

Novel Nonaqueous Liquid–Liquid Biphasic Solvent for Energy-Efficient Carbon Dioxide Capture with Low Corrosivity

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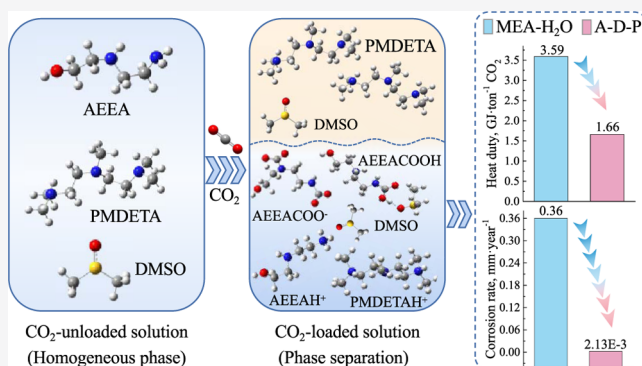


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ABSTRACT: To address the problems of the relatively high energy penalty and corrosivity of aqueous biphasic solvents, a novel nonaqueous biphasic solvent composed of 2-((2-aminoethyl)-amino)ethanol (AEEA), dimethyl sulfoxide (DMSO), and *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA) was proposed for CO₂ capture. With optimization, this novel AEEA–DMSO–PMDETA (A–D–P) biphasic solvent could achieve a high CO₂ loading of 1.75 mol·mol^{−1}, of which 96.8% of the absorbed CO₂ was enriched in the lower phase with only 49.6% of the total volume. ¹³C NMR analysis and quantum calculations revealed that A–D–P could absorb CO₂ to form not only carbamate but also carbamic acid species, which were stabilized by DMSO via hydrogen-bonding interactions. Most products were highly polar and preferred to dissolve in polar DMSO rather than the less polar PMDETA, thus leading to the phase change. The thermodynamics results showed that the heat duty of A–D–P was only 1.66 GJ·ton^{−1} CO₂ (393.15 K), which was significantly lower than that of the benchmark MEA (3.59 GJ·ton^{−1} CO₂) and the reported aqueous biphasic solvents. Moreover, A–D–P presented a noncorrosive behavior to steel after CO₂ saturation, clearly showing its superiority over MEA and the aqueous biphasic solvents. Therefore, with superior properties of energy savings and noncorrosiveness, the A–D–P biphasic solvent could be a promising candidate for CO₂ capture.



1. INTRODUCTION

The consumption of fossil fuels for energy leads to massive anthropogenic emissions of carbon dioxide (CO₂), which aggravates global warming.^{1,2} The development of efficient carbon capture, utilization, and storage (CCUS) technologies is a crucial remedial measure to address the problem of CO₂ emissions.³ The key step of CCUS technologies is to capture CO₂ from flue gas. Chemical absorption, especially monoethanolamine (MEA)-based absorption, is currently the most advanced method for capturing CO₂.^{4–6} However, the MEA-based process is limited in industrial applications because of its downside of a high energy penalty for solvent regeneration. For example, the benchmark 30 wt % MEA aqueous solution suffers from a high regeneration energy requirement of 3.7 GJ·ton^{−1} CO₂, which accounts for 60–80% of the total energy consumption.^{7,8} A large quantity of energy is consumed in the heating and vaporization of the solvent water.⁹ Thus, the development of energy-efficient absorbents is urgently required.

In recent years, biphasic solvents have been proposed as potential candidates for energy-efficient CO₂ capture. This new type of absorbent mainly contains three categories: thermomorphic biphasic solvents,^{10,11} liquid–solid biphasic solvents,^{12,13} and liquid–liquid biphasic solvents.^{14–16} Among these, the liquid–liquid biphasic solvent has received the most

attention.^{15,16} Typically, it can undergo a phase transition from one homogeneous phase to two immiscible liquid phases after loading CO₂, and the majority of the absorbed CO₂ is enriched in one phase (a CO₂-rich phase).^{17,18} Therefore, the energy requirement for solvent regeneration will be significantly reduced because only the CO₂-rich phase needs to be sent to the desorber.

In general, the liquid–liquid biphasic solvent is an aqueous amine blend, which can be prepared by dissolving a primary amine and a tertiary amine in water. The primary amine functions as an absorption accelerator to provide a high CO₂ absorption rate, and the tertiary amine mainly serves as a CO₂ sink to facilitate the formation of two phases, while the solvent water is responsible for reducing the viscosity of the solution.¹⁹ To date, biphasic solvents such as triethylenetetramine (TETA)-2-((diethylamino)ethanol)-H₂O,^{20–22} TETA-*N,N*-dimethylcyclohexylamine-H₂O,²³ diethylenetriamine (DETA)-

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N,N,N',N'',N'' -pentamethyldiethylenetriamine (PMDETA)- H_2O ,²⁴ TETA- N,N,N',N' -tetramethyl-1,3-propanediamine- H_2O ,²⁵ and so forth, have been proposed to achieve a relatively low regeneration heat of 1.83–2.50 GJ·ton^{−1} CO₂ for CO₂ capture. However, for these biphasic solvents, in almost all cases, their CO₂-rich phases were aqueous, and a considerable energy requirement was inevitably consumed in the heating and vaporization of water during CO₂ desorption because of the high heat capacity and vaporization enthalpy of water.²⁶ In addition, like the benchmark MEA aqueous solution, the aqueous CO₂-rich phase of these biphasic solvents might still suffer from non-negligible equipment corrosivity.^{15,27} Therefore, it is essential to improve the biphasic solvent in terms of the regeneration heat duty and corrosivity.

