

Comparison of CO₂ absorption performance between methyl-di-ethanolamine and tri-ethanolamine solution systems and its analysis in terms of amine molecules

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Abstract: The present study analyzes the features of chemical CO₂ absorption using tertiary amine solvents by comparing the absorption performance and electrical properties between methyl-di-ethanolamine (MDEA) and tri-ethanolamine (TEA) systems. The results are mostly attributed to the different structures of the two amine molecules. Absorption performance is significantly affected by the molecular structure and water concentration in the amine solution. The absorption performance of the MDEA system is better than that of TEA, which is basically ascribed to the MDEA molecule's more asymmetric and irregular shape than that of TEA, which thus enhances the catalytic activity of MDEA and the reactivity of the –OH moiety in water. The difference of electrical properties such as ionic conductivities (ICs) of the two protonated amines and real ionic activity coefficients (RIAC) between the two systems might be also caused by the different molecular structures of the two amines. The IC of protonated MDEA is estimated to be 23.70% higher than that of protonated TEA, because of the higher ionic mobility and charge density of MDEA. The RIAC of the MDEA system is higher than that of TEA, which is explained by the different physicochemical interactions between the molecules in the two systems. Since water is one of the reactants in the absorption, its concentration in solution significantly affects the results of the systems. In addition, the absorption using tertiary amine is a base-catalyzed reaction, and thus variations of the overall absorption rate follow a parabolic curve. Therefore, it is maximized to be 14.2 and 9.8 mmol CO₂·L⁻¹·min⁻¹ in the 15 wt% MDEA and TEA solutions, respectively. Finally, the correlated equations for *in situ* estimation of chemical absorption capacity by electrical conductivity measured during the absorption are derived in the two systems. © 2021 The Authors. *Greenhouse Gases: Science and Technology* published by Society of Chemical Industry and John Wiley & Sons, Ltd.

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Received August 26, 2020; revised February 23, 2021; accepted February 26, 2021

Published online at Wiley Online Library (wileyonlinelibrary.com). DOI: 10.1002/ghg.2059

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Keywords: Carbon capture and storage; chemical CO₂ absorption; electrical conductivity; ionic conductivity; methyl-di-ethanolamine; tri-ethanolamine

Introduction

The increase of anthropogenic CO₂ emission is causing serious global warming.^{1–3} Carbon capture and storage (CCS), one of the available options to reduce CO₂ emissions,^{4–6} is a technology to selectively capture CO₂ from the flue gas generated in various industrial processes with a CO₂ concentration range of about 4 (natural gas power plant) ~30 mol% (maximum in cement plant) in order to reduce atmospheric emissions.⁷ Among the many CCS technologies based on physicochemistry that have been developed, chemical absorption using alkanolamine-based solvents is the most representative and has already entered large-scale commercialization combined with enhanced oil recovery systems in the United States and Canada.^{8–11}

The commercialization of the MEA-based absorption process has been based on the solvent's high reactivity with CO₂ and low price.^{12–15} However, the remaining disadvantages include large energy consumption for solvent regeneration, corrosion of process equipment, and continuous make-up of monoethanolamine (MEA) during the operation due to its high volatility and low thermal stability. Therefore, various alternative solvents incorporating NH₃, polyethylene glycol, piperazine, and so on have been proposed to overcome the disadvantages of MEA-based absorbent.^{16–20}

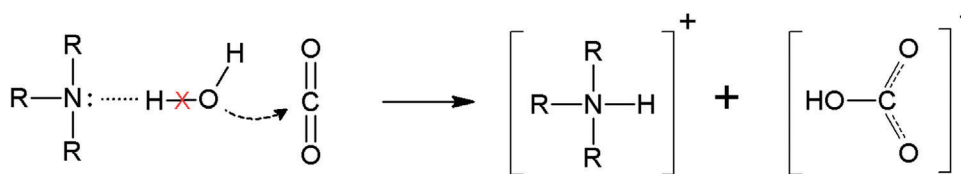
Methyl-di-ethanolamine (MDEA) and tri-ethanolamine (TEA) are tertiary amine solvents with the chemical structure of R₃N, where one R is methyl (–CH₃) and the other two R moieties are –C₂H₄OH for MDEA, and all the R groups are –C₂H₄OH for TEA. These solvents are considered to have promising characteristics to address the aforementioned shortcomings of MEA systems.^{21,22} Nevertheless, these two tertiary amines are not used as the main solvents to absorb CO₂ in the process due to their slow absorption rate. Therefore, tertiary amines have not been significantly studied as the independent absorbents, but rather as subsidiary solvents to improve the absorption performance and the stability of the process using other main solvents.^{23–25} However, the CO₂ absorption capacity of MDEA and TEA solutions can be theoretically maximized to 1.0 mol CO₂·mol^{–1} amine even with a high-concentration

solution because they follow different absorption mechanisms from primary and secondary amine systems. Therefore, many studies on tertiary amine solutions have recently been published in terms of absorption performance and some of these have compared the systems using MDEA and TEA solutions as the main solvent for absorption.^{26–29}

El Hadri *et al.* investigated the effect of the amine molecular structure on the CO₂ absorption performance by comparing the CO₂ solubility of 30 different amine solutions, and then evaluated the thermodynamics and kinetic properties of each system.³⁰ Xiao *et al.* reported the equilibrium solubility of CO₂ measured in five different tertiary amine solvents, including MDEA and TEA, and compared them to the predicted value using the Modified Kent–Eisenberg (M-KE) model. In addition, they presented the correlation between their CO₂ equilibrium solubility and the molecular structure, and then claimed that the stronger electron donating groups (e.g., ethyl group) substantially increased the CO₂ equilibrium solubility in the solutions.³¹

Although many other studies have examined the tertiary amine solvents, few have attempted to quantitatively compare the MDEA and TEA systems in terms of the correlation between the absorption performance and the electrical properties of the two systems.^{32–35} Specifically, the present study reports the correlations between the amount of CO₂ absorbed and the variation of electrical properties in each system, while also attempting to explain why their correlations differ substantially according to their different molecular structures and sizes. Our investigation is important since better understanding the correlation between absorption performance and electrical properties will be very beneficial for controlling the process with the aim of increasing its efficiency and simplicity. The CO₂ absorption capacity of the systems can be readily estimated *in situ* by measuring the electrical conductivity (EC) of the solution during the process. In addition, the relation between the electrical properties of tertiary amines and their molecular structure could be informative to investigate the properties of other solvent systems for absorption.

In the present study, therefore, the CO₂ absorption performance, such as chemical absorption capacity

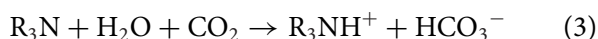
Figure 1. Chemical CO₂ absorption mechanism using tertiary amine solvent.

(CAC_{chem}), amine utilization, and overall absorption rate (OAR) of the MDEA and TEA systems, as well as their electrical properties, was investigated and the results were systematically compared and analyzed based on amine molecular structure and size. In addition, the ionic conductivity (IC) of protonated MDEA and the real ionic activity coefficient (RIAC) in high-concentration MDEA solutions were estimated using the EC of the solution measured during the absorption, which were also compared to those of TEA system.³⁶ Finally, the equations were generalized to enable *in situ* estimation of CAC_{chem} by measuring EC in high-concentration MDEA and TEA solutions.

Theory

Absorption mechanism using tertiary amine aqueous solution

The reactions involved in CO₂ absorption using tertiary amine solvent, including the dissociation and bicarbonation reaction, are summarized in Eqns (1)–(3).



Here, if all R groups are $-C_2H_4OH$ moieties, the amine is TEA, but if one R is a $-CH_3$ moiety and the other two Rs are $-C_2H_4OH$, it is MDEA.

