

# DIAMINE VERSUS AMINES BLEND FOR CO<sub>2</sub> CHEMICAL ABSORPTION

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## Abstract

The present work analyses the behaviour of aqueous solutions of N,N-dimethylethylenediamine as chemical solvent for carbon dioxide separation by gas-liquid absorption. The interest of this molecule is centred on the presence of different types of amino centres that confer the capability to act as typical solvent based on mixtures of amines taking into account the suitable behaviour of some mixtures. For this reason a comparison between diamine and amine blend solvents has been carried out in order to understand the differences between these solvents using absorption and NMR studies. This experimental work analyses the influence of amine type, concentration and ratio between different amines. Also, the effect of gas flow rate used in the bubble column reactor upon the absorption kinetics has been analysed.

## 1. Introduction

It is clearly established that the use of chemical absorption processes for carbon dioxide separation is considered as a mature technique with a relatively low cost that allows the treatment of gas streams with high flow rates.<sup>1</sup> This type of operation for carbon dioxide separation implies the use of chemical solvents, generally based on amines. In general, the use of primary and secondary amines is highly recommended, taking advantage of the high reaction rate with carbon dioxide in aqueous solution and the low cost.<sup>2</sup> One of the most important limitations of this type of solvents is related to the low carbon dioxide loading that can be reached, limited by the reaction mechanism based on the production of carbamate.<sup>3,4</sup> Another negative characteristic of this type of solvents that includes primary and secondary amines is the high cost associated to solvent regeneration procedures<sup>5,6</sup> that generally accounts for 70% of the costs of the overall absorption/desorption process.<sup>7</sup> In addition other researchers<sup>8</sup> consider that a higher stability of solvents can be reached avoiding the use secondary centres due to the formation of nitrosamines.

Taking into account these negative characteristics the development of new solvents tries to reach: (i) high absorption rate and carbon dioxide loading and (ii) negligible solvent degradation, corrosion and energy consumption. To reach these aims one of the proposed alternatives is the use of solvents that include a mixture of amines.<sup>9</sup> The aim of using this type of mixtures is centred on taking advantage of the positive characteristics of tertiary or sterically hindered amines that can overcome the negative aspects of primary and secondary amines, previously commented. It must be taken into account that solvents based on tertiary amines have shown a low reaction rate in comparison to primary and secondary amines.<sup>10</sup> Moreover this type of solvents can reach higher values of carbon dioxide loading, thus leading to a better regeneration process that implies lower costs, degradation and corrosion.<sup>11</sup> Several studies have been carried out in order to analyse the behaviour of mixtures of amines in the carbon dioxide absorption process comparing their performance to those obtained for the individual amines reaching in certain cases better results than the conventional solvent.<sup>12-14</sup> Also a research line with very interesting results is centered on the use of di- or polyamines. One of the most important molecules in this research line is piperazine that has been used in an important number of research studies and papers, from basic studies to industrial applications.<sup>15,16</sup>

Present research work evaluates other type of chemical solvents different than conventional ones, trying to take advantage of combining different amine centres in the same solvent, inspired by promising results obtained while working with mixtures of different amines. A previous study analysed the use of diamines in the chemical solvents for carbon dioxide absorption using mineralisation for solvent regeneration.<sup>17</sup> This work shows fast kinetics and low energy requirements that indicate this type of solvents as promising ones. A previous work<sup>18</sup> of our team showed that a diamine allows to reach similar values that amines blends for absorption rate and carbon dioxide loading. Taking into account these previous results, present work is focussed on solvents with N,N-dimethylethylenediamine (a diamine with different amino centres - primary and tertiary) that has been considered as a promising diamine for chemical solvent formulation.<sup>17</sup> Our work is centred on a comparison with the solvent based on amines blends (maintaining type and concentration) in order to evaluate the strength and weakness of this type of solvents. The influence of amine ratio, concentration and gas flow rate over the absorption process has been analysed.