Nonaqueous absorbents, which are composed of amines and organics, have recently attracted increasing attention. Researchers found that using organics as diluents could significantly save energy associated with absorbent regeneration because the organic diluents possessed a lower heat capacity, vapor pressure, and vaporization enthalpy compared to water.^{28–30} Moreover, in the absence of water, amines could absorb CO₂ to generate noncorrosive products via specific reaction pathways. As a result, nonaqueous absorbents could have a significant advantage of a low corrosivity compared to aqueous absorbents.^{31,32} Inspired by the above findings, it will be of great significance to develop nonaqueous liquid–liquid biphasic solvents, which are expected to combine the advantages of the nonaqueous absorbent and the biphasic solvent, achieving energy-efficient and noncorrosive CO₂ capture. However, to date, information about nonaqueous liquid–liquid biphasic solvents is sparse in the open literature.

Therefore, the present work attempts to develop a nonaqueous liquid–liquid biphasic solvent, which is expected to achieve energy-efficient and noncorrosive CO₂ capture. To develop this novel biphasic solvent, the key is to find a suitable combination of an absorption accelerator, a CO₂ sink, and an organic diluent from numerous chemicals. After an elaborate screening, a novel nonaqueous biphasic solvent composed of 2-((2-aminoethyl)amino)ethanol (AEEA), dimethyl sulfoxide (DMSO), and PMDETA is proposed for CO₂ capture in this work. AEEA with two amino groups serves as the absorption accelerator to ensure a high CO₂ absorption rate and loading.^{33,34} DMSO, which has a low heat capacity and vaporization enthalpy and a high chemical stability,³⁵ acts as the diluent to reduce the energy consumption, and PMDETA functions as the phase-splitting agent. For this novel biphasic solvent, the relationship between the phase change behavior and the CO₂ absorption performance was first investigated. Then, ¹³C nuclear magnetic resonance (¹³C NMR) and quantum chemistry calculations were conducted to verify the reaction products and their interactions. Based on the analysis, the reaction mechanism and phase-changing mechanism of CO₂ absorption into the biphasic solvent were comprehensively elucidated. Moreover, the thermodynamics and corrosivity of the biphasic solvent were also evaluated.

2. MATERIALS AND METHODS

2.1. Materials. AEEA (98.0 wt % purity), DMSO (99.8 wt % purity), PMDETA (99.0 wt % purity), MEA (99.0 wt % purity), deuterated methanol (CD₃OD-*d*₄, 99.9 wt % purity), and deuterated DMSO-*d*₆ (99.9 wt % purity) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.,

China. CO₂ and N₂ (99.999 vol % purity) were supplied by Guilin Ruyi Biotechnology Co., Ltd., China.

2.2. CO₂ Absorption and Desorption. The novel nonaqueous biphasic solvent, which was named AEEA–DMSO–PMDETA (abbreviated as A–D–P), was prepared by dissolving AEEA (0.5–2.0 mol·L^{−1}, M) in a mixture of DMSO and PMDETA (V/V, 10:0 to 0:10). CO₂ absorption into the A–D–P biphasic solvent (25 mL) was performed in a homemade bubbling reactor at 313.15 K. The schematic of the absorption apparatus is shown in Figure S1. To facilitate the performance testing of the novel absorbent, pure CO₂ was used in this work. The flow rate of the CO₂ gas at the inlet of the reactor was kept at 80 mL·min^{−1} via a mass flow controller, and the gas flow rate at the outlet was measured by a soap-film flowmeter. The CO₂ absorption rate (r_{ab} , mol·mol^{−1}·min^{−1}) was calculated by the difference between the inlet and outlet gas flow rates. The CO₂ absorption loading (mol·mol^{−1}) can then be obtained from the integral of the absorption rate versus the absorption time. It should be noted that tertiary amines are not able to react with CO₂ in nonaqueous solutions.³⁶ Therefore, it could be considered that the tertiary amine PMDETA contributed very little to the CO₂ loading in the A–D–P biphasic solvent. As a result, only the AEEA content was taken into consideration for the calculation of the absorption rate and loading.

When the A–D–P biphasic solvent was saturated, two immiscible phases (a CO₂-lean phase and a CO₂-rich phase) formed, which were separated by a separating funnel. The properties of both phases, including volume percentage, CO₂ content, and viscosity, were analyzed successively. Subsequently, only the CO₂-rich phase was used for CO₂ desorption. The desorption was conducted in an oil bath with magnetic stirring at a desired temperature (373.15–393.15 K) (Figure S2). The CO₂ release rate at different desorption times was then measured using a soap-film flowmeter. By integrating the CO₂ release rate versus the desorption time, the CO₂ cyclic loading (mol·mol^{−1}) can be obtained. Detailed calculations are described in Supporting Information.

2.3. Evaluation of the Regeneration Heat and Corrosion. The heat duty associated with absorbent regeneration mainly consists of three parts: the reaction heat of absorption (Q_{rxn}), the sensible heat (Q_{sen}), and the latent heat (Q_{latent}).²³ The definition and calculation process of these three parameters are presented in Supporting Information.