In tertiary amine solution before absorption, R_3N first dissociates to protonated amine (R_3NH^+) and OH^- by Eqn (1). The concentrations of the generated R_3NH^+ and OH^- can be determined by the dissociation constant (pK), and the pK values of MDEA and TEA are 8.54 and 7.72, respectively.³⁷ When CO₂ is injected into the solution for absorption, OH^- , which is a strongly basic ion, firstly reacts with CO₂ to generate HCO_3^- (Eqn (2)), and then primary absorption is conducted by R_3N via Eqn (3). The absorption mechanism of Eqn (3) is based on a catalyst reaction in which amine does not directly react with CO₂, as shown in Fig. 1.³⁸

R_3N catalyzes the formation of OH^- by reacting with the water directly due to the attraction force exerted between a noncovalent pair of N atoms and the proton, and then CO₂ is combined with the OH^- . As a result, R_3NH^+ and HCO_3^- are generated when CO₂ is absorbed in a tertiary amine solution, and the theoretical molar ratio between the absorbed CO₂ and R_3N is 1.0 mol CO₂·mol⁻¹ amine. In addition to Eqn (3), water molecules can independently and additionally absorb a certain amount of CO₂ and this is regarded as the physical absorption capacity of water in amine systems. This capacity was measured as $2.34 \cdot 10^{-2}$ mol CO₂·L⁻¹ water (0.52 g CO₂·500 mL⁻¹ water) through the carbonation with 500 mL water under CO₂ at a partial pressure of 33.4 kPa at 25 °C.

Calculation of electrical conductivity (EC)

The equations used to calculate the EC of the MDEA, and TEA solutions are presented in Eqns (4)–(9).³⁹

$$EC = k_o \gamma^2 \quad (4)$$

$$k_o = \sum z_i \lambda_i c_i \quad (5)$$

$$IS = 5 \times 10^{-4} \sum c_i z_i^2 \quad (6)$$

$$\log \gamma = -0.509 z_+ z_- \sqrt{IS} \quad IS < 0.01 \quad (7)$$

$$\log \gamma = -0.5 z_+ z_- \frac{\sqrt{IS}}{1 + \sqrt{IS}} \quad 0.01 \leq IS \leq 0.1 \quad (8)$$

$$\log \gamma = -0.5 z_+ z_- \left(\frac{\sqrt{IS}}{1 + \sqrt{IS}} - 0.2 IS \right) \quad 0.1 < IS < 0.5 \quad (9)$$

The EC of the solution ($S \cdot m^{-1}$) is the product of the EC of an infinitely diluted solution (k_o ; $S \cdot m^{-1}$) and the square of the ionic activity coefficient (IAC; γ) of the solution as expressed in Eqn (4). Here, k_o is an ideal value that any interactions between ions and molecules are not exerted in the solution, which can be calculated by Eqn (5) using the concentration (c_i ; mol·m⁻³), absolute value of electric charge (z_i), and IC (λ_i ; $S \cdot m^2 \cdot mol^{-1} \cdot z^{-1}$) of every ion present in the solutions.

Table 1. Molar concentrations and their corresponded mass concentrations of the MDEA and TEA solutions.

MDEA		TEA		Classified concentration range
Molar concentration (mol·L ⁻¹)	Mass concentration (wt%)	Molar concentration (mol·L ⁻¹)	Mass concentration (wt%)	
0.01	0.12	0.01	0.15	Very low-concentration
0.02	0.24	0.02	0.30	
0.03	0.36	0.03	0.45	
0.04	0.48	0.04	0.60	
0.05	0.60	0.05	0.75	
0.1	1.19	0.1	1.49	Low-concentration
0.2	2.38	0.2	2.97	
0.3	3.57	0.3	4.45	
0.4	4.76	0.4	5.93	
0.5	5.94	0.5	7.40	
1.27	15.0	1.02	15.0	High-concentration
1.90	22.5	1.55	22.5	
2.55	30.0	2.08	30.0	

Practically, however, the interactions in real solutions depend on the ionic concentration in the solutions and the extent of interactions is determined by the γ value of the solutions. Generally, the IAC of the solutions can be calculated by using Debye–Huckel (Eqn (7)), Guntelberg (Eqn (8)), and Davies equation (Eqn (9)) according to the ionic strength (IS) of the solution estimated using Eqn (6).^{40–42}

However, when the IS of solution (mol·L⁻¹) is higher than 0.5 as the ionic concentration increases, Eqns (7)–(9) cannot be employed to calculate the EC of the solution since IS out of the available range. In this case, RIAC (γ_c) was calculated by Eqn (10) shown below, which is a modified equation by substituting directly measured EC (EC_m) from the absorption for the EC of Eqn (4) and k_o calculated via Eqn (5).

$$\gamma_c = \sqrt{\frac{EC_m}{k_o}} \quad \text{in high-concentration solution} \quad (10)$$

The process regarding these calculations was detailed in our previous works.³⁶

Experimental section

Thirteen different concentration solutions of MDEA and TEA were prepared for absorption. The molar

concentrations of the solutions and their corresponded mass concentrations (wt%) are summarized in Table 1.

To analyze the experimental results systematically, the solutions were classified into the following three categories according to the amine concentration of the solution: very low, low, and high. Very low-concentration solutions were used to estimate the IC of protonated MDEA (MDEAH⁺) and TEA (TEAH⁺). The ICs were verified by applying them to derive the correlation between the absorption performance and the electrical properties of the low- and high-concentration solution systems. In addition, the results of the overall absorption capacity (CAC_{total}) and IAC were also obtained in the low- and high-concentration solution systems and compared.

A schematic diagram of the absorption experiment is shown in Fig. 2.

The solutions of 500 mL for absorption were put in a cylindrical Pyrex reactor (D , 110 mm; h , 80 mm; total volume, 760 cm³) equipped with a water jacket to maintain the reactor temperature at 25 °C. The reactor was completely sealed and the empty spaces in the reactor and all gas lines were purged with pure N₂ gas (99%) before CO₂ was injected.

A gas mixture composed of 33.3 mol% CO₂ and balanced N₂ was used for absorption. CO₂ and N₂ gas

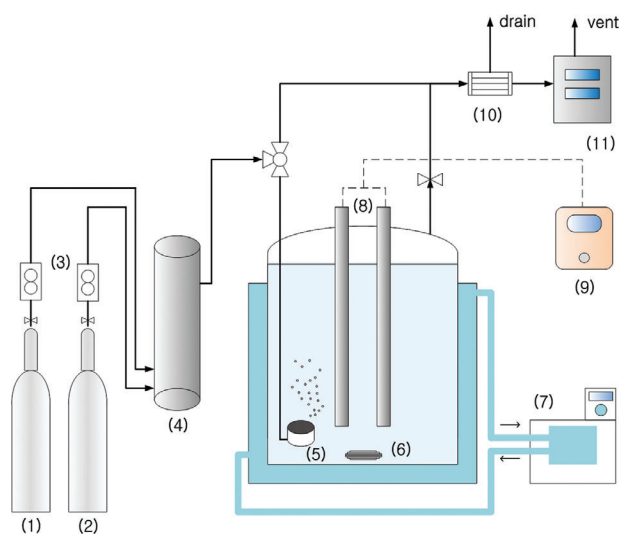


Figure 2. Schematic diagram of CO₂ absorption with tertiary amine solutions: (1) N₂ cylinder, (2) CO₂ cylinder, (3) mass flow controller (MFC), (4) gas mixer, (5) sparger, (6) magnetic stirrer, (7) water circulator, (8) pH/EC meter, (9) pH/EC recorder, (10) condenser, and (11) gas analyzer.

entered the SUS-made gas mixer (D , 90 mm; h , 400 mm; total volume, 2545 cm³) at a flow rate of 1.0 and 2.0 L·min⁻¹, respectively, using a mass flow controller (MFC; TSC-220, MKP, South Korea) to ensure uniform mixing.

