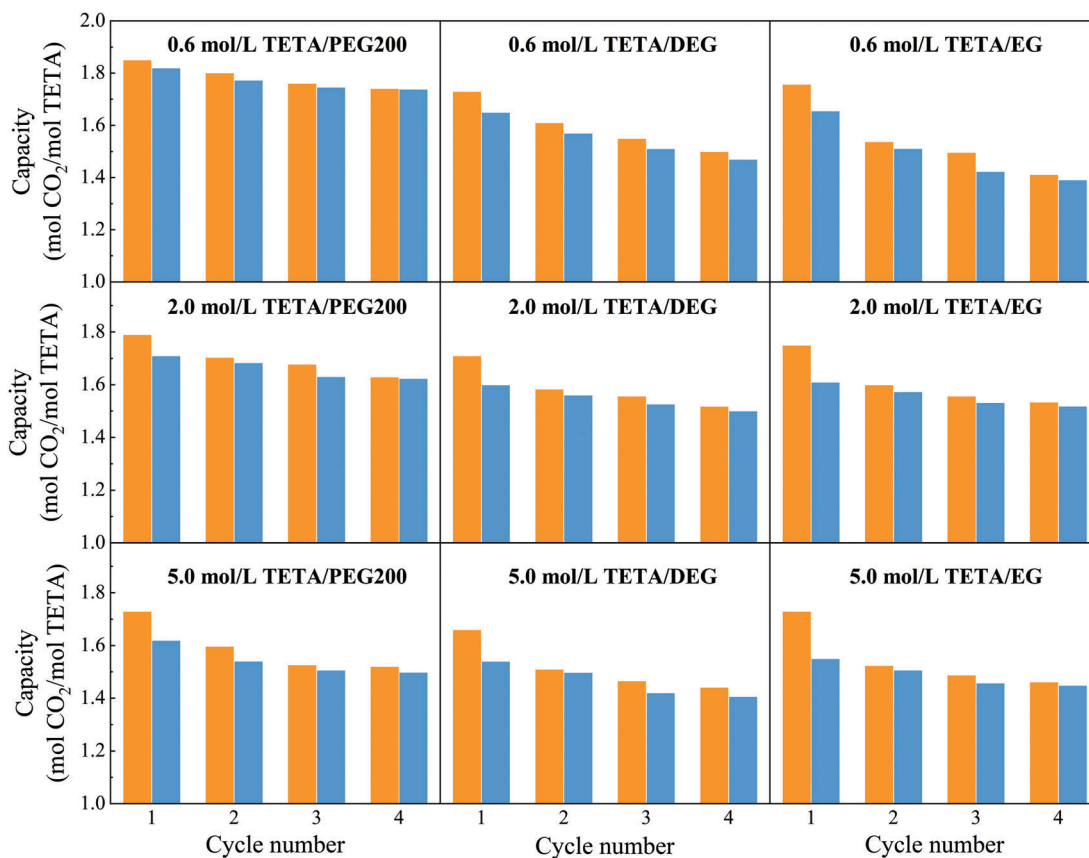


Figure 5. Absorption (orange bars) and desorption (blue bars) capacity of CO₂ for cyclic runs of TETA nonaqueous solution with different concentration at 120°C by microwave regeneration.

Figure 5 show that the absorption–desorption capacity of TETA nonaqueous solutions with three concentrations became relatively stable during the third and fourth cycles. The CO₂ recovery of 0.6, 2.0, and 5.0 M solutions over four cycles maintains a range

of 82.9–93.9, 82.9–90.7, and 82.0–86.6%, respectively, which are much higher than that found for a 30 wt% MEA aqueous solution (about 50%).⁴³ It can be seen that microwave heating regeneration has a very good regeneration effect for organic-amine nonaqueous

Table 3. Microwave regeneration and conduction heating regeneration performance of TETA/PEG200.

Concentration (mol/L)	Microwave heating			Conductive heating		
	time (min)	RE ^a (%)	EC ^b (kJ/g CO ₂)	time (min)	RE (%)	EC (kJ/g CO ₂)
0.6	10.5	94.22	32.04	35.4	42.35	93.83
2.0	19.1	91.54	24.91	49.8	36.51	132.31
5.0	29.7	84.73	31.26	85.4	21.42	224.15

^a RE: CO₂ recovery.
^b EC: energy consumption.