20# carbon steel, which has good toughness, plasticity, and weldability, is a low-cost equipment material that is commonly used in CO₂ capture facilities. In the present work, the corrosivity of the A–D–P biphasic solvent was evaluated by determining the corrosion rate of 20# carbon steel in the test solution. Corrosion experiments were conducted using an electrochemical workstation (CHI660, Shanghai Chenhua Instrument Co., Ltd., China). In brief, a three-electrode electrochemical cell (50 mL) with approximately 30 mL of the test solution was first placed in a thermostat to ensure a constant temperature. A 20# carbon steel coupon, which was used as the working electrode, was then immersed in the solution. After that, a Tafel curve measurement was performed. The corrosion rate of the carbon steel coupon can be calculated by the Tafel extrapolation method from the Tafel curve. A more detailed description of the corrosion experiment can be found in a previous study.³⁷

2.4. ¹³C NMR Characterization. The ¹³C NMR spectra were recorded on a 500 MHz Bruker AVANCE NMR

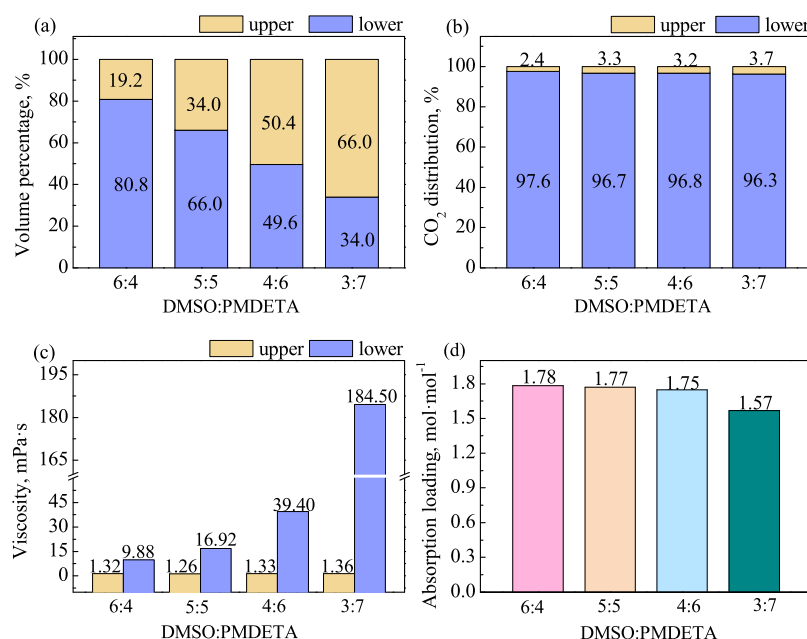


Figure 1. CO₂ absorption performance of A–D–P biphasic solvents with different ratios of DMSO to PMDETA, (a) volume percentage, (b) CO₂ distribution, (c) viscosity, and (d) CO₂ loading. (C_{AEEA} : 1.0 M; V_{solution} : 25 mL; $T_{\text{absorption}}$: 313.15 K; Q_{CO_2} : 80 mL·min⁻¹).

spectrometer. To prepare a sample for detection, the test solution was introduced into a 5 mm-diameter NMR tube. In addition, the deuterated solvent (CD₃OD-*d*₄ or DMSO-*d*₆) was added into the tube to mix with the test solution for obtaining signal locks. In the present work, 0.4 mL of the test solution and 0.2 mL of the deuterated solvent were used. Under such conditions, the test solution could completely dissolve in the deuterated solvent, and the concentration of the analyte could reach the detection limit of the spectrometer.

2.5. Quantum Chemical Calculation. The quantum chemical calculations were performed using the Gaussian 09 package. Based on density functional theory (DFT), the calculations, including the optimized geometries of the reactants and products, molecular dipole moment, and intermolecular hydrogen, were achieved at the level of B3LYP/6-311++G(d,p).³⁸

3. RESULTS AND DISCUSSION

3.1. Phase Change Behavior and the CO₂ Absorption Performance. Phase change behavior is regarded as one of the most essential properties for a biphasic solvent.^{19,21} According to the prescreening study, it was determined that the phase change of the A–D–P biphasic solvent was mainly affected by the DMSO and PMDETA content. Therefore, the A–D–P biphasic solvent with an appropriate DMSO/PMDETA ratio should be optimized. For this purpose, the molar concentration of AEEA was fixed at 1.0 M, and the volume ratio of DMSO/PMDETA varied between 10:0 and 0:10 (V/V). The results shown in Figure S4 revealed that the phase change behavior could be tuned by altering the DMSO/PMDETA ratio. For the tested solvents, not all of them could become dual liquid phases after CO₂ absorption, and only those with DMSO/PMDETA ratios of 6:4, 5:5, 4:6, and 3:7 presented two immiscible phases (upper and lower phases). Given this, to optimize the absorbent, the A–D–P biphasic solvents with the ability of phase change were selected for further investigation in terms of the CO₂ absorption performance.

Figure 1 depicts the CO₂ absorption performance of various A–D–P biphasic solvents. As previously mentioned, the phase separation was remarkably affected by the DMSO and PMDETA content. Herein, the volume percentage of the lower phase significantly decreased from 80.8 to 34.0% as the DMSO/PMDETA ratio changed from 6:4 to 3:7 (Figure 1a). However, the variation in the DMSO/PMDETA ratio did not show an obvious influence on the CO₂ distribution in the two phases. For all of the A–D–P biphasic solvents, more than 96% of the absorbed CO₂ was enriched in the lower phase (Figure 1b). Figure 1c shows the viscosity of the A–D–P biphasic solvent at different DMSO/PMDETA ratios. For different biphasic solvents, the viscosities of the upper phases were close to one another (approximately 1.30 mPa·s), while those of the lower phases dramatically increased from 9.88 to 184.50 mPa·s as the DMSO/PMDETA ratio changed from 6:4 to 3:7. Associated with the results in Figure 1a, the increase in viscosity should be a result of the absorbed CO₂ being concentrated in the decreased volume of the lower phase. As is known, an increase in viscosity would have a negative impact on the CO₂ absorption.³⁹ Consequently, the CO₂ absorption loading of the biphasic solvents decreased from 1.78 to 1.57 mol·mol⁻¹ as the DMSO/PMDETA ratio changed from 6:4 to 3:7 (Figure 1d).