## 2. Experimental Section

### 2.1. Materials

Carbon dioxide was supplied by Praxair with a purity of 99.998%. The chemical solvents employed in carbon dioxide chemical absorption experiments were based on the use of N,N-dimethylethylenediamine (DMEDA), monoethanolamine (MEA) and dimethylethanolamine (DMEA) that were purchased from Alfa Aesar with purities of 95%, [?]99% and [?]98% respectively. Aqueous solutions of these amines were prepared on mass with double distilled water.

### 2.2. Carbon dioxide absorption studies

The different studies carried out in this work were performed in a bubble column reactor with a square geometry (side length = 4 cm; height = 65 cm) made in methacrylate and with a working volume of liquid phase of 0.9 L. The gas phase was fed in bubbles shape using a five-holes sparger built in Teflon<sup>®</sup>. This phase consisted on pure carbon dioxide saturated with water to avoid the influence of other mass transfer phenomena upon carbon dioxide mass transfer rate. The gas flow rate ( $Q_G$ ) range used in this work was 0.1-0.3 L·min<sup>-1</sup>. These studies were based on the analysis of absorption rate and carbon dioxide loading using different reagents at varied concentrations and gas flow rates. The inlet and outlet gas flow rates were controlled and measured with two mass flow controllers (Alicat Scientific MC-5SLMP-D) previously calibrated by the supplier for the gas employed in these experiments at the working range for flow rates and pressures, thus allowing the calculation of the absorbed flow rate of carbon dioxide ( $q_a$ ). Also, Flow Vision SC software package (Alicat Scientific) was used to record the carbon dioxide flow rate during the experiments. The working regime was continuous in relation to the gas phase and batch regarding the absorbent liquid one.

### 2.3. Speciation studies

<sup>1</sup>H and <sup>13</sup>C NMR spectroscopy was applied to qualitatively study the substances present in the liquid phase inside the bubble column reactor during the chemical absorption of carbon dioxide for the different solvents used in this work. The MestrReC 4.7 software developed by MestreLab Research was used for spectra processing. Spectra were acquired on 300 MHz Varian Mercury spectroscopy. Samples of amine solution were taken from the middle zone of reactor system. Deuterated water (D<sub>2</sub>O) was used as internal reference for the processing of <sup>1</sup>H NMR and tetradeuterated methanol (CD<sub>3</sub>OD) as internal reference for the processing of <sup>13</sup>C NMR.

### 2.4. Steady state regime studies

These carbon dioxide capture studies were carried out using the experimental set-up shown in Figure 1 employing the same bubble column reactor and gas flow rate mass controllers as previously described in section 2.2. The lean solvent was fed to the top of the bubble column reactor, while the gas stream entered the absorber at the bottom. The lean solvent was maintained at the desired temperature (40 @C) by using a cryostat (Selecta Frigiterm). The CO<sub>2</sub>-enriched solvent present in the bottom of the absorber was withdrawn

from the bubble column reactor using a peristaltic pump (Selecta Percom N-M). After being heated until the target temperature (90 @C), it was fed into the top of a stripping section, where a packed column was employed to increase the contact between vapor and liquid phases. Thus, while descending through the packed column, this CO<sub>2</sub>-enriched solvent was stripped by the steam generated in the reboiler. A magnetic stirrer hot plate (Selecta Agimatic-N was used to boil the solvent and generate the vapor stream in the stripper. After leaving the reboiler and being cooled down to 25@C, the regenerated solvent re-entered the bubble column reactor thus completing the process of steady state regime absorption. Different gas and liquid flow rates were used for these experiments to evaluate their influence upon the overall carbon dioxide absorption performance.

### 3. Results and Discussion

The main aim of present research work is establish a comparison between diamine-based solvents and a blend of amines that employ the same type and number of amino groups. Figure 2 shows the absorption curves corresponding to DMEDA+water solvent using different diamine concentration. The shape of these curves were similar, reflecting the total absorption of the carbon dioxide fed to the gas-liquid contactor at the beginning of the experiments, thus indicating suitable characteristics regarding both the reaction rate and mass transfer. After this constant-absorption rate period a monotonic decrease was observed until solvent saturation was reached.