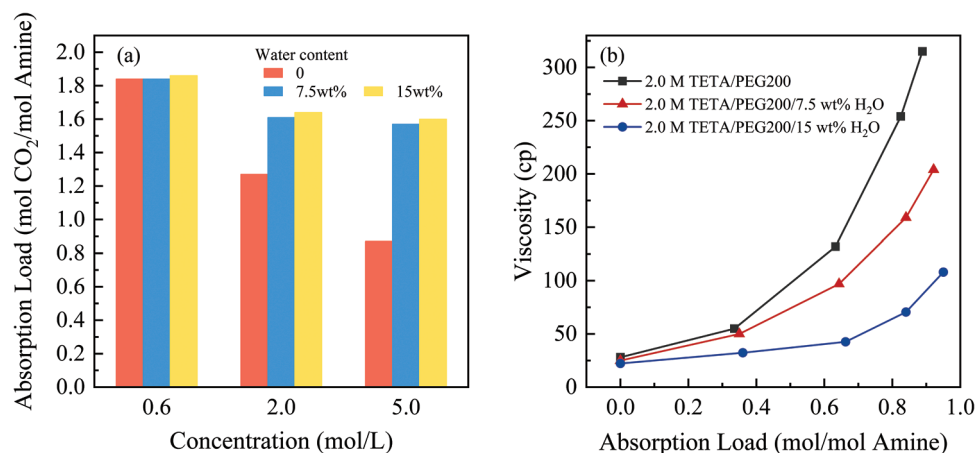


Figure 6. (a) The absorption load of TETA/PEG200 with different concentrations and water contents in 120 min; (b) Absorbent viscosity-absorption load curves of 2.0 M TETA/PEG200 with different water content (60°C).

absorbents. Unless the viscosity of the absorption product is too large (> 1000 cp), increasing the concentration can slightly reduce the CO₂ recovery in exchange for lower regeneration energy consumption.

Comparison of microwave and conduction heating regeneration

TETA/PEG200, considering its better regeneration performance, was selected to compare the performance of microwave and conduction heating regeneration under 400 W and 120°C. The results are shown in Table 3. For the TETA/PEG200, microwave heating has obvious advantages over traditional conduction heating regeneration. When the concentration is 0.6, 2.0, and 5.0 M, the CO₂ recovery of microwave regeneration is 2.22, 2.51, and 3.96 times that of conduction heating regeneration, respectively, and the energy consumption is reduced by 65.9, 81.2, and 86.0%.

The advantages of microwave heating over conduction heating regeneration increase with the

increase of concentration. This is mainly because the heat of microwave heating comes from the collision and vibration of the molecules. Thus, the heating is uniform, and the surface and interior of solutions begin to heat up at the same time. Although there is microwave loss, it is less affected by the physical properties of solutions compared to the conduction heating that gradually heats solutions from the outside to the inside. The high-concentration absorbents are not suitable for conductive heating due to high viscosity. While the microwave heating will be less affected by viscosity, and the advantages will be more obvious.

Effect of water vapor on TETA nonaqueous absorbents

Effect on absorption performance

Typical flue gas in postcombustion process usually contains 5–7 wt% water vapor.⁴⁴ The TETA/PEG200 of different concentrations was mixed with 7.5 and 15

wt% water to simulate an absorbent that enriched a certain amount of water after a period of absorption–desorption cycles. The results in Figure 6(A) show that water can accelerate the absorption rate of TETA/PEG200, increase the absorption load, and has a more obvious impact on high-concentration absorbents. When the 2.0 M and 5.0 M TETA/PEG200 are mixed with 7.5 wt% water, the absorption load is increased by 27 and 80%, respectively, compared with nonaqueous absorbent. As the water content is further increased to 15 wt%, the absorption load only increases slightly. It can be seen that the presence or absence of water has a greater impact on the absorption load, but the impact of water content is not obvious.

The absorption products of 2.0 M TETA/PEG200 with three water contents were tested by ¹³C-NMR, and the results are shown in Figure 7. The four groups of peaks in the range of 163.74–164.77 ppm are formed by the carboxyl carbon in the carbamate, indicating that the product contains a variety of carbamates, which are formed by the combination of different amino groups in TETA molecule and CO₂. The carbonyl carbon signal at 160.31 ppm is the peak formed by alkyl carbonate, which proves that PEG200 not only acts as a solvent but also participates in the CO₂ absorption reaction as a reactant.²¹ The comparison of the three graphs shows that adding water to TETA/PEG200 does not affect the types of products obtained from the absorption reaction.