The concentration of CO₂ in the gas mixture was confirmed to be 33.3 mol% by direct injecting into a nondispersive infrared (NDIR) CO₂ gas analyzer (GA; maMos-200, Madur Electronics, Poland) that measures CO₂ concentration every second. After verifying the gas concentration that was kept constant for 10 min, the gas was used for absorption. In addition, to improve the accuracy of the CO₂ concentration measured during the experiment, the humidity in the gases was removed by a condenser using iced water as the circulating fluid, which was equipped in front of the gas analyzer.

The gas mixture was injected into the solutions through a 1 μ m pore-sized sparger and the absorption was carried out in the reactor with a magnetic bar rotating at a stirring rate of 180 rpm. The EC and pH of the solution were measured every 5 s during the absorption using a pH/EC meter (Orion 4 Star, Thermo Scientific, USA). The concentration of the outlet gas after passing the solutions for absorption was analyzed by using the GA, following the previously mentioned procedures, and when it was equal to the feed gas concentration, the absorption was regarded as being completed. All *in situ* measured data, including

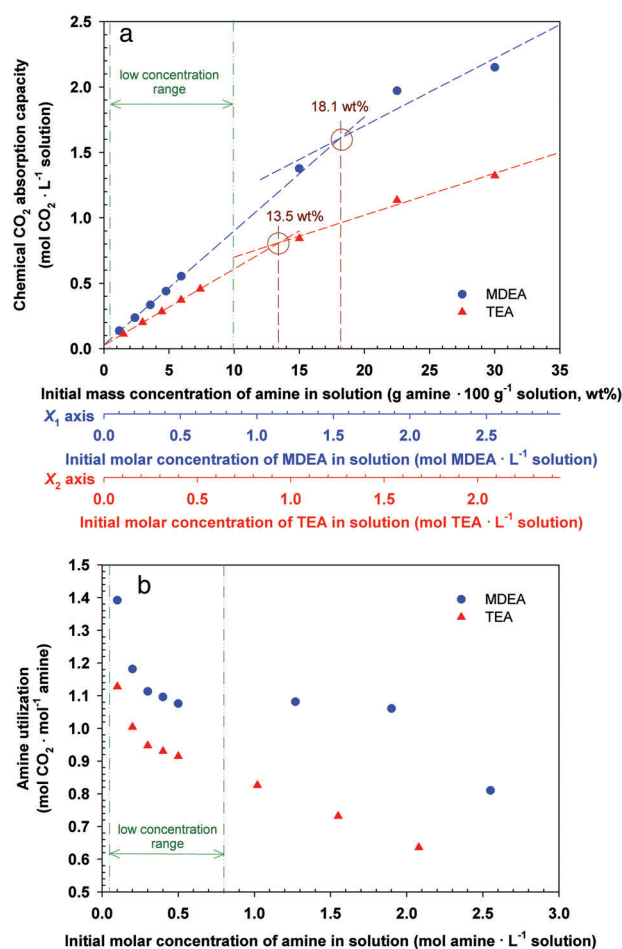


Figure 3. (a) Chemical CO₂ absorption capacity and (b) amine utilization according to initial molar concentration of MDEA and TEA solutions.

CO₂ concentration in the gas mixture and the pH and EC values of the solutions, were automatically recorded using the data acquisition systems for analysis.

Results and discussion

CO₂ absorption performance of MDEA and TEA solutions

Chemical CO₂ absorption capacity and amine utilization

The chemical CO₂ absorption capacity (CAC_{chem} ; mol CO₂·L⁻¹ solution) and amine utilization (mol CO₂·mol⁻¹ amine) of the low- (0.1–0.5 M) and high- (15.0–30.0 wt%) concentration MDEA and TEA solutions are shown in Fig. 3a and b, respectively. CAC_{chem} indicates the amount of CO₂ chemically absorbed according to Eqn (3), and it is calculated by subtracting the physical absorption capacity (CAC_{phy})

Table 2. Increasing ratio of chemical CO₂ absorption capacity (CAC_{chem}) to initial amine mass concentration in low- and high-concentration solutions of the MDEA and TEA systems.

System	Increasing ratio of CAC_{chem} (mmol CO ₂ ·L ⁻¹ ·g ⁻¹ amine)	
	Low-concentration range 0.1–0.5 M	High-concentration range 15.0–30.0 wt%; 1.3–2.6 M MDEA 1.0–2.1 M TEA
MDEA	8.71	5.15
TEA	5.83	3.20

from CAC_{total} experimentally measured by the gas analyzer. The CAC_{phy} of each amine solution was calculated based on the water concentration and the total amount of CO₂ absorbed of pure water, which were reported in our previous works.³⁶

In Fig. 3a, CAC_{chem} of the MDEA system was larger than that of the TEA system for all the same mass concentration solutions. The increasing ratio of CAC_{chem} to the concentration (slope at Fig. 3a) was different at low- (0.1–0.5 M) and high- (15.0–30.0 wt%) concentration ranges, as summarized in Table 2.

The increasing ratio of CAC_{chem} in low- and high-concentration ranges of the MDEA system was 49 and 61% larger than that of the TEA system, respectively. This phenomenon is primarily ascribed to the different molecular weights of the two amines: with the same mass concentration of the two amines, the molar concentration of MDEA is larger than that of TEA because the molecular weight of MDEA is relatively low. Therefore, theoretical CAC_{chem} and the increasing ratio of CAC_{chem} according to mass concentration were larger in the MDEA system. The initial molar concentrations of the MDEA and TEA solutions (C_{ini}) corresponding to their mass concentrations (X axis) are shown at the bottom of the X axis as X_1 and X_2 axis, respectively, in Fig. 3a. Therefore, CAC_{chem} and the increasing ratio of CAC_{chem} in the MDEA system should theoretically be 1.26 times larger than those of the same mass concentration solution points in the TEA system if Eqn (3) occurred completely. However, in the low- and high-concentration ranges, the real increasing ratio of CAC_{chem} in the MDEA system was 1.49 and 1.61 times larger than that in the TEA system, respectively, because the ratio of effective TEA molecules participating in absorption is further decreased than in the MDEA system. This point is detailed in Fig. 3b shown below.

Although the increasing ratio of CAC_{chem} (slope) of the two systems should be theoretically constant in the

low- and high-concentration ranges because the absorption is carried out by Eqn (3) in the two systems, the real increasing ratio of CAC_{chem} in the low-concentration range was larger than that in the high-concentration range. This phenomenon is primarily because as amine concentration of the solution increases the interaction between the amine molecules strengthens and the water concentration decreased in the high-concentration solution. At this condition, that is, the distance between the amine molecules is further decreased, which increases the interaction between the molecules, which substantially decreased the amine molecules to participate in the absorption reaction. In addition, the decreased water concentration, which is one of the reactants, might reduce the extent of reaction, thereby decreasing the increasing ratio of CAC_{chem} at the high-concentration range. C_{ini} point, which divides such low- and high-concentration ranges, could be obtained by crossing the two different regression lines of the increasing ratio of CAC_{chem} according to C_{ini} in the two systems. The points of the MDEA and TEA systems were determined to be 18.1 and 13.5 wt%, respectively, as shown in Fig. 3a.

To quantify the ratio of effective amines participating in the reaction in both systems, the molar concentration of effective amines, which was stoichiometrically calculated using Eqn (3) with CAC_{chem} obtained in each solution, was divided by C_{ini} . This factor was called the amine utilization (mol CO₂·mol⁻¹ amine) and is shown in Fig. 3b for all solutions in the two systems. The amine utilization does not theoretically exceed 1.0, based on Eqn (3). However, CO₂ might be trapped in the free space present between amine and water molecules in a low-concentration tertiary amine solution because the amine molecule is larger, and its structure is more complex compared to primary and secondary amines. Therefore, amine utilization can be slightly over 1.0 in

the low-concentration MDEA and TEA systems because free spaces can be filled with a small amount of additionally absorbed CO₂.