The CO₂ absorption performance of the A–D–P biphasic solvent with different AEEA concentrations was also investigated. The results show that altering the AEEA concentration rarely affected the phase change behavior or CO₂ distribution in the two phases (Figure S5). Nevertheless, an obvious decrease in the CO₂ absorption loading and a significant increase in the viscosity of the lower phase occurred as the AEEA concentration increased from 0.5 to 2.0 M. With a comprehensive consideration of the CO₂ absorption performance, the A–D–P biphasic solvent with an AEEA concentration of 1.0 M and a DMSO/PMDETA ratio of 4:6 was considered the optimal absorbent [denoted as A–D–P (1.0 M, 4:6)], which possessed a relatively low viscosity (39.40 mPa·s) of the lower phase and a high CO₂ loading of 1.75 mol·mol⁻¹.

By comparison, the CO₂ loading of A–D–P (1.0 M, 4:6) was much higher than that of aqueous MEA (and most reported biphasic solvents^{22–24}) and comparable to that of the [DETA][Tz]-1-propanol-H₂O biphasic solvent reported by Zhan et al.²⁶ (see Figure S6). It is worth noting that for A–D–P (1.0 M, 4:6), more than 96% of the CO₂ loading accumulated in the lower phase, which was only 49.6% of the total solution volume. As was already stated, only the rich phase of biphasic solvents is required for CO₂ stripping. This implies that the volume of the A–D–P biphasic solvent for regeneration could be reduced by 50.4% compared with the benchmark MEA process. Therefore, the A–D–P biphasic solvent would be conducive to reduce the regeneration energy penalty for CO₂ capture.

Moreover, CO₂ absorption into the A–D–P biphasic solvent within a wide temperature range of 303.15–333.15 K was investigated. The results showed that the A–D–P biphasic solvent could present an excellent phase separation after loading CO₂ within the investigated temperature range (Figure S7). The CO₂ absorption loading slightly decreased as the temperature increased, but it remained as high as 1.22 mol·mol^{−1} (Figure S8). These results indicated that the A–D–P biphasic solvent could adapt to temperature fluctuations (313.15–323.15 K) after the flue gas desulfurization process.

3.2. CO₂ Desorption Performance. Desorption performance is another crucial criterion for evaluating a novel absorbent. In this study, the desorption of A–D–P (1.0 M, 4:6) was investigated in the temperature range of 373.15–393.15 K. For comparison, an investigation of the benchmark aqueous MEA was also performed. As shown in Figure 2, the

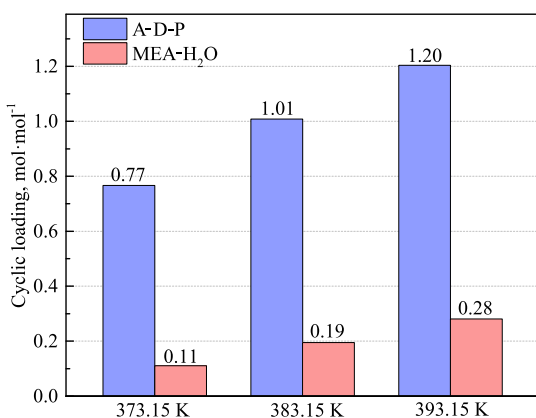


Figure 2. Comparison of the CO₂ cyclic loading between the A–D–P biphasic solvent and MEA aqueous solution at different temperatures. (*C*_{AEEA}: 1.0 M; DMSO:PMDETA = 4:6; *C*_{MEA}: 5.0 M; desorption time: 30 min).

CO₂ cyclic loading of both A–D–P (1.0 M, 4:6) and MEA increased as the desorption temperature increased, indicating that high temperature favored CO₂ stripping. Surprisingly, at the same temperature, the cyclic loading of A–D–P (1.0 M, 4:6) was much higher than that of MEA. For example, 1.20 mol·mol^{−1} of the cyclic loading for A–D–P (1.0 M, 4:6) was achieved at 393.15 K, which was nearly five times as high as that of MEA (0.28 mol·mol^{−1}). This result indicated the superior desorption performance of the A–D–P biphasic solvent. It is important to note that a high CO₂ cyclic loading is beneficial for saving energy,³⁹ meaning that the A–D–P

biphasic solvent would enable a significant reduction in energy consumption during solvent regeneration.

The long-term stability of the A–D–P biphasic solvent was also investigated, and the results are presented in Figure S9. It was determined that the CO₂ cyclic loading of the A–D–P biphasic solvent did not show a significant change as the number of absorption–desorption cycles increased, and it still retained 1.18 mol·mol^{−1}, even after the fifth cycle. This result indicated that the A–D–P biphasic solvent had stable regenerability and could be repeatedly used after multiple thermal desorption.

3.3. Mechanism Analysis. **3.3.1. ¹³C NMR Analysis.** To understand the mechanism of CO₂ capture by the A–D–P biphasic solvent, qualitative ¹³C NMR measurements were used to identify the product species and composition distribution in the upper and lower phases. Because the components of the A–D–P biphasic solvent are quite soluble in both CD₃OD-*d*₄ and DMSO-*d*₆, either of them could be used as a solvent for NMR analysis.