The promoting effect of water on absorption may be due to the decrease in the viscosity of the water-less absorbent, which reduces the mass transfer resistance. As shown in Figure 6(B), the viscosity of the absorbent decreases with the increase of water content. It is known that the viscosity of the solution is closely related to the viscosity of each component (background viscosity) and interactions among molecules. The viscosity of H₂O, TETA and PEG200 is respectively 1.0, 28.2, and 62.2 cp at 20°C as measured by a digital viscometer. Therefore, the background viscosity of TETA/PEG200 solution decreases greatly with the addition of water. In addition, the number of hydrogen bonds in the system with different water contents was studied by molecular dynamics simulation. The details of calculation method are given in the supporting Information. The viscosity of PEG200 being a self-associated liquid is very high because of a good hydrogen bond ability.^{45,46} The hydroxyl and ether bonds in PEG200 and the amine groups in TETA can

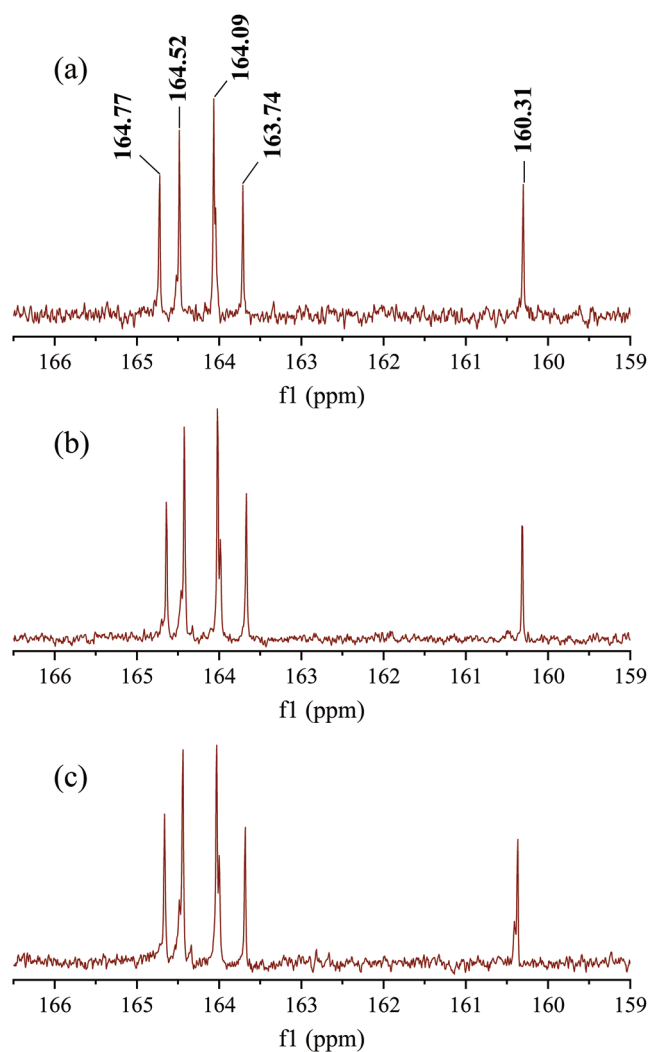


Figure 7. ¹³C NMR spectra of products after CO₂ absorption by TETA/PEG200 with different water contents: (a) none water; (b) 7.5 wt%; (c) 15 wt%.

form intermolecular hydrogen bonds well. Results in Table S2 show that the number of hydrogen bonds in PEG200-PEG200 and TETA-PEG200 interactions decreases as the water content increases. This demonstrates that the intermolecular hydrogen bond network in TETA/PEG200 is disrupted when H₂O is introduced, which may result in the decrease of viscosity.