The area under the absorption curve increased with amine concentration due to a higher number of amino centres available to react with physically absorbed carbon dioxide. This value is related with an important parameter in this kind of studies: carbon dioxide loading ( $\alpha$ ), defined as the ration between mol of absorbed CO<sub>2</sub> and mol of amino groups in the tested solvent. The evolution of this parameter is also included in Figure 2 and shows a stable increase until a constant value ins reached, being this value related with the overall reaction mechanism stoichiometry. At low amine concentration, the carbon dioxide loading was higher due to the importance of physical absorption upon the overall process, but an increase in amine concentration allowed to reach a constant value close to 0.55 mol CO<sub>2</sub>-mol amine group<sup>-1</sup>. Taking into account previous studies<sup>14</sup> a carbon dioxide loading similar to the obtained for DMEDA aqueous solutions implies the reaction mechanism shown in reaction 1.



The behaviour observed in Figure 2 is commonly associated to primary or secondary amines acting as chemical solvent absorption. However the final constant value of carbon dioxide loading obtained in these experiments was not compatible to those reached at the end of experiments involving those types of amines, where larger values were reached. This higher carbon dioxide loading can be achieved due to the existence of carbamate hydrolysis processes, where the hydrolysis degree depends on different aspects e.g. the steric hindrance of amine.<sup>19,20</sup> For instance, monoethanolamine aqueous solutions (primary amine) reach carbon dioxide loading close to 0.7 mol CO<sub>2</sub>-mol amine group<sup>-1</sup> due to partial carbamate hydrolysis.<sup>21</sup>. Considering that the diamine employed in present work involves the presence of both a primary and a tertiary amino group, the expected carbon dioxide loading could be 0.75 mol CO<sub>2</sub>-mol amine group<sup>-1</sup> (avoiding the carbamate hydrolysis).

Moreover, the influence of gas flow rate fed to bubble column reactor upon absorption rate has been analysed (see Figure 3). In this type of biphasic reactors, the gas flow rate can play an important role upon absorption rate, since it can not only affect phase mixture but also interfacial area. Generally, an increase in the amount of gas fed to reactor causes an increase in both parameters; a higher agitation that increases mass transfer rate, and also increasing gas hold-up in the bubble column. This last parameter generally causes an important enhance in gas-liquid interfacial area. For this reason, the experiments shown in Figure 3 indicated a high absorption rate when gas flow-rate fed to column contactor increases. This solvent allowed the absorption of all carbon dioxide flow rate fed to the reactor.

As previously commented, the use of diamine aqueous solutions must be compared with the behaviour of amine blends in order to select the solvent with better characteristics, taking into account that previous

studies<sup>22,23</sup> suggested that amine blends contribute to better properties for carbon dioxide chemical absorption than single-amine solvents. For these reasons, the same type of experiments has been performed using a mixture of alkanolamines that maintain the same type and concentration of amino groups than the diamine aqueous solutions. The selected mixture was composed of monoethanolamine (MEA) and dimethylaminoethanol (DMEA). Figure 4 shows the absorption curve corresponding to a 50% mixture of each amine to maintain the same amine group concentration in comparison to the diamine aqueous solutions. A similar trend was observed in comparison to the previously commented diamine experiments. At the beginning of the experiments the amine-blend solvent absorbed all the carbon dioxide fed to the reactor and after this period a continuous decrease was observed. Moreover, Figure 4 shows the effect of different ratios between both alkanolamines upon the absorption of carbon dioxide. Revealing that an increase in the proportion of primary amine groups (corresponding to higher monoethanolamine concentration) led to an increase in the absorption rate, maintaining the total absorption of carbon dioxide during a higher period of time, however displaying similar absorption rate decreases after that time. Consequently, amine blends did not show important differences upon the absorption curves in comparison to the use of diamine solvent.