To avoid the interference of the deuterated reagent in the composition distribution analysis, CD₃OD-*d*₄ prior to DMSO-*d*₆ was used for signal locks because of the presence of DMSO in the biphasic solvent. Figure 3a shows the ¹³C NMR spectra of the A–D–P biphasic solvent before and after CO₂ absorption. In the upper-phase spectrum, carbon signals for DMSO and PMDETA were detected, indicating that the upper phase contained PMDETA and DMSO. Compared with the result for the fresh solution, the intensity of the carbon signal for DMSO was relatively weak in the upper-phase spectrum, which revealed that PMDETA was dominant in the upper phase. It should be noted that no visible peak for the CO₂ products could be observed in the spectrum of the upper phase, which might be a result of the extremely low concentration of the CO₂ products. For the lower-phase spectrum, the characteristic signals assigned to AEEA, PMDETA, and DMSO were all detectable. Interestingly, the signals for AEEA and PMDETA shifted upfield to a certain degree, which was likely a result of the formation of protonated amines or amine-CO₂ products.³⁹ In the meantime, two new signals appeared at 163.8 and 159.3 ppm, which corresponded to the carbonyl carbon in carbamate and the alkyl carbonate species, respectively.⁴⁰ This proved that the lower phase was a CO₂-rich phase. However, amines that react with CO₂ were unable to form alkyl carbonate species, which was supposed to be derived from the reaction of the carbamate with CD₃OD-*d*₄. Similar results were also reported by Barzagli et al.²⁹ and Liu et al.;⁴¹ in their studies, a carbamate could react with alcohol to form an alkyl carbonate.

To eliminate the effect of CD₃OD-*d*₄ on the reaction products, another sample of the lower phase was dissolved in DMSO-*d*₆ for NMR analysis to verify the products, with the results shown in Figure 3b. Two visible signals emerged at 160.0 and 161.3 ppm. The former corresponded to the carbonyl carbon of the carbamic acid species.^{28,36} Because the predicted ¹³C NMR resonance of the carbamate species is usually at 163–165 ppm, the signal observed at 161.3 ppm could be interpreted as carbamate and carbamic acid species in a fast exchange through rapid proton transfer. Given the above results, it could be concluded that CO₂ was absorbed in the forms of carbamate and carbamic acid species in the A–D–P biphasic solvent.

3.3.2. Reaction Mechanism. Based on the ¹³C NMR analysis, the reaction mechanism of CO₂ absorption into the

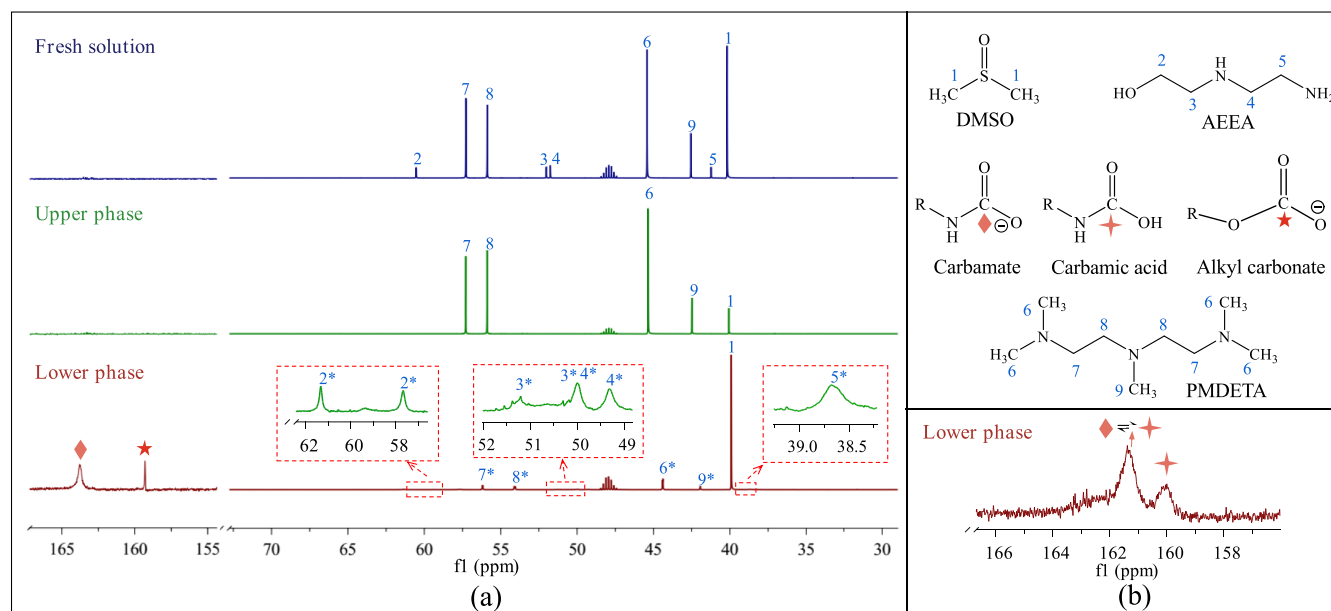
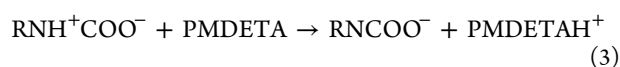


Figure 3. ^{13}C NMR spectra of the A–D–P biphasic solvent, (a) using $\text{CD}_3\text{OD}-d_4$ for signal lock; (b) lower phase using $\text{DMSO}-d_6$ for signal locks. (Asterisks denote the chemical shifts of the carbon backbones of the AEEA and PMDETA species).

