



Correlation of CO₂ absorption performance and electrical properties in a tri-ethanolamine aqueous solution compared to mono- and di-ethanolamine systems

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Abstract

The study investigates the correlation of CO₂ absorption performance and electrical properties in a tri-ethanolamine (TEA) aqueous solution compared to the mono-ethanolamine (MEA) and di-ethanolamine (DEA) systems. While the absorption rate of the MEA and DEA systems varies with amine concentration, and the maximum rate is observed at 30.0 and 50.4 wt% amine solution, respectively, the rate of the TEA system according to concentration follows a parabolic curve and the maximum rate is observed at 15.0 wt% solution. The ionic conductivity of carbamic acid in the TEA system is estimated to be the smallest with 37.60 S cm²/mol z and the decreasing ratio of ionic activity coefficient according to the concentration is the largest. The results are mostly attributed to differences in amine molecular structure and the unique reaction mechanism. Finally, based on these values, the correlation equations are obtained to estimate CO₂ absorption capacity by measuring electrical conductivity in situ.

Keywords Carbon capture and utilization/storage · Alkanolamine · Absorption · Electrical conductivity · Ionic conductivity · Ionic activity coefficient

Introduction

CO₂ chemical absorption is one of the most representative carbon capture, utilization, and storage (CCUS) technologies in response to climate change caused by anthropogenic CO₂ emissions (Smith et al. 2014; Wang and Oko 2017; Ramírez-Santos et al. 2018; Bian et al. 2019; Ho et al. 2019; Kusin et al. 2020). The technology focuses primarily on selective absorption of CO₂ using solvents in flue gas including 15–35 CO₂ vol% emitted from coal-fired power plant, cement production, and steel industries. Various types of solvents (or absorbents) have been examined to selectively react with CO₂ during the chemical absorption (Shen et al. 2017; Zareie-kordshouli et al. 2017; Lai et al. 2019; Xu et al. 2019). The most commonly used absorbent is an alkanolamine-based aqueous solution.

Alkanolamines are chemical compounds that contain both amino (–NH₂, –NHR, and –NR₂) and hydroxyl (–OH) groups. Alkanolamines are classified into primary (RNH₂), secondary (R₂NH), and tertiary (R₃N) compounds depending on the number of R groups, i.e., hydroxy-methyl or hydroxy-ethyl groups containing –OH, attached to nitrogen atom. Mono-ethanolamine (MEA) is the most widely used alkanolamine-based absorbent (Sabouni et al. 2014; Smith et al. 2014; Bhatti et al. 2019; Guo et al. 2019).

MEA is a primary amine carrying two hydrogen and one C₂H₄OH groups (R) attached to nitrogen atoms. The advantages of MEA include high absorption capacity, rapid reaction rate, lower molecular weight, and relatively low cost compared to other alkanolamines. However, the disadvantages include loss of MEA due to high vapor pressure and thermal (or oxidative) decomposition as well as high energy consumption to regenerate MEA in addition to its high corrosivity to steel equipment (Kladkaew et al. 2009; Handojo et al. 2018; Ling et al. 2019). Therefore, studies have been conducted to develop new chemical absorbents to enhance the advantages and compensate for the disadvantages of MEA (Hartono et al. 2014; Li et al. 2018; Shen et al. 2018; Yusuf et al. 2019; Zhang et al. 2019).

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At the same time, studies are needed to minimize the operating costs by further optimizing the operation variables in the process. For example, quantification of the amount of CO₂ absorbed or desorbed in real time during the operation and correlation of the reaction performance with electrical properties may facilitate the monitoring and control of the reaction variables for further optimization.

Thus, previous studies reported the correlation between variation in electrical conductivity (EC) and amounts of CO₂ absorbed using MEA and di-ethanolamine (DEA) aqueous solutions as absorbents (Han and Wee 2013, 2016, 2017). The amount of CO₂ absorbed can be accurately determined in situ by measuring the EC variation of the two amine systems. In particular, the ionic activity coefficient (IAC) of solutions with varying amine concentrations during the absorption was estimated, and the ionic conductivities of carbamic acid and carbamate generated by CO₂ absorption in MEA and DEA aqueous solutions were reported.