Effect on desorption performance

The TETA/PEG200 solutions with different water content and concentration were regenerated by microwave heating at 400 W and 120°C, and the results are shown in Figure 8. As explained in section 3.2, aqueous absorbents are not suitable for microwave

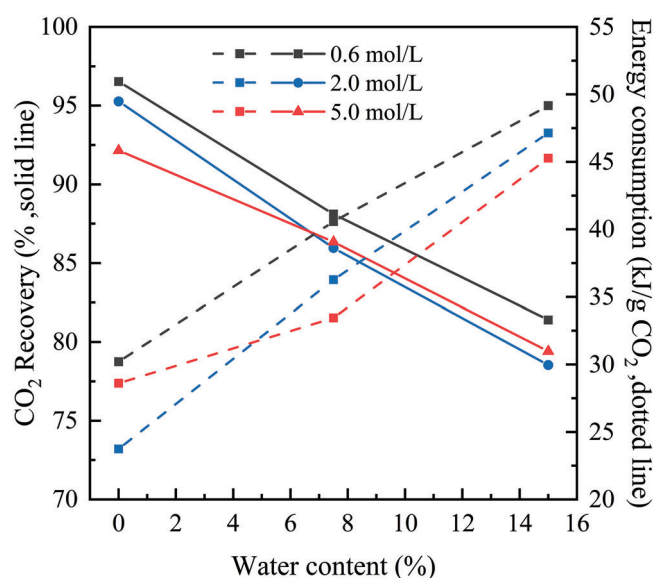


Figure 8. CO₂ recovery and energy consumption of TETA/PEG200 with different concentration and water content.

regeneration. Therefore, the addition of water in TETA/PEG200 will inevitably lead to a decrease in CO₂ recovery and an increase in energy consumption. But in the low water content range (e.g., 0–7.5 wt%), the effect on the high-concentration absorbent is relatively small. It can be seen from Figure 8 that when the water content of the solution increases from 0 to 7.5 wt%, the energy consumption of TETA/PEG200 at 5.0 M increases by 16.9%, which is significantly less than 34.3% at 0.6 M and 52.8% at 2.0 M.

Therefore, for low-concentration absorbents, it should be considered in practical applications to remove water and control a certain amount of water after the water content in the absorbent reaches a certain level. However, when the concentration of the absorbent required by the process is very high, a small amount of water (e.g., 0–7.5 wt%) in the absorbent has less effect on regeneration performance compared with low-concentration absorbent. But it can effectively improve its absorption performance and improve the physical properties of the absorbent (mainly to avoid the formation of paste solid with extremely high viscosity during the absorption process).

Conclusion

Developing nonaqueous absorbents for CO₂ capture have received lots of attentions in recent years. However, there are still great differences between

current research conditions and industrial application, such as the low amine concentration used, the single regeneration route, and the influence of flue gas impurities. Based on these problems, this work studied the absorption and microwave regeneration performance of three typical TETA nonaqueous absorbents at high concentrations and the influence of water vapor. The results indicated that high-concentration TETA nonaqueous absorbents had obvious advantages in absorption rate, and the average absorption rate of 2.0 mol/L and 5.0 mol/L TETA/EG was 2.84 and 4.70 times that of 0.6 mol/L, respectively. High-concentration absorbents showed lower regeneration energy consumption. For TETA/DEG and TETA/EG, the regeneration energy consumption was reduced by 25.6 and 29.4% as the concentration increased from 0.6 to 5.0 M. The advantages of microwave heating over conduction heating regeneration increased with the increase of concentration. When the concentration of TETA/PEG200 was 0.6, 2.0, and 5.0 M, the energy consumption of microwave regeneration was reduced by 65.9, 81.2, and 86.0% compared with conduction heating, and CO₂ recovery of microwave regeneration was 2.22, 2.51, and 3.96 times that of conduction heating. However, the absorption load decreased due to the increase of viscosity of high-concentration absorbents. The flue gas usually contains water vapor, which reduced the viscosity of high-concentration nonaqueous absorbent and increased the absorption load but did not affect the types of reaction products. The addition of water in TETA/PEG200 led to a decrease in CO₂ recovery and an increase in energy consumption. But in the low water content range (e.g., 0–7.5 wt%), the effect on the high-concentration absorbent is relatively small. These results indicate that high-concentration TETA nonaqueous absorbents have the potential to capture CO₂ with high efficiency and low energy consumption.

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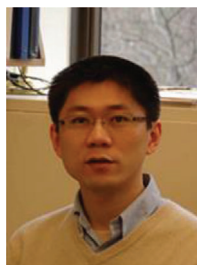
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