A–D–P biphasic solvent could be elucidated. There were two kinds of amines in the absorbent, that is, AEEA and PMDETA. The tertiary amine PMDETA, which had no active proton on its amino groups, was unable to directly react with CO_2 .²⁹ The diamine AEEA with two active amino groups could attack free CO_2 to form an unstable zwitterion,⁴² and the reaction could be expressed as follows (RNH denotes AEEA)

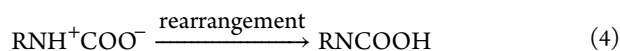


In general, the unstable zwitterion was then rapidly deprotonated by a base (proton acceptor) to form a carbamate.³⁶ It should be noted that, in addition to AEEA, PMDETA, a strong Brønsted base, could also behave as a proton acceptor to despoil the proton from the unstable zwitterion



The formation of the protonated PMDETA (PMDETAH^+) in eq 3 was in accordance with the ^{13}C NMR results in Figure 3a, wherein the carbon signals for PMDETA shifted after CO_2 absorption.

Moreover, the zwitterion could also undergo rearrangement to form a carbamic acid via intramolecular proton transfer in the nonaqueous A–D–P biphasic solvent³⁶



Like the zwitterion, the carbamic acid was also unstable and prone to deprotonation by another amine molecule to form a carbamate. However, the carbamic acid firmly stayed in the CO_2 -saturated biphasic solvent, as previously confirmed. Kortunov et al.³⁶ suggested that some polar organic solvents were capable of stabilizing the carbamic acid in nonaqueous systems. Therefore, it could be speculated that an interaction might exist between carbamic acid and DMSO in the A–D–P system because DMSO is a polar and nucleophilic solvent. To

test this hypothesis, the interaction between the carbamic acid and DMSO molecules was simulated by the DFT method with the B3LYP/6-311++G(d,p) basis set. It should be noted that both monocarbamic acid and bicarbamic acid species could exist in the solvent because AEEA has two amino groups, both of which can react with CO_2 . Therefore, the interactions between DMSO and these two types of carbamic acid species were investigated. As shown in Figure 4, a hydrogen bond with

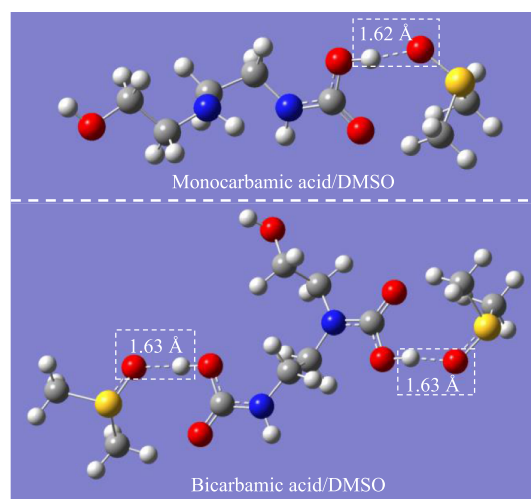


Figure 4. Hydrogen-bonding interaction between carbamic acid species and DMSO.

a short length of approximately 1.6 Å formed between the $-\text{COOH}$ group of carbamic acid and the $-\text{S}=\text{O}$ group of DMSO, which proved to be a strong interaction between carbamic acid and DMSO molecules. With the help of hydrogen-bonding interactions, the AEEA-carbamic acid could thus stably exist in the biphasic solvent.

The reaction mechanism of CO_2 absorption into the A–D–P biphasic solvent is summarized in Figure S10. In brief, AEEA first attacked free CO_2 to form the unstable zwitterion species.

A portion of the zwitterion was then directly deprotonated by AEEA or PMDETA to form the carbamate species. Simultaneously, some fraction of zwitterion species rapidly rearranged into carbamic acid, which was stabilized by DMSO via hydrogen-bonding interactions. Theoretically, the CO_2 loading of AEEA for the formation of carbamate species was approximately $1.0 \text{ mol} \cdot \text{mol}^{-1}$ and that for the formation of carbamic acid species could approach $2.0 \text{ mol} \cdot \text{mol}^{-1}$. In this regard, the CO_2 loading of AEEA would vary between 1.0 and $2.0 \text{ mol} \cdot \text{mol}^{-1}$ in the case where both carbamate and carbamic acid species were produced. This was in agreement with the results in Figure 1, in which the CO_2 loading was found to be $1.75 \text{ mol} \cdot \text{mol}^{-1}$.

3.3.3. Phase Change Mechanism. Previous studies suggested that the phase change behavior of biphasic solvents might be related to the polarity difference between different components.²⁶ According to the above results and analysis, the fresh A–D–P biphasic solvent consisted of AEEA, DMSO, and PMDETA, and the CO_2 -loaded solvent contained DMSO, PMDETA, and reaction products such as carbamate species, carbamic acid species, AEEAH^+ , and PMDETAH^+ . To understand the phase change mechanism, it is essential to investigate the polarities of various components. Generally, the polarity of a substance is positively correlated with its dipole moment. Hence, the dipole moments of various components in the A–D–P biphasic solvent were investigated.