In Fig. 3b, the MDEA utilization was higher than that of TEA in all solutions. However, the ratio of MDEA to TEA utilization remained almost constant—about 1.17 times higher in the low-concentration range below 0.5 M. This phenomenon is ascribed to the fact that amine utilization in the low-concentration solution is further dependent on the water concentration than that of amine in both systems. Meanwhile, although the TEA utilization over 0.5 M solutions considerably decreased lower than 1.0, the MDEA utilization was maintained higher than 1.0 even in the high-concentration solution of 1.90 M (22.5 wt%). This might be because the MDEA system has more spaces to trap CO₂ between amine and water molecules in the high-concentration solutions because the MDEA molecule, which has two C₂H₄OH and one CH₃ moieties, is more asymmetric and irregular in terms of molecular structure than TEA composed of three C₂H₄OH moieties; which might basically lead to the small different steric hindrance of MDEA and TEA systems.

Therefore, the amine utilization of the MDEA and TEA solutions of the same molar concentration is significantly affected by the amine molecular structure. For chemical absorption in a tertiary amine solution, a substantial attraction force is firstly exerted between the unpaired electrons of the N atom and one proton of water, which is larger in the MDEA system because the catalytic activity of the MDEA molecule is higher than that of the TEA molecule.⁴³ Therefore, the reactivity of water and CO₂ is relatively higher in the MDEA system, which results in a higher MDEA utilization in the same molar concentration solutions.

Overall absorption rate

With CAC_{chem} and total absorption time obtained in the two systems, CAC_{chem} per unit time, termed as OAR, was calculated and they are shown in Fig. 4.

OAR increased according to C_{ini} in the low-concentration range in the two systems, and its maximum value of the 15 wt% MDEA and TEA solutions was 14.2 and 9.8 mmol CO₂·L⁻¹·min⁻¹, respectively. Thereafter, OAR decreased as C_{ini} increased, resulting in a parabolic curve over the full concentration range. The curved variation of OAR occurs because the chemical absorption with tertiary amine is followed by a base-catalyzed mechanism, in which CO₂ directly reacts with water to generate

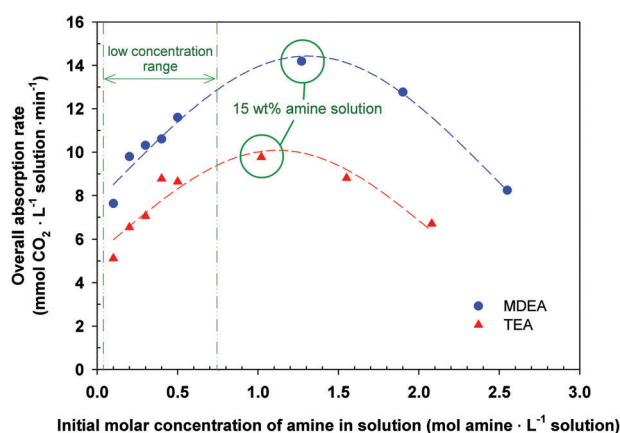


Figure 4. Overall absorption rate according to initial molar concentration of MDEA and TEA solutions.

HCO₃⁻, and tertiary amine acts as a catalyst in the reaction, as shown in Fig. 1. Therefore, the water concentration in the amine solution is one of the important factors that strongly affect the absorption performance, including OAR, in the two systems. In addition, the OAR of the MDEA system was always higher than that of TEA at all concentrations due to the properties resulting from the structure of the MDEA molecule, which can increase the reactivity of -OH moieties in water for absorption. Based on the parabolic curve of the OAR results, the mass concentration that maximizes OAR is 15.0 wt% in the two systems, which equates to C_{ini} values in the MDEA and TEA systems of 1.3 and 1.0 M, respectively.

Electrical properties of the MDEA and TEA systems

IC of MDEAH⁺ and TEAH⁺

The IC of MDEAH⁺ and TEAH⁺ are summarized in Table 3. The IC and absolute value of electric charge of OH⁻ and HCO₃⁻ involved Eqns (1) and (3) are listed in Table 3.^{44,45}

Very low-concentration solutions were used for absorption to estimate the IC of MDEAH⁺ and TEAH⁺ to minimize interaction between ions or molecules in the solutions. Before CO₂ is injected in the MDEA and TEA solutions, the fresh solutions dissociates the R₃NH⁺ of amine and OH⁻ by Eqn (1) and their concentrations can be calculated based on the pK values, as aforementioned. Thereafter, as CO₂ is absorbed, R₃NH⁺ and HCO₃⁻ begin to be generated by Eqn (3), and their *in situ* concentrations can be calculated by Eqn (3) with CAC_{chem} values measured every second during the absorption. Therefore, the

Table 3. Ionic conductivity (IC) and absolute value of electric charge (z) of ions involved in chemical CO₂ absorption in the MDEA and TEA solutions.

Ions	absolute value of electric charge (z)	Ionic conductivity (S·cm ² ·mol ⁻¹ ·z ⁻¹)
OH ⁻	+1	198.6 ⁴⁴
HCO ₃ ⁻	+1	44.50 ⁴⁵
MDEAH ⁺	+1	46.51 ^a
TEAH ⁺	+1	37.60 ^b

^a Estimated in present works.
^b Estimated in previous works.³⁶

concentration of all ions, such as R₃NH⁺, OH⁻, and HCO₃⁻, contained in fresh and CO₂ absorbed solutions can be determined. In addition, the IC of OH⁻ and HCO₃⁻ are already known and if the IC of R₃NH⁺ was reasonably estimated, the *in situ* EC values in all CO₂ absorbed solutions can be calculated (EC_c) via Eqns (4)–(9).

The calculation to verify the IC of the two R₃NH⁺ ions obtained from the estimated values was iterated with MATLAB programs until the IC satisfied the certain point that minimizes the calculation deviation between EC_m and EC_c values in all CO₂ absorbed solutions of the two systems. As a result, the IC of MDEAH⁺ and TEAH⁺ was calculated to be 46.51 and 37.60 S·cm²·mol⁻¹·z⁻¹, respectively, and the minimum calculation deviation was 9.2 and 14.73%.³⁷

The IC of MDEAH⁺ is about 1.24 times larger than that of TEAH⁺, which was attributed to the different molecular (or ionic) weight and volume of the two R₃NH⁺ ions. IC is strongly affected by ionic weight and volume, which are directly related to ionic mobility and charge density, respectively. The ionic weight of TEAH⁺ and MDEAH⁺ is 150.19 and 120.16 g·mol⁻¹, respectively, and the ionic volume of MDEAH⁺ is smaller than that of the TEAH⁺. Therefore, the mobility and ionic charge density of MDEAH⁺ are larger than those of TEAH⁺.

Comparison of measured (EC_m) and calculated EC (EC_c) variation during absorption in very low-concentration (0.01–0.05 M) MDEA and TEA solutions

For the very low-concentration MDEA and TEA solutions, variation of EC_c calculated based on the

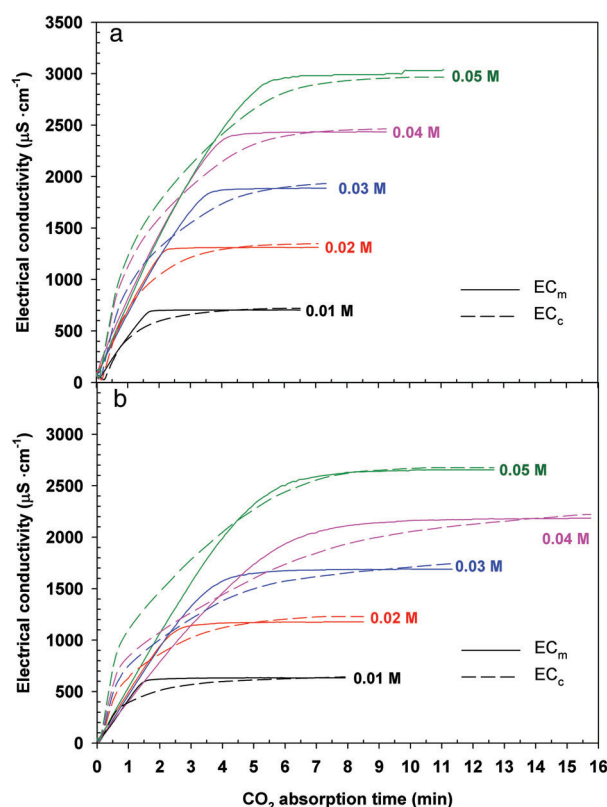


Figure 5. Variation of measured (EC_m) and calculated (EC_c) electrical conductivity according to absorption time in very low-concentration (0.01–0.05 M) (a) MDEA and (b) TEA solutions.

determined IC of MDEAH⁺ and TEAH⁺ and variation of EC_m directly measured during the absorption are shown in Fig. 5a and b.