Analysing the behaviour of the value of carbon dioxide loading for both solvents based on the mixture of amines (MEA and DMEA), a similar behaviour was also observed. Both systems reached values close to 0.95 mol CO<sub>2</sub>·mol amine group<sup>-1</sup>. The use of a higher amount of MEA in the mixture caused a slight decrease in the value of carbon dioxide loading probably due to an increase in the amount of carbamate formed in the liquid phase.

In order to carefully analyse the behaviour of amines mixture solvents, both amines have been studied individually in carbon dioxide absorption experiments. Figure 5 shows a comparison between the use of amine blend solvent (at 50% of each amine) and single amine solutions. These experiments showed a very different behaviour. The primary amine (MEA) reached a high absorption rate at the beginning of the experiment, absorbing the total carbon dioxide flow rate during a period of time similar to that observed for the blended solvent. After that, a dramatic decrease in absorption rate was observed and the mixture of amines reached an important enhancement in absorption rate. On the other hand, the tertiary amine showed the lowest absorption rate, mostly due to the different reaction mechanism that characterises carbon dioxide absorption by tertiary amines,<sup>24</sup> thus affecting the reaction rate and hence influencing the overall process. Taking into account this comparison, it is possible to conclude that the mixture of MEA and DMEA showed a significant better behaviour than the use DMEDA-based solvents. This mixture reached higher absorption rates similar to those observed for the primary amine, being even better in certain parts of the experiments. In relation to carbon dioxide loading, this blended solvent reached intermediate values between both systems, but close to 1 mol CO<sub>2</sub>·mol amine group<sup>-1</sup> in all cases.

When a comparison between both systems (diamine and blend of amines) is performed (see Figure 6), the solvent based on DMEDA showed a very important and negative difference in the value of carbon dioxide loading. As previously commented in Figure 1, diamine aqueous solutions reached value of carbon dioxide loading close to 0.55 mol CO<sub>2</sub>·mol amine group<sup>-1</sup>. This value was significantly lower than in alkanolamine mixture solvents. Figure 6 shows a similar absorption rate when amine concentration is high but the decrease in the absorption rate corresponding to the saturation of solvent was produced in a lower experiment time. A similar conclusion was reached by analysing the evolution of carbon dioxide loading that displayed a similar slope but reached a significant lower amount of carbon dioxide chemically absorbed at the end of experiments.

The reason of this difference in the amount of carbon dioxide captured per amino group cannot be explained only based on absorption experiments, and for this reason, several speciation studies were carried out focusing on <sup>1</sup>H and <sup>13</sup>C NMR. This type of experiments tried to identify the reaction products present in the liquid phase during the absorption experiments, thus allowing to explain the absorption rate and also the carbon dioxide loading on the basis of the weight of each reaction in the overall reaction mechanism. This technique allowed to analyse how the different carbons present in amines were involved in the reaction by detecting changes on the chemical shifts associated to each carbon atom. Figure 7 shows the <sup>13</sup>C NMR spec-

tra corresponding to the liquid phase during the chemical absorption of carbon dioxide in DMEDA aqueous solution. At the beginning of the carbon dioxide absorption process ( $\alpha=0$  mol CO<sub>2</sub>·mol amine group<sup>-1</sup>), three signals were observed at chemical shifts of 38, 44 and 60 ppm that corresponded to carbons of the DMEDA molecule. The additional peak observed but was related to deuterated methanol (used as reference), thus its chemical shift was not indicated in Figure 7 to avoid confusion.