Tri-ethanolamine (TEA) is a tertiary amine composed of three C₂H₄OH moieties representing the R groups and is also one of CO₂ absorbents (Xiao et al. 2016). TEA has low energy consumption for solvent regeneration and exhibits less corrosivity and solvent loss as well as high resistance to solvent degradation (Derks et al. 2006; López et al. 2015; Narimani et al. 2017). However, it has been used as a reaction additive in most studies than as a primary chemical absorbent for CO₂ absorption due to its very slow rate of absorption (Conway et al. 2015; Rosli et al. 2017; Mouhoubi et al. 2018; Hou et al. 2019). Therefore, the TEA characteristics in terms of CO₂ absorption performance have yet to be elucidated. In addition, the ionic conductivity (IC) of ions generated in the CO₂ absorption reaction, the IAC, and EC variation have yet to be reported.

A few studies analyzed the CO₂ absorption systems using MEA, DEA, and TEA aqueous solution, which solely differ in the number of C₂H₄OH groups within the same molecular structure. They have mostly focused on the performance and characteristics of the CO₂ chemical absorption system under specific conditions (Bernhardsen and Knuutila 2017; Hwang et al. 2018; Ling et al. 2019).

In the present study, the overall performance of CO₂ absorption system using TEA aqueous solution was investigated, including total CO₂ absorption capacity (CAC), absorption completion time, and overall absorption rate (OAR). In addition, the study reported the IC of carbamic acid of TEA (R₃NH⁺) by analyzing chemically absorbed CAC (CAC_{chem}) and EC variation during the absorption and the electrochemical properties such as IAC of the solution according to the TEA concentration in the absorption system. Based on these results, the CAC_{chem} was correlated with EC, to estimate the amount of CO₂ absorbed in situ by measuring the EC variation during the absorption, across all TEA concentrations. Thereafter,

these results were systematically compared to those of the MEA and DEA systems reported previously (Han and Wee 2013, 2016, 2017). The comparative results explain the factors underlying the substantial differences in their CO₂ absorption performance in terms of molecular structure and electrical properties. Hence, the study contributes significantly to optimization of the operation conditions to enhance the absorption performance.

Theory

CO₂ absorption reaction mechanism of amine aqueous solutions

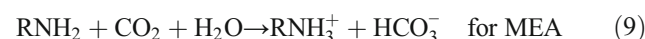
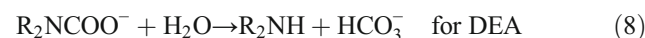
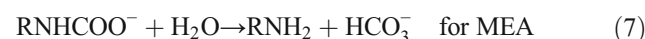
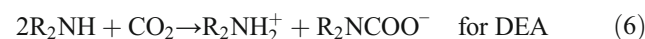
As chemical solvents for CO₂ absorption, the three amines of MEA, DEA, and TEA in aqueous solution were first dissociated to generate carbamic acids of amine and OH[−] around the water molecules, as expressed by Eqs. (1)–(3), respectively.



Subsequently, when CO₂ was injected into each amine aqueous solution under these conditions, the OH[−] group reacted first with CO₂ in all the three amine solutions due to its strong basicity to generate HCO₃[−], as shown in Eq. (4).



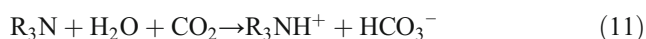
The CO₂ absorption reaction in the aqueous solution involves amine and the reaction mechanism in MEA and DEA systems differs from that of the TEA system. First, the individual reaction mechanism in the MEA and DEA systems is summarized in Eqs. (5)–(8). The overall reaction of each system is expressed by Eqs. (9) and (10).



In MEA and DEA aqueous solutions, the carbamates are generated by the direct reaction of CO₂ and amine according to Eqs. (5) and (6), which represent the primary reaction. Therefore, the theoretical molar ratio of CO₂ absorbed to the

amine is 0.5 mol CO₂/mol amine. However, when water concentration in the solution is elevated (i.e., amine concentration is low) or the CO₂ partial pressure is high, the carbamate is hydrolyzed to produce free amine as shown in Eqs. (7) and (8). Then, CO₂ can be additionally absorbed by the free amine generated, and therefore, the theoretical molar ratio between the amine and the CO₂ absorbed is increased more than 0.5. Crooks and Donnellan reported the absorption mechanisms of the DEA system, as listed in Eqs. (6) and (8), resulting in their molecule structure as shown in Fig. 1 (Crooks and Donnellan 1989).