To accurately calculate the CAC_{chem} values, which is critical for estimating the concentration of all ions in the solutions, the amount of CAC_{phy} was assumed to be proportional to the amount of CAC_{total}, which is measured at the absorption completion point, with a constant ratio. For example, the amount of CAC_{total} measured and CAC_{phy} assumed at the completion point was 53.4 and 23.4 mmol CO₂·L⁻¹ in 0.03 M MDEA solution, respectively, and thus CAC_{phy} was about 43.8% of CAC_{total}. Therefore, this ratio was applied to all CO₂ absorbed solutions during the reaction, and thus the amount of CAC_{chem} of all solutions was assumed to be 56.2% of the CAC_{total} measured during the reaction. Therefore, CAC_{chem} was finally determined, and thus the concentrations of other ions in Eqns (2) and (3) were stoichiometrically calculated.

In Fig. 5a and b, EC_m in the initial period of reaction of all solutions was linearly increased over time. Afterwards, the increasing ratio of EC_m over time was

Table 4. Time observed according to the difference between EC_c and EC_m, as well as CAC_{total}, CAC_{chem}, real CAC_{chem} and their ratio at that time in the 0.03 M MDEA and TEA solutions.

Comparison of EC _c and EC _m	EC _c > EC _m		EC _c = EC _m		EC _c < EC _m	
	MDEA	TEA	MDEA	TEA	MDEA	TEA
Time observed from absorption start (min)	1.0	1.0	2.5	2.3	4.0	4.0
CAC _{total} (mmol CO ₂ ·L ⁻¹)	22.4	20.3	38.3	30.3	46.7	40.4
CAC _{chem} (mmol CO ₂ ·L ⁻¹)	12.7 (56.2)*	11.5 (56.2)*	21.7 (56.2)*	17.2 (56.2)*	26.5 (56.2)*	22.9 (56.2)*
Real CAC _{chem} (mmol CO ₂ ·L ⁻¹)	8.9 (39.4)*	7.1 (34.6)*	21.7 (56.2)*	17.2 (56.2)*	28.9 (61.4)*	26.6 (65.2)*

^a In parenthesis; ratio of CAC_{chem} or real CAC_{chem} to CAC_{total}, (%).

significantly decreased at certain time, and then the absorption was completed after EC_m was maintained constant for some time. On the other hand, EC_c increased relatively rapidly, and thus it was slightly higher than EC_m in the initial period for every solution. Subsequently, the increasing ratio of EC_c decreased over time and EC_c became smaller than EC_m. Finally, EC_m and EC_c of each solution were almost the same at the absorption completion point. This difference between EC_c and EC_m in each solution during the reaction was tentatively attributed to the varying ratio of CAC_{phy} to CAC_{total} throughout the reaction, unlike the aforementioned assumption.

For example, the EC_c value of the 0.03 M MDEA solution at 1 min was larger than the EC_m of the same solution at that time. Here, the amount of CAC_{total} of the solution was measured as 22.6 mmol CO₂·L⁻¹. Applying the aforementioned assumption, the amount of CAC_{chem} at this time point was calculated to be 12.7 mmol CO₂·L⁻¹. When considering the CAC_{chem} and Eqn (3), the concentrations of MDEAH⁺ and HCO₃⁻ in the solution could be calculated. Therefore, applying these concentrations to Eqns (4)–(9), the EC_c value of the 0.03 M MDEA solution at 1 min was calculated to be 913 μS·cm⁻¹. However, the EC_m was measured to be 667 μS·cm⁻¹ for the MDEA solution, which was substantially smaller than the EC_c value. Inversely, if the EC_m values were used instead of the EC term in Eqn (4) and combining it with Eqns (5)–(9), the concentrations of MDEAH⁺ and HCO₃⁻ in the solutions could be calculated as the unknown variables of the combined equation. Therefore, using these two concentrations and via Eqn (3), the amount of real CAC_{chem} was calculated to be 8.9 mmol CO₂·L⁻¹ in the 0.03 M MDEA solution, which was 39.4% of the

CAC_{total} amount. Since this ratio was lower than the previously assumed value by 16.8%, EC_m was smaller than EC_c in the solutions. Therefore, the real CAC_{chem} and its ratio to CAC_{total} could be calculated at every time point in all solutions based on their EC_m values measured during the absorption, and thus some EC_c values were equal to EC_m, while the other EC_c was smaller or larger than EC_m. Considering this calculation process, EC_c calculated based on CAC_{chem} and the real CAC_{chem} calculated based on EC_m were compared and the results are summarized in Table 4, with their ratios to CAC_{total} in the 0.03 M MDEA and TEA solutions.

Considering the results presented in the Table 4, the ratio of real CAC_{chem} to CAC_{phy} according to time was not constant in the MDEA and TEA systems, and the ratios of real CAC_{chem} to CAC_{total} were calculated comparing the EC_m and EC_c values at each time. The ratio of real CAC_{chem} amount of the 0.03 M MDEA and TEA solutions was calculated and was lowest at 45 and 50 s, respectively, which was about 37.7 and 30.1% of their CAC_{total}. As a result, the ratio of real CAC_{chem} amount was relatively low in the initial period, and then gradually increased according over time. Finally, the ratio of real CAC_{chem} amount decreased again and the absorption was completed

Application of ICs of protonated amine to the low-concentration (0.1~0.5 M) MDEA and TEA solutions

EC_c variation of the low-concentration MDEA and TEA solutions according to absorption time was calculated using the determined IC of MDEAH⁺ and TEAH⁺ and the result are shown in Fig. 6 with the EC_m values.

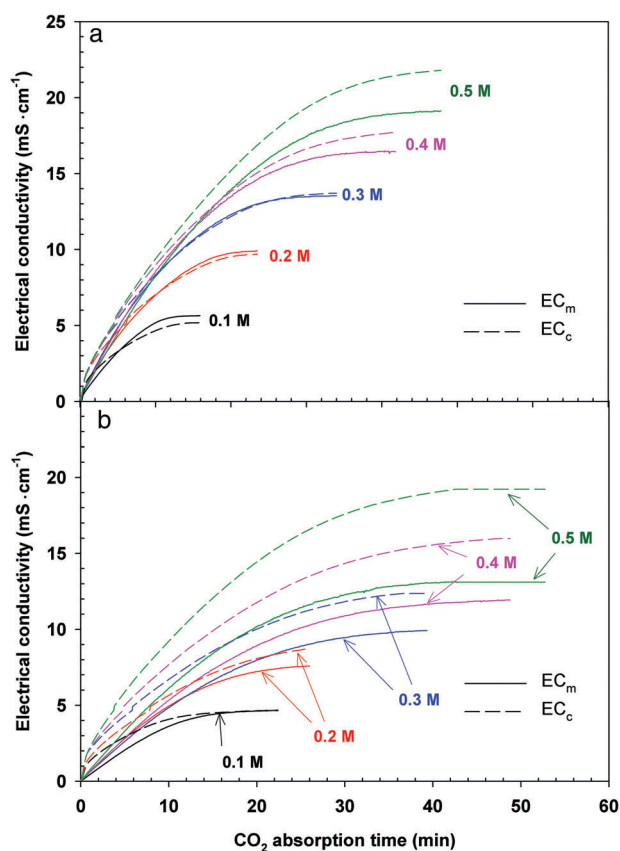


Figure 6. Variation of measured (EC_m) and calculated (EC_c) electrical conductivity according to absorption time in low-concentration (0.1–0.5 M) (a) MDEA and (b) TEA solutions.