The successive spectra included in Figure 7 correspond to the solvent when different amounts of carbon dioxide were absorbed using the carbon dioxide loading data. When a carbon dioxide loading of 0.08 mol CO<sub>2</sub>·mol amine<sup>-1</sup> was reached, new signals appeared close to the previously analysed peaks of DMEDA. On the basis of previous studies<sup>25</sup> this type of signals was in agreement with the spectrum for carbamate. This conclusion was supported by the presence of a peak at 164.6 ppm that corresponded to the carbon atom of the carbon dioxide when it reacts with the amine centre. It is well-known<sup>26</sup> that the reaction of carbon dioxide with primary and secondary amines to produce carbamate is faster than the reaction with tertiary amines producing bicarbonate. Figure 7 shows the same behaviour when a diamine is used, since carbon dioxide preferably reacted with the primary amine centres of this diamine. The same behaviour and reaction mechanism was observed during the main part of the chemical absorption experiment, However, in the last part of this experiment a new signal appeared with a chemical shift of 160 ppm, which corresponds to the bicarbonate molecule.<sup>25</sup> The presence of bicarbonate in the solvent could be cause by different types of reactions: (i) carbamate hydrolysis and (ii) reaction between carbon dioxide and tertiary centres. Considering that tertiary centres in this molecule has the same concentration as primary ones at the beginning of experiments, a higher weight of the direct reaction of carbon dioxide with tertiary centres than here observed could be expected. The presence of low amounts of bicarbonate at the end of experiments (close to solvent saturation) allowed to conclude that this product was mainly caused by carbamate hydrolysis, because bicarbonate only appeared when high concentrations of carbamate were reached.

In order to fully understand the reaction mechanism of carbon dioxide with aqueous solutions of DMEDA, further studies using a chemical solvent based on a blend of MEA and DMEA were performed. These compounds were chosen to maintain both the same type and concentration of each amino centre present in DMEDA. Figure 8 shows the spectra obtained during carbon dioxide chemical absorption using this blended solvent. At the beginning, five peaks were observed: carbons corresponding to MEA (43 and 60 ppm) and DMEA (45, 59 and 63 ppm). As in the analysis of spectra in Figure 7 for DMEDA, new signals corresponding to MEA carbamate (duplicity of signals and the creation of a peak close to 165 ppm) appeared in the NMR spectra during the carbon absorption process. One of the most important differences observed when comparing the spectra corresponding to diamine and that of amine blends is the presence of bicarbonate at relatively low carbon dioxide loadings (in comparison with the final value) in the solvent based on amine blend. Specifically, bicarbonate appeared at 0.67 mol CO<sub>2</sub>·mol amine<sup>-1</sup>, and at the end of the experiment the carbon dioxide loading reached the value of 0.94 mol CO<sub>2</sub>·mol amine<sup>-1</sup>.

As previously commented, the presence of bicarbonate can be due to either the reaction of carbon dioxide with tertiary centres (DMEA) or the hydrolysis of carbamate. In this case the final value of carbon dioxide loading is close to 1 mol CO<sub>2</sub>·mol amine<sup>-1</sup> thus indicating that both reactions take place completely.

On the basis of the experimental results of speciation studies in these solvents (diamine and amines blend), it is possible to conclude that diamine-based solvent generated some type of inhibition of chemical reaction of carbon dioxide with tertiary centre, because the maximum value of carbon dioxide loading was significantly lower in comparison with the use of the same type of centres and radicals in a blend of amines. This behaviour is in agreement with a previous study<sup>27</sup> that detects an important influence of electronic environment in the diamine when the length of the alkyl spacer is small.

The overall experimental data allowed to propose that the decrease in carbon dioxide loading with the diamine-based solvent was due to the lack of chemical reaction in the tertiary centre, because reached values are comparable to those obtained considering the use of aqueous solutions of MEA as chemical solvent for carbon dioxide chemical absorption. The inhibition of chemical reaction in the tertiary centre was caused by the interactions of this centre with either other parts of the same molecule or other molecule. Previous

work<sup>28</sup> indicated that the use of a diamine with two primary amino centres can lead to a cycled structure after the reaction of one of them with carbon dioxide. This fact can also stabilize the carbamate, reducing the hydrolysis processes. The reaction mechanism here proposed is in agreement with the previously detected reduction in carbon dioxide loading and the low presence of bicarbonate in the reaction products. Additional speciation experiments using different amine ratios for the amine blend-based solvent (MEA/DMEA ratio of 5) showed behaviour in agreement with the previous discussion maintaining the same concentration of primary and tertiary centres (see figure 9).