In Fig. 1, R denotes the functional group of C₂H₄OH. If one of the two Rs is H, it is a MEA molecule. On the other hand, the CO₂ absorption mechanism of the TEA system differs completely from that of the MEA and DEA systems and directly reacts with CO₂. The CO₂ absorption of TEA is a base-catalyzed reaction in which TEA molecules convert CO₂ to HCO₃[−]. Donaldson and Nguyen explained this reaction mechanism as listed in Eq. (11) and as shown in Fig. 2 (Donaldson and Nguyen 1980). Therefore, when CO₂ is absorbed in TEA aqueous solution for capture, carbamic acid and HCO₃[−] are solely generated.



Calculation of electrical conductivity

Many equations are used to calculate EC in CO₂ absorption system using TEA aqueous solution as listed in Eqs. (12)–(17).

$$EC = k_0 \gamma^2 \quad (12)$$

$$k_0 = \sum z_i \lambda_i c_i \quad (13)$$

$$IS = 500 \sum c_i z_i^2 \quad (14)$$

$$\log \gamma = -0.509 z_+ z_- \sqrt{IS} \quad IS < 0.01 \quad (15)$$

$$\log \gamma = -0.5 z_+ z_- \frac{\sqrt{IS}}{1 + \sqrt{IS}} \quad 0.01 \leq IS \leq 0.1 \quad (16)$$

$$\log \gamma = -0.5 z_+ z_- \left(\frac{\sqrt{IS}}{1 + \sqrt{IS}} - 0.2 IS \right) \quad 0.1 < IS < 0.5 \quad (17)$$

In Eqs. (12)–(17), EC is the electrical conductivity (S/m), k_0 is the electrical conductivity of infinitely diluted solution (S/m), γ is the ionic activity coefficient, z_i is the absolute value of electric charge of ion i , λ_i is the ionic conductivity of ion i (S m²/mol z), c_i is the ionic concentration of ion i (mol/m³), and IS is the ionic strength of the solution (mmol/m³).

EC is the product of k_0 and γ^2 as listed in Eq. (12) and k_0 can be readily calculated by Eq. (13) based on the ionic concentration and electric charge in the aqueous solution as well as the IC. k_0 is the estimated value assuming that the solution represents an ideal state without ionic interaction. However, the extent of interaction depends on the ionic concentration of the solution and is directly related to IAC (γ) calculated using Eqs. (15)–(17) known as the Debye–Hückel, Gutenberg, and Davies equations (Debye and Hückel 1923; Davies 1962; Stumm and Morgan 1970). The three equations are selectively applied according to the range of IS calculated via Eq. (14) using the ionic concentration and electric charge in the solution. Therefore, the factors required to calculate the EC using Eqs. (12)–(17) include ionic concentration, electric charge, and IC in the solution within the IS range less than 0.5 M.

Meanwhile, the IS ranges mentioned above are more valid at small and general ions such as H⁺, K⁺, Ca²⁺, Cl[−], and NO₃[−].