In Fig. 6, the EC_m and EC_c values in the initial period of the MDEA and TEA solutions below 0.2 M were not significantly different, as in very low-concentration solutions. However, the difference between EC_m and EC_c gradually increased as C_{ini} and the time increased. In particular, the difference between EC_m and EC_c in the TEA system was even larger than that in the MDEA system, and thus the difference of two EC values of the 0.5 M TEA solution averaged 60% during the absorption. On the other hand, the average difference of the two EC values in the 0.1–0.5 M MDEA solutions was 13.7%. Considering the results, the IC of MDEAH⁺ could be confirmed to be substantially valid because the difference between EC_m and EC_c , which is calculated by applying it to the MDEA system, was relatively very small in all MDEA solutions below 0.5 M. In addition, the interaction between ions or molecules was verified to be so small in the MDEA solution below 0.5 M that it was considered to have little influence on EC_m in the solutions. On the other

hand, the difference between the two EC values was very large in the TEA solution above 0.3 M, which was attributed to the fact that the TEA molecule is larger than MDEA. That is, in the TEA solution over 0.3 M, the interaction between ions or molecules of TEA could be substantially intensified due to their large size, which rapidly reduced the EC_m increase according to amount of CO₂ absorbed in the solution. These results could be explained by the difference between the IAC calculated by Eqns (7)–(9) and the real IAC based on EC_m in the solution. As the interaction between ions or molecules increases in solution, IAC in the solution becomes smaller because it is directly related to interaction. However, the interactions were considerably negligible in the MDEA solutions below 0.5 M. In addition, although the EC_c in the 0.1, 0.2 M MDEA and 0.1 M TEA solutions at the absorption completion point were similar or slightly smaller than the EC_m in the same solutions, the EC_c values in the MDEA and TEA solutions over 0.2 M and 0.1 M, respectively, were a little larger than the EC_m and the difference between the two EC gradually increased according to C_{ini} . This is because the interaction, which is practically exerted between molecules or ions such as R₃NH⁺ and HCO₃[−] generated by Eqn (3), was not considered in calculating EC_c . Practically, however, the interaction is intensified according to the amine concentration and the amount of zwitterion (R₃NH⁺·HCO₃[−]) increased. Furthermore, MDEAH⁺ and TEAH⁺ include three elongated large R moieties, which may lead to physical entanglements with them in high-concentration solution, and thus the impact of molecules or ions on EC_m can be substantially decreased. Therefore, the increasing ratio of EC_m was even further decreased relative to that of EC_c as the amine concentration increased at the absorption completion point with the larger molecules. As a result, the difference between EC_m and EC_c of the TEA system was always larger than that of the MDEA system for the same concentration solutions, and their difference in the 0.5 M TEA solution at the absorption completion point was the largest.

Ionic activity coefficient in the high-concentration (15.0–30.0 wt%) MDEA and TEA solutions

The IAC of the high-concentration 15–30 wt% MDEA and TEA solutions cannot be calculated via Eqns (7)–(9) because their IS values are always much higher

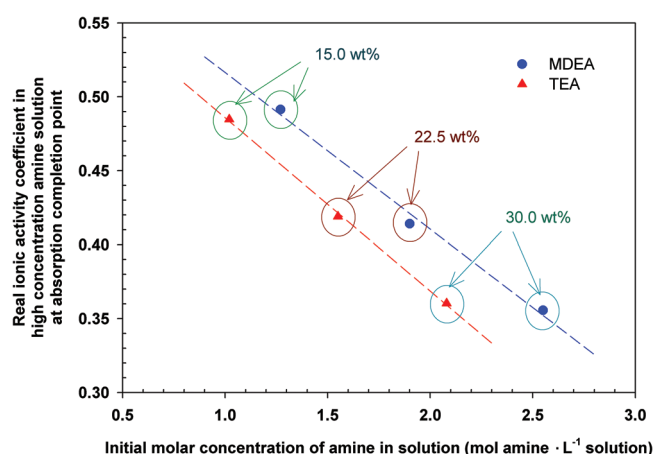


Figure 7. Real ionic activity coefficient (RIAC) and their regression results at the absorption completion point in high-concentration MDEA and TEA solutions.

than 0.5. Therefore, RIAC was calculated by applying EC_m to Eqn (10) with k_o calculated by Eqn (5). The RIAC results of the 15–30 wt% MDEA and TEA solutions at the absorption completion point are shown in Fig. 7 with the regression results.

Firstly, the RIAC of the MDEA system was about 10% higher than that of TEA in the same molar concentration solutions. In addition, RIAC linearly decreased according to C_{ini} in both systems, and thus its decreasing ratio of the MDEA system ($10.60 \cdot 10^{-2} \text{ L} \cdot \text{mol}^{-1} \text{ amine}$) was smaller than that of the TEA system ($11.72 \cdot 10^{-2} \text{ L} \cdot \text{mol}^{-1} \text{ amine}$). RIAC is one of the most representative factors to affect the performance of the reaction. Therefore, the RIAC difference of the high-concentration solution between the two systems could be explained due to the previously described several effects such as the intensity of the interaction, molecule or ion size and their physical entanglements, and the amount of zwitterions and water molecules in the solutions.

Correlation of CAC_{chem} and EC_m in the MDEA and TEA systems

Variation of CAC_{chem} and EC_m according to absorption time

The variation of CAC_{chem} and EC_m according to time in the low- (0.1–0.5 M) and high- (15–30 wt%) concentration MDEA and TEA solutions are shown in Fig. 8.

CAC_{chem} increased rapidly in the initial period of absorption of the two systems, as shown in Fig. 8a and c, respectively, and the reaction approached the

completion point as the absorption rates gradually decreased in both systems. The absorption rate, however, was the highest in the 15 wt% solution among the high-concentration solutions, because the absorption using the MDEA and TEA solutions is a base-catalyzed reaction, as aforementioned in the Overall Absorption Rate section. In Fig. 8b and d, the trend of EC_m variation according to time was very similar to that of CAC_{chem} . This indicates that CAC_{chem} is very directly related to EC_m that is strongly proportional to the concentrations of ions. However, the increasing ratio of CAC_{chem} to EC_m according to time began to decrease in the solution over 22.5 wt%, unlike the relative low-concentration solutions. For example, EC_m of the 30 wt% MDEA and TEA solutions at the absorption completion point was 24.65 and 13.90 $\text{mS} \cdot \text{cm}^{-1}$, respectively, which were lower than that of the two 22.5 wt% solutions (29.90 and 16.61 $\text{mS} \cdot \text{cm}^{-1}$, respectively). This is due to the rapid decrease in RIAC in high-concentration solutions (over 22.5 wt%), which significantly reduces EC_m of the solutions.

Correlation of CAC_{chem} and EC_m

Nevertheless, the variations of CAC_{chem} and EC_m according to time exhibited a similar trend and they were directly proportional to each other in the two systems. This was confirmed in Fig. 9a and c, which shows the variation of CAC_{chem} according to EC_m in the low- and high-concentration MDEA and TEA solutions. Therefore, the relation could be linearly correlated, and the results are shown in Fig. 9b and d.