As shown in Figure 5, the dipole moments of AEEA, DMSO, and PMDETA were close to one another but relatively low

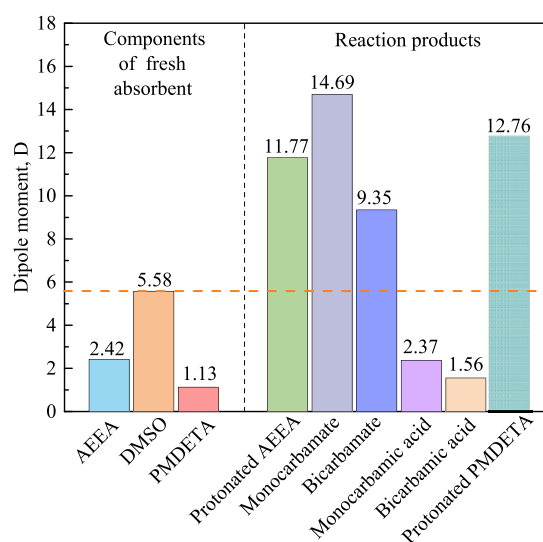


Figure 5. Dipole moments of different molecules.

(below 5.6 D), indicating the relatively low polarities of these three components. In contrast, the dipole moments of the reaction products (except for the carbamic acid species) were all at a relatively high level (above 9.3 D), meaning that most products had high polarities. Normally, the mutual solubility of different components is significantly influenced by their polarities. According to the similarity intermiscibility theory, it could be inferred that the close polarities enabled AEEA, DMSO, and PMDETA to mix uniformly before CO_2 absorption. After CO_2 absorption, highly polar products formed in the biphasic system. Because DMSO had a higher polarity than PMDETA, the polar products were supposed to have a better mutual solubility with DMSO. In addition, the

quantum chemical calculation results showed that the polar product and DMSO could attract one another via hydrogen bonds, but there was no stable hydrogen-bonding interaction between the product and the PMDETA molecules (Figure S11). Given this, it was reasoned that the polar products would prefer to dissolve in the polar solvent of DMSO, rather than the less-polar PMDETA. It should be noted that the carbamic acid species would theoretically dissolve in PMDETA because of its low polarity. However, it could fortunately also dissolve in DMSO with the help of the hydrogen-bonding interaction, as previously mentioned in Section 3.3.2. Eventually, PMDETA would be solely separated from the mixture of DMSO and the reaction products, and then the A–D–P biphasic solvent split into two immiscible phases after CO_2 absorption. Because the density of PMDETA ($0.85 \text{ g} \cdot \text{cm}^{-3}$, 313.15 K) was relatively smaller than that of the mixture of DMSO and the reaction products ($1.11 \text{ g} \cdot \text{cm}^{-3}$, 313.15 K), PMDETA transferred to the upper phase, while the mixture stayed in the lower phase. The schematic diagram of the phase separation of CO_2 absorption into the A–D–P biphasic solvent is vividly depicted in Figure 6. It is worth noting that it

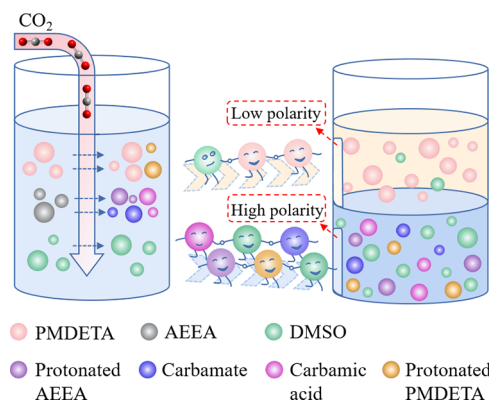


Figure 6. Schematic diagram of the phase separation of CO_2 absorption into the A–D–P biphasic solvent.

was reasonable for a small amount of DMSO to be brought to the upper phase because DMSO and PMDETA had a certain degree of mutual solubility, as verified by ^{13}C NMR analysis.

4. REGENERATION HEAT DUTY AND CORROSIVITY

Regeneration energy penalty and corrosivity are two crucial items when assessing the application potential of absorbents in a CO_2 -capturing process.⁴³ In this study, the regeneration heat duty and corrosivity of the A–D–P biphasic solvent were investigated.

As stated, the regeneration heat duty consists of Q_{rxn} , Q_{sen} , and Q_{latent} . The Q_{rxn} value could be calculated by the vapor–liquid equilibrium (VLE) data. The VLE data of CO_2 absorption into the A–D–P biphasic solvent are depicted in Figure S12. In addition, the parameters for estimating Q_{sen} and Q_{latent} are presented in Tables S1 and S2. Accordingly, the heat duty of the A–D–P biphasic solvent at different regeneration temperatures could be determined, and the results are shown in Figure 7. In the meantime, the results for the aqueous MEA are also presented. As can be seen, the heat duty of the aqueous MEA estimated in this work was in good agreement with the data reported in the literature,^{21,23} indicating the reliability of the calculation method. The heat duty of the two absorbents decreased as the regeneration temperature

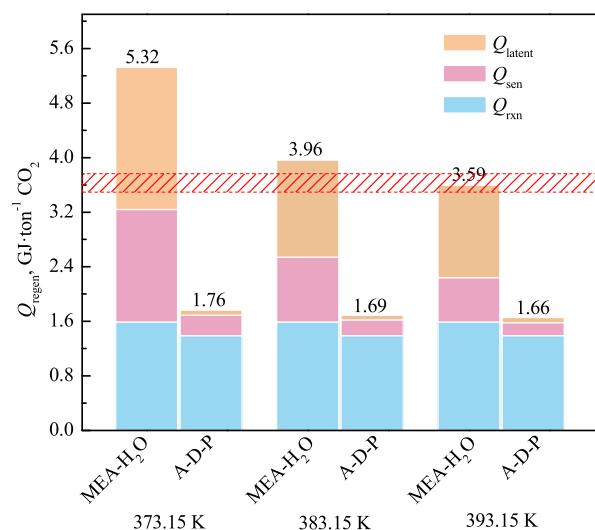


Figure 7. Heat duties of the A–D–P biphasic solvent and MEA aqueous solution at different regeneration temperatures. The red dashed bar represents the regeneration heat duty (393.15 K) of the aqueous MEA reported in the literature.^{21,23}