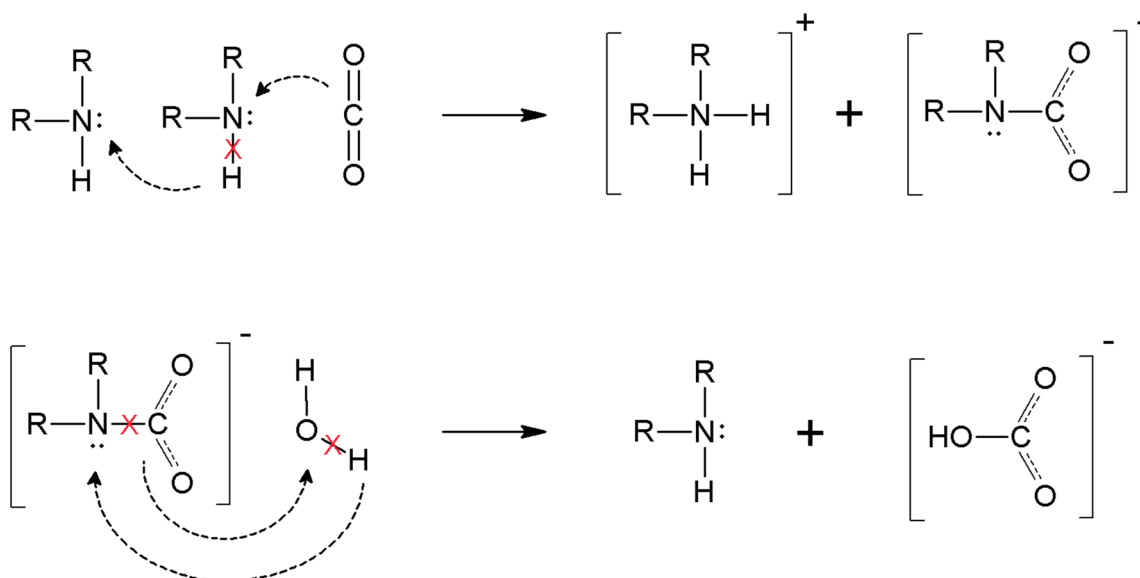


Fig. 1 CO₂ absorption mechanism using DEA aqueous solution as solvent (Crooks and Donnellan 1989)

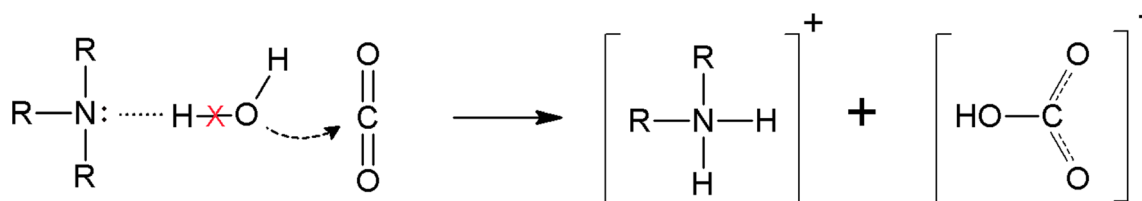


Fig. 2 CO₂ absorption mechanism using TEA aqueous solution as solvent (Donaldson and Nguyen 1980)

However, because of the relatively larger ion size of carbamic acid of TEA generated by CO₂ absorption compared to the size of the general ions, the physicochemical interaction between the ions is very large at similar concentrations of the general ions. Furthermore, in highly concentrated amine solutions, the interaction between ions is even higher, such that the γ calculated using Eqs. (15)–(17) differs significantly from the real values measured during the absorption. Therefore, the EC calculated under these conditions can be substantially different from the EC measured. Therefore, the real activity coefficient in highly concentrated solution (γ_c) is calculated via Eq. (18), which is modified from Eq. (12) by substituting EC and γ with EC_m and γ_c , respectively. In particular, when the TEA concentration of aqueous solution exceeds 0.1 M, the following Eq. (18) can be used effectively to calculate γ_c .

$$\gamma_c = \sqrt{\frac{EC_m}{k_0}} \quad \text{In highly concentrated aqueous solution} \quad (18)$$

Experimental methods

Thirteen types of concentrated TEA aqueous solution were prepared by mixing TEA with deionized water for CO₂ absorption. The molar concentrations of 13 TEA aqueous solutions and their corresponding mass (or weight) concentrations (wt%) are summarized in Table 1. In addition, the molar concentrations of MEA and DEA aqueous solutions used in the absorption reaction in previous studies are also listed in Table 1 for comparison of the TEA systems (Han and Wee 2013, 2016, 2017).

The solutions were used as a chemical absorbent to absorb CO₂ and a schematic diagram of the absorption is presented in Fig. 3.

For absorption, 0.5 L TEA aqueous solution was filled in a cylindrical Pyrex reactor (*D*, 110 mm; *h*, 80 mm) equipped with a water jacket to maintain a temperature of 25 °C. Before the CO₂ absorption was conducted, all empty spaces in the reactor and the gas lines were washed with N₂ gas, and the reactor inside was filled with N₂.