In Fig. 9a and c, CAC_{chem} is linearly proportional to EC_m in the MDEA and TEA solutions above 0.1 M. This is because the EC of the solution is strongly dependent on the concentration of ions, as presented in Eqns (4) and (5), and the concentrations are directly correlated with CAC_{chem} . However, the slope of correlated equation, that is, the slope of CAC_{chem} according to EC_m , (SCE) was different for each solution, and SCE was increased as C_{ini} increased. This indicates that the amount of CAC_{chem} required to increase the same amount of EC was increased as C_{ini} increased. For example, CAC_{chem} required to increase EC by 10 $\text{mS} \cdot \text{cm}^{-1}$ was 0.566 $\text{mol CO}_2 \cdot \text{L}^{-1}$ in the 15 wt% MDEA solution, it was 1.62 times larger, 0.915 $\text{mol CO}_2 \cdot \text{L}^{-1}$, in the 30 wt% MDEA solution. This result was attributed to the decrease of RIAC as C_{ini} increased. In the high-concentration solution therefore, CAC_{chem} required to increase the ratio of effective ion concentration, which directly affects EC_m

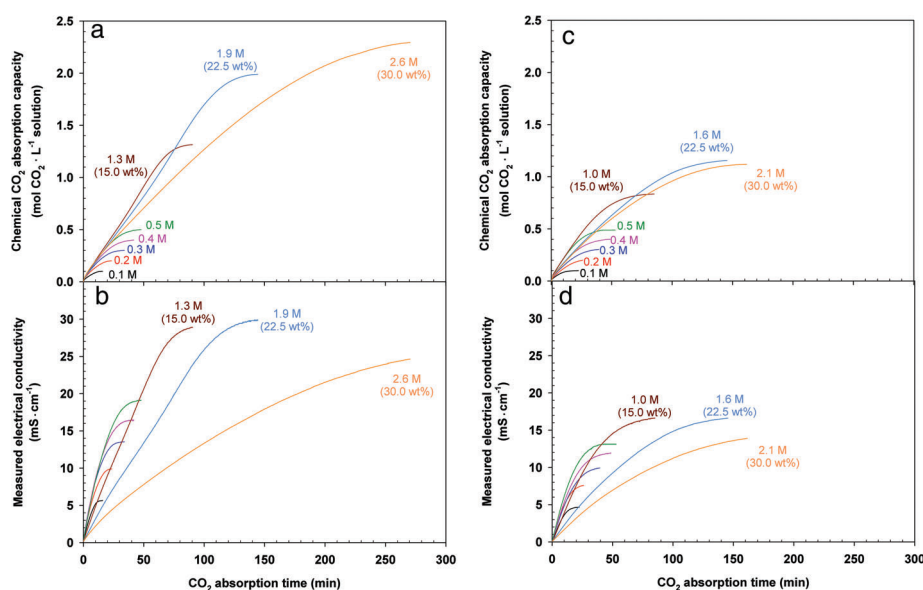


Figure 8. Chemical CO₂ absorption capacity and measured electrical conductivity (EC_m) according to absorption time in (a and b) MDEA and (c and d) TEA solutions.

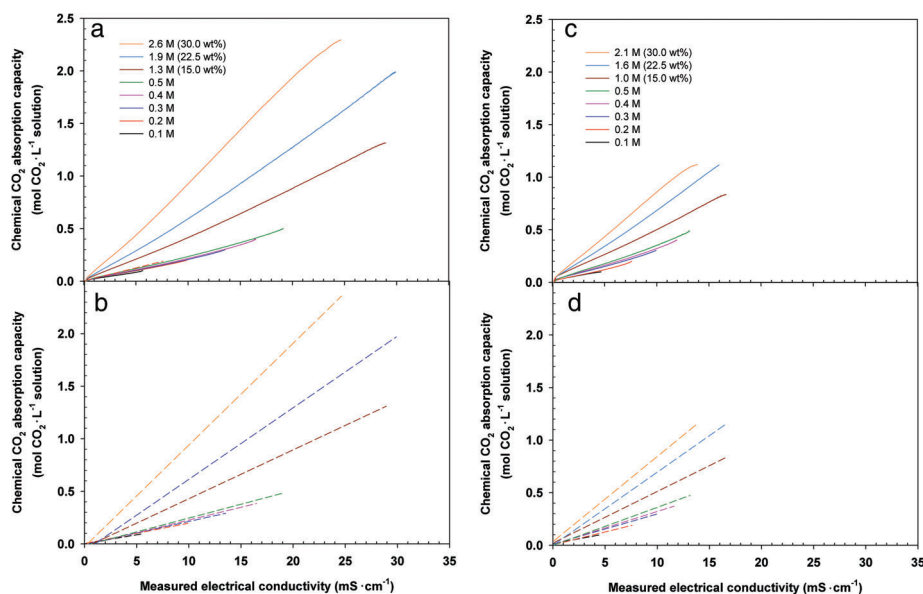


Figure 9. Correlation between chemical CO₂ absorption capacity and measured electrical conductivity (EC_m) and their regression results in (a and b) MDEA and (c and d) TEA solutions.

in the solution, is relatively larger than that of the low-concentration solution.

Generalized correlation equations between CAC_{chem} and EC_m

From the regression results between CAC_{chem} and EC_m that are shown in Fig. 9b and d, the equation to correlate CAC_{chem} with EC_m in both systems could be

generalized as presented in Eqn (11).

$$\begin{aligned} & \text{CAC}_{\text{chem}} \text{ of } n \text{ M solution} \\ & = a \times (\text{EC}_m \text{ of } n \text{ M solution}) + b \quad (11) \end{aligned}$$

where 'a' is the slope of CAC_{chem} to EC_m (SCE) and 'b' is the y-intercept (ICE). SCE and ICE values according to the C_{ini} of the two systems, which are obtained from

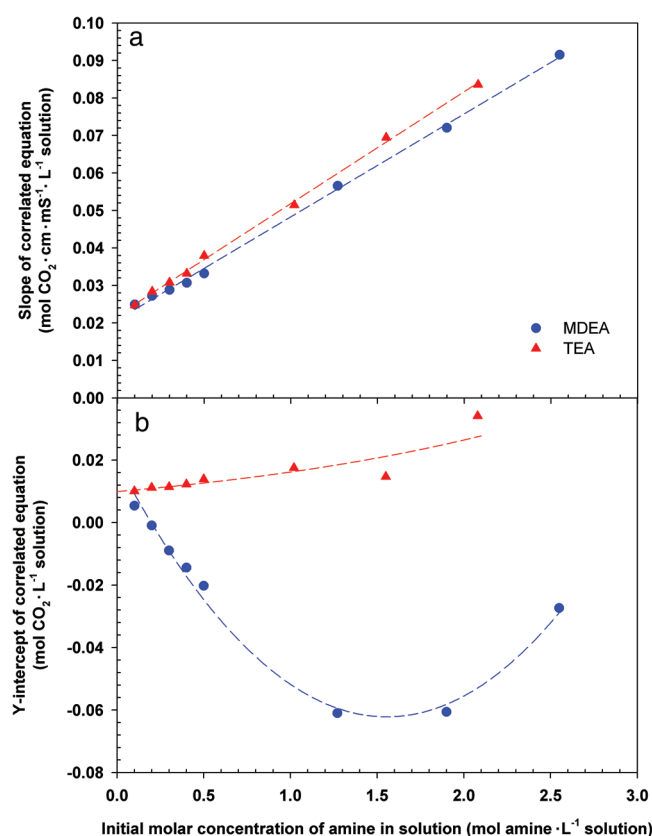


Figure 10. Variation of (a) slope (SCE) and (b) y-intercept (ICE) in correlated equation according to initial molar concentration of MDEA and TEA solutions.

the correlated line in Fig. 9b and d, are shown in Fig. 10a and b, respectively.