In the first part of this manuscript the carbon dioxide chemical absorption behaviour using different solvents has been analysed taking into account the type of solvent, the concentration of amine or blend of amines and gas flow rate, explaining these behaviours on the basis of the reaction mechanism determined by nuclear magnetic resonance spectroscopy. Additionally, several studies in steady state regime have been performed comparing the different solvents previously analysed. In this part of the experimental work, the role of regeneration processes by stripping can influence the overall behaviour of chemical solvents. An example of the experimental results obtained in this type of experiments is shown in Figure 10 for DMEDA aqueous solutions. The influence of gas flow rate fed to bubble column reactor and solvent flow rate was analysed in this figure; in relation to the first variable (gas flow rate) an increase in the amount of carbon dioxide absorbed in the bubble column reactor was observed, but no effect was observed when the influence of liquid phase flow rate ( $Q_L$ ) was studied.

Moreover, a comparison between the different solvents employed in the present work was carried out in Figure 11. In all cases, an increase in gas flow rate fed to bubble column reactor caused an increase in the amount of carbon dioxide transferred to the liquid phase. Though the previous commented studies carried out in semi batch regime allowed to conclude that the solvents based on the use of blends of amines contribute better carbon dioxide absorption results, the experimental data obtained in steady state regime (see Figure 11) showed a different behaviour.

The diamine-based solvent obtained higher carbon dioxide absorption rates than the other solvents based on the mixture of amines with the same functional groups. This difference can be due to the special characteristics corresponding to the steady state regime. In this type of configuration, the carbon dioxide loading reached by the solvent during the chemical absorption is relatively low. This fact can explain the higher absorption rate for diamine-based solvents, because the reaction rate corresponding to the formation of carbamate is higher than the ones corresponding to the systems where the final product is the bicarbonate ion. This behaviour is in agreement with previously shown results included in Figure 6, that showed a high absorption rate for DMEDA solutions when carbon dioxide loading was lower than  $0.4 \text{ mol CO}_2 \cdot \text{mol amine}^{-1}$ .

#### 4. Conclusions

Present work compares the carbon dioxide chemical absorption using the same type of amino centres being part of a diamine (DMEDA) and a mixture of amines (MEA+DMEA). On one hand, the studies corresponding to the use of amine blends showed that changes in the amine ratios did not lead to important changes in the absorption curves and carbon dioxide loading, though a higher presence of MEA increased both parameters. For instance, a chemical solvent composed of an aqueous solution of MEA/DMEA (ratio of 1) showed a very similar behaviour than a MEA-based solvent.

The use of DMEDA (diamine) showed a different performance than the use of amine blends-based solvents, though the same concentration of each type of amino centres was employed. The diamine-based solvent showed an important decrease in the carbon dioxide loading that caused also a decrease in the absorption rate (caused by a lower driving force).

Speciation studies using both type of solvents allowed to conclude that significant differences in the reaction mechanism were produced. A reduction in the production of bicarbonate ion was observed when using DMEDA as chemical absorbent. This fact was produced by the interaction between amino centres during the chemical absorption, that caused both the stabilization of the carbamate produced through the reaction of carbon dioxide with primary amino groups (avoiding its hydrolysis) and an inhibition of the reaction

of carbon dioxide with the tertiary centres. This fact caused an important decrease in the carbon dioxide loading reached by this type of solvent.

The last part of the work focused on steady state experiments by accomplishing a stripping-based solvent regeneration unit. In contrast to batch experiments, the experimental results here obtained showed higher absorption rates for the diamine-based solvent. For this configuration, this type of behaviour was caused by a lower carbon dioxide loading values being reached in the absorber, which corresponded to only carbamate being produced, as determined in speciation studies for this carbon dioxide loading range. The chemical reaction rate was higher for carbamate production than for bicarbonate, thus allowing higher absorption rates when using the solvent based on diamine in comparison to those based on amine blends. It allows to consider DMEDA-based solvents as potential ones to be used in carbon dioxide separation units.