A mixture of N₂ and CO₂ was prepared to simulate the high CO₂ concentration (33.3 vol%) of gases emitted by the cement industry, and the gas was used as the feeding

gas for absorption. The flow rate of N₂ and CO₂ gases was controlled at 2.0 L/min and 1.0 L/min, respectively, using a mass flow controller (MPR-200, MKP) to maintain consistent levels of CO₂ concentration in the gas mixture. Before injecting the gas mixture, the CO₂ concentration was confirmed by directly feeding the mixture into a nondispersive infrared (NDIR) gas analyzer (maMos-200, Madur Electronics) bypassing the reactor using a three-way valve attached to the top of a reactor cap. The CO₂ concentration analyzed every second by the gas analyzer was monitored. Subsequently, the gas mixture with sufficiently stabilized CO₂ concentration was used in the absorption experiment. The flow rate of the sampling pump in the gas analyzer required to directly feed the NDIR sensor with the gas mixture was set to 1.5 L/min, and a condenser was installed to eliminate humidity in the gas mixture before entry into the sampling pump.

After stabilizing the concentration and flow rate of the gas mixture, the mixture was injected into the reactor through a sparger made of a glass filter for CO₂ absorption. Simultaneously, the solutions were uniformly mixed at the stirring speed of 180 rpm. The pH and EC of the solution were measured every 5 s using a pH/EC meter (Orion 4 Star, Thermo Scientific) during the absorption.

The concentration of the outlet gas passed through the reactor was analyzed in situ via the same method using the gas analyzer as mentioned earlier. The absorption completion was determined when the outlet CO₂ concentration equaled the initial CO₂ concentration in the gas mixture before injection into the reactor. All parameters (CO₂ concentration, pH, and EC) were obtained using a computerized data acquisition system.

The total amount of CO₂ absorbed was calculated based on the outlet CO₂ concentration and gas flow rate. The methodology to calculate the CAC was detailed in our previous paper (Han et al. 2011). Also, in this study, the amount of CO₂ absorbed in freshwater at 25 °C and 33.43 kPa of CO₂ partial pressure was assumed to be the capacity of the CO₂ physical absorption in water, which is 23.4 mmol CO₂/kg water (0.52 g CO₂/500 mL).

Standard uncertainties (*u*) of the measured data for mass (*m*), volume (*V*), temperature (*T*), pressure (*P*), CO₂ concentration (*C*), and EC in the work are *u*(*m*) = 0.001 g, *u*(*V*) = 0.3 mL, *u*(*T*) = 0.1 K, *u*(*P*) = 0.01 kPa, *u*(*C*) = 0.01 vol%, and *u*(EC) = 0.01 μS/cm.

Table 1 Molar concentrations of MEA, DEA, and TEA in amine aqueous solutions, corresponding mass concentrations, and the role of solutions used

Molar and mass concentrations of amine in solution; mol/L solution (wt%)			Role of solutions in CO ₂ absorption
MEA	DEA	TEA	
0.1 (0.6)	0.1 (1.1)	0.01 (0.15)	To estimate ionic conductivity of carbamic acid and carbamate in each amine system
0.2 (1.2)	0.2 (2.1)	0.02 (0.30)	
0.3 (1.8)	0.3 (3.2)	0.03 (0.45)	
0.4 (2.4)	0.4 (4.2)	0.04 (0.60)	
0.5 (3.1)	0.5 (5.2)	0.05 (0.75)	
1.0 (6.1)	1.0 (10.4)	0.1 (1.5)	To compare CO ₂ absorption performance and electrical properties in the three systems
2.0 (12.2)	2.0 (20.6)	0.2 (4.0)	
3.0 (18.3)	3.0 (30.7)	0.3 (4.5)	
4.0 (24.4)	4.0 (40.6)	0.4 (5.9)	
5.0 (30.4)	5.0 (50.4)	0.5 (7.4)	
		1.0 (15.0)	
		1.6 (22.5)	
		2.1 (30.0)	

Results and discussion

The study parameters including the CAC_{chem} , absorption completion time, OAR, and IAC varied remarkably at specific amine concentrations in each system and the results differed

slightly. Therefore, the results are explained in two sections based on ‘low’ and ‘high’ concentration ranges. The two concentration ranges used to obtain the results are summarized in Table 2.

Fig. 3 Schematic diagram representing CO₂ absorption in an amine aqueous solution: (1) N₂ cylinder, (2) CO₂ cylinder, (3) mass flow controller (MFC), (4) gas mixer, (5) water circulator, (6) sparger, (7) magnetic stirrer, (8) pH/EC meter, (9) condenser, (10) gas analyzer, (11) pH/EC recorder, (12) computer for data acquisition