increased. This was because the increased temperature could lead to a higher CO₂ desorption efficiency, which was conducive to the reduction in the regeneration heat. Surprisingly, at the same temperature, the heat duty for the A–D–P biphasic solvent was much lower than that for the aqueous MEA. For example, the A–D–P biphasic solvent could achieve a heat duty as low as 1.66 GJ·ton^{−1} CO₂ at 393.15 K, which was 53.8% lower than the 3.59 GJ·ton^{−1} CO₂ requirement for the aqueous MEA. This could be attributed to the low heat capacity and vaporization enthalpy of the DMSO organic solvent, which enabled the A–D–P biphasic solvent to have extremely low Q_{sen} and Q_{latent} values (0.19 and 0.08 GJ·ton^{−1} CO₂, respectively). The aqueous MEA unfortunately suffered from high Q_{sen} and Q_{latent} values (0.64 and 1.35 GJ·ton^{−1} CO₂, respectively) because a large quantity of energy was consumed in the heating and vaporization of the solvent water.⁹ It is worth noting that the heat duty for A–D–P did not noticeably vary in the temperature range of 373.15 to 393.15 K, meaning that a relatively low regeneration temperature could be used for CO₂ stripping from A–D–P. Furthermore, the regeneration heat duty of the A–D–P biphasic solvent was also lower than that of the AEEA aqueous solution and most aqueous biphasic solvents reported in the literature (Table S3). This result revealed that the novel A–D–P biphasic solvent was promising from the perspective of saving energy.

The corrosivity of the A–D–P biphasic solvent was evaluated by determining the corrosion rate of 20# carbon steel in the solution, with the results shown in Figure 8. Additionally, the corrosion rates for the benchmark aqueous MEA and some reported aqueous biphasic solvents were presented for comparison. As can be seen from the figure, the corrosion rates of 20# carbon steel in all fresh absorbents were extremely low (close to zero mm·year^{−1}). However, an obvious difference in the corrosion rate between the A–D–P biphasic solvent and other absorbents appeared after CO₂ absorption. In the case of CO₂ saturation, the aqueous MEA and aqueous biphasic solvents exhibited high corrosion rates to 20# carbon steel. In contrast, the CO₂-saturated A–D–P biphasic solvent still retained a low corrosion rate to 20# carbon steel, as did

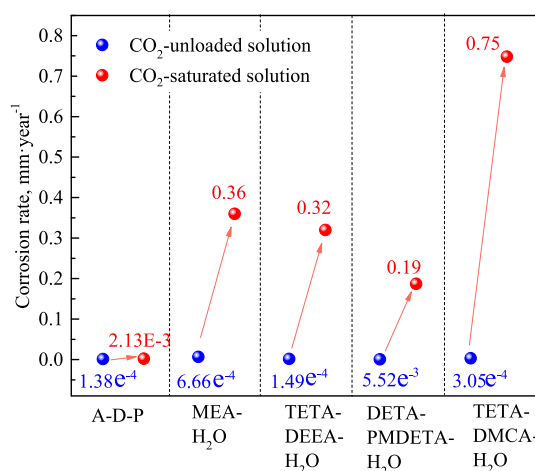


Figure 8. Comparison of the corrosion rate of A–D–P with aqueous MEA and biphasic solvents reported in the literature. (T: 313.15 K).

the fresh solution. Wu et al.³⁷ and He et al.⁴⁴ found that in an absorbent, HCO₃[−] and H⁺ were two important substances that could promote the corrosion rate of iron. It has been proven that HCO₃[−] and H⁺ can be easily generated via the hydrolysis of carbamate and the hydration reaction of CO₂ in the aqueous MEA and aqueous biphasic solvents.⁴⁵ However, in non-aqueous biphasic solvents, the hydrolysis of carbamate and the hydration reaction of CO₂ were unable to occur in the absence of water.⁴⁶ Therefore, the corrosion rate of 20# carbon steel in the CO₂-saturated A–D–P biphasic solvent was undoubtedly lower than that in the aqueous MEA and aqueous biphasic solvents. The lower the corrosion rate, the lower the corrosivity.³⁷ In this regard, the A–D–P biphasic solvent with low corrosivity is conducive to industrial applications.

In summary, the proposed A–D–P nonaqueous biphasic solvent exhibited a superior CO₂ capture performance in terms of the CO₂ absorption loading and cyclic loading. After absorption, the majority of the absorbed CO₂ was enriched in the lower phase, which was only half of the total volume. Because of the decreased volume for regeneration and the low heat capacity and vaporization enthalpy, the regeneration heat duty of this novel absorbent was significantly lower than that of the benchmark MEA and aqueous biphasic solvents reported in the literature. Moreover, the corrosivity of the A–D–P biphasic solvent was proven to be extremely low. Therefore, the novel A–D–P nonaqueous biphasic solvent could be a promising alternative to the benchmark MEA for energy-efficient and noncorrosive CO₂ capture.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.0c05774>.

Additional details on the experimental procedure, calculation method of parameters, schematic diagrams of experimental apparatuses, absorption and desorption data, schematic diagram of the reaction mechanism, VLE data, and parameter data for calculating regeneration heat (PDF)

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Notes

The authors declare no competing financial interest.

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