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### Figure Captions

Figure 1. Experimental set-up for steady state experiments. (1) mass flowmeter/controller, (2) bubble column, (3) peristaltic pump, (4) heater, (5) condenser, (6) packed column, (7) reboiler, (8) cooler, (9) data acquisition software.

Figure 2. Influence of diamine (DMEDA) concentration upon absorption curves and carbon dioxide loading.  $Q_G = 0.2 \text{ L}\cdot\text{min}^{-1}$ . (○)  $C_B = 0.2 \text{ M}$ ; (◐)  $C_B = 0.6 \text{ M}$ ; (◑)  $C_B = 1.2 \text{ M}$ .

Figure 3. Effect of gas flow rate upon absorption curves using DMEDA solvent.  $C_B = 0.6 \text{ M}$ . (○)  $Q_G = 0.1 \text{ L}\cdot\text{min}^{-1}$ ; (◐)  $Q_G = 0.2 \text{ L}\cdot\text{min}^{-1}$ ; (◑)  $Q_G = 0.3 \text{ L}\cdot\text{min}^{-1}$ .

Figure 4. Effect of mixture ratio upon absorption curves and carbon dioxide loading.  $C_B = 0.6 \text{ M}$ .  $Q_G = 0.2 \text{ L}\cdot\text{min}^{-1}$ . [DMEA]/[MEA] ratio: (○) 1; (◐) 5.

Figure 5. Comparison between absorption rate of amines blend and individual amine solutions.  $Q_G = 0.3 \text{ L}\cdot\text{min}^{-1}$ .  $C_B = 0.6 \text{ M}$ . (○) Amines blend (50%/50%); (□) MEA; (△) DMEA.

Figure 6. Comparison of experimental behaviors (absorption rate and carbon dioxide loading) between amines blend and diamine solvents.  $Q_G = 0.3 \text{ L}\cdot\text{min}^{-1}$ .  $C_B = 1.2 \text{ M}$ . (○) amines blend (50%/50%); (□) diamine.

Figure 7.  $^{13}\text{C}$  NMR spectra corresponding to samples from carbon dioxide absorption in DMEDA aqueous solution.  $Q_G = 0.3 \text{ L}\cdot\text{min}^{-1}$ .  $C_B = 0.6 \text{ M}$ .

Figure 8.  $^{13}\text{C}$  NMR spectra corresponding to samples from carbon dioxide absorption in MEA and DMEA blend solvent. MEA/DMEA ratio = 1.  $Q_G = 0.3 \text{ L}\cdot\text{min}^{-1}$ .  $C_B = 0.6 \text{ M}$ .

Figure 9.  $^{13}\text{C}$  NMR spectra corresponding to samples from carbon dioxide absorption in MEA and DMEA blend solvent. MEA/DMEA ratio = 5.  $Q_G = 0.3 \text{ L}\cdot\text{min}^{-1}$ .  $C_B = 0.6 \text{ M}$ .

Figure 10. Influence of liquid phase and gas flow rates upon carbon dioxide absorption rate.  $C_B = 1.2 \text{ M}$ . (○)  $Q_L = 96 \text{ mL}\cdot\text{min}^{-1}$ ; (□)  $Q_L = 72 \text{ mL}\cdot\text{min}^{-1}$ ; (△)  $Q_L = 45 \text{ mL}\cdot\text{min}^{-1}$ .

Figure 11. Influence of gas flow rate and type of solvent upon carbon dioxide absorption rate.  $Q_L = 72 \text{ mL}\cdot\text{min}^{-1}$ .  $C_B = 1.2 \text{ M}$ . (○) diamine, (□) MEA/DMEA ratio = 1, (△) MEA/DMEA ratio = 5.