Fig. 10a shows that SCE of the two systems is increased proportionally to C_{ini} and depicts the slopes of SCE (SSCE), which is another parameter indicating the ratio of SCE variation according C_{ini} of the solutions to characterize the amine-based absorption system. SSCE is dependent on the conductivity and concentration of effective ions present in the solutions. The EC variation become relatively large as the conductivity and concentration of effective ions increased, which increased the SCE value in the solution. Therefore, the SSCE of the MDEA system was $0.027 \text{ mol CO}_2 \cdot \text{cm} \cdot \text{mS}^{-1} \cdot \text{mol}^{-1}$ amine, which was lower than $0.030 \text{ mol CO}_2 \cdot \text{cm} \cdot \text{mS}^{-1} \cdot \text{mol}^{-1}$ amine of the TEA system, because the IC (Table 3) and RIAC (Fig. 7) of the MDEA system were larger than those of TEA.

Fresh amine solutions that have not absorbed CO₂ have a certain EC value. However, the ICE shown in Fig. 10b is the value obtained through the regression of

the results shown in Fig. 9b and d, which indicates the amount of CAC_{chem} when EC in solution is $0 \text{ mS} \cdot \text{cm}^{-1}$. The ICE values, therefore, are an insignificant mathematical parameter to solely express the generalized equations. When correlating ICE with the C_{ini} of the TEA system through regression by applying the first-order and exponential function, the regression coefficient (r^2) was 0.747 and 0.815 for the first-order and exponential functions, respectively. Therefore, although the relationship between ICE and C_{ini} in TEA seemed to be linear, it could be favorably expressed in the exponential form. On the other hand, the ICE variation of the MDEA system followed the form of a parabolic curve.

Finally, SCE and ICE could be correlated with the C_{ini} of solution and the final equations can be expressed as Eqns (12)–(15) for the MDEA and TEA systems.

$$\text{SCE of MDEA} = 0.027 \cdot C_{ini} + 0.021 \quad r^2 \text{ is } 0.993 \quad (12)$$

$$\text{SCE of TEA} = 0.030 \cdot C_{ini} + 0.022 \quad r^2 \text{ is } 0.999 \quad (13)$$

$$\begin{aligned} \text{ICE of MDEA} &= 0.0337 \cdot C_{ini}^2 - 0.1049 \cdot C_{ini} \\ &\quad + 0.0194 \quad r^2 \text{ is } 0.988 \end{aligned} \quad (14)$$

$$\text{ICE of TEA} = 10^{0.213 \cdot C_{ini} + 0.997} \quad r^2 \text{ is } 0.815 \quad (15)$$

Finally, when 'a' and 'b' in Eqn (11) are replaced with the SCE and ICE values of the MDEA and TEA systems, as summarized in Eqns (12)–(15), the overall equation to estimate CAC_{chem} of each system can be represented as only the C_{ini} and EC_m values measured during the absorption, and they are generalized as presented in Eqns (16) and (17) for the MDEA and TEA systems, respectively.

$$\begin{aligned} \text{CAC}_{chem} \text{ of MDEA} \\ &= (0.027 \cdot C_{ini} + 0.0214) \cdot EC_m \\ &\quad + 0.0337 \cdot C_{ini}^2 - 0.1049 \cdot C_{ini} + 0.0194 \end{aligned} \quad (16)$$

$$\begin{aligned} \text{CAC}_{chem} \text{ of TEA} \\ &= (0.030 C_{ini} + 0.022) \cdot EC_m + 10^{0.213 \cdot C_{ini} + 0.997} \end{aligned} \quad (17)$$

With the variation of EC_m during the absorption, therefore, CAC_{chem} of the MDEA and TEA solutions of an arbitrary C_{ini} value could be estimated *in situ* using Eqns (16) and (17), respectively.

Summary of results

For convenience of understanding, the comparative results of the MDEA and TEA systems in terms of the

Table 5. Summary of comparative results in terms of CO₂ absorption performance and electrical properties of the MDEA and TEA systems.

		MDEA	TEA
Molecular weight (g·mol ⁻¹)		119.16	149.18
Molar volume (cm ³ ·mol ⁻¹)		114.6	132.0
CAC _{chem} (mol CO ₂ ·L ⁻¹ solution)		Relatively higher	Relatively lower
Increasing ratio of CAC _{chem} (mmol CO ₂ ·L ⁻¹ solution·g ⁻¹ amine)	Low-concentration	8.71	5.15
	High-concentration	5.83	3.20
Amine utilization (mol CO ₂ ·mol ⁻¹ amine)		Relatively higher	Relatively lower
Maximum overall absorption (mmol CO ₂ ·L ⁻¹ ·min ⁻¹) and its observed initial amine concentration in solution (M; wt%)		14.2 (1.27; 15.0)	9.8 (1.02; 15.0)
Ionic conductivity of protonated amine (S·cm ² ·mol ⁻¹ ·z ⁻¹)		46.51	37.60
Decreasing ratio of RIAC (L·mol ⁻¹ amine)		10.60 × 10 ⁻²	11.72 × 10 ⁻²
SSCE (mol CO ₂ ·cm·mS ⁻¹ ·mol ⁻¹ amine)		0.027	0.030

CO₂ absorption performance and electrical properties are summarized in Table 5.

Conclusions

The present study has described the features of chemical CO₂ absorption using tertiary amine solutions as absorbents by comparing the absorption performance and electrical properties in the MDEA and TEA systems. The results were mostly explained by the different structures of the two amine molecules. The study conclusions are as follows:

1. The CO₂ absorption performance, as CAC_{chem}, its increasing ratio according to mass concentration of amine in solution, amine utilization, and OAR, was higher in the MDEA system than in the TEA system. This performance difference was attributed to the more asymmetric and irregular structure of the MDEA molecule compared to the TEA molecule, which enhances the catalytic activity of MDEA and the reactivity of the -OH moiety in water. In addition, as the physically absorbed CO₂ might become further trapped in the free spaces formed between MDEA and water molecules in the low-concentration solution, the amine utilization was slightly larger than the theoretical value (1.0 mol CO₂·mol⁻¹ amine). The water concentration in the amine solution significantly affected the influence of the absorption performance on the interaction between ions or molecules in the solutions. In addition, the variation of OAR of the two systems, where water is also a reactant, followed

a parabolic curve according to C_{ini} because the absorption is a base-catalyzed reaction. Therefore, the OAR value of the MDEA and TEA systems was maximized in the 15 wt% solution at 14.2 and 9.8 mmol CO₂·L⁻¹·min⁻¹, respectively.

2. The IC of MDEAH⁺ was estimated to be 46.51 S·cm²·mol⁻¹·z⁻¹, which was 1.24 times larger than that of TEAH⁺ and which was attributed to the higher ionic mobility and charge density of MDEAH⁺ resulting from its relatively small weight and volume compared to those of TEAH⁺. The RIAC value of the MDEA system was larger than that of the TEA system in the same concentration solution. RIAC was linearly decreased according to C_{ini} in both solutions and the decreasing ratio of the MDEA system was smaller than that of the TEA system. These results were explained by the relatively smaller intensity of the physicochemical interaction between the molecules or ions in the MDEA system in the same concentration solutions.
3. Finally, based on the aforementioned results, the correlations between the absorption performance and the variation of electrical properties were derived in both systems. Therefore, the overall equation for *in situ* estimation of CAC_{chem} by measuring the EC variation of the solutions during the absorption was generalized in the MDEA and TEA systems. In the equation, SCE, which indicates the increasing ratio of CAC_{chem} according to EC_m was proportional to the C_{ini} of the solution, and its slope, which is the increasing ratio of SCE (SSCE) according to C_{ini} in the TEA system (0.030 mol

CO₂·cm·mS⁻¹·mol⁻¹ amine), was higher than that in the MDEA system (0.027 mol CO₂·cm·mS⁻¹·mol⁻¹ amine). This is because when the amount of CO₂ absorbed is the same in the two identical initial amine concentration solutions, the EC variation is larger in the MDEA system due to the relatively larger IC of MDEAH⁺ and RIAC in solution compared to the TEA system.

Acknowledgments

This research was supported by Basic Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2017R1D1A1B03033107) as well as supported by the Catholic University of Korea, Research Fund, 2019.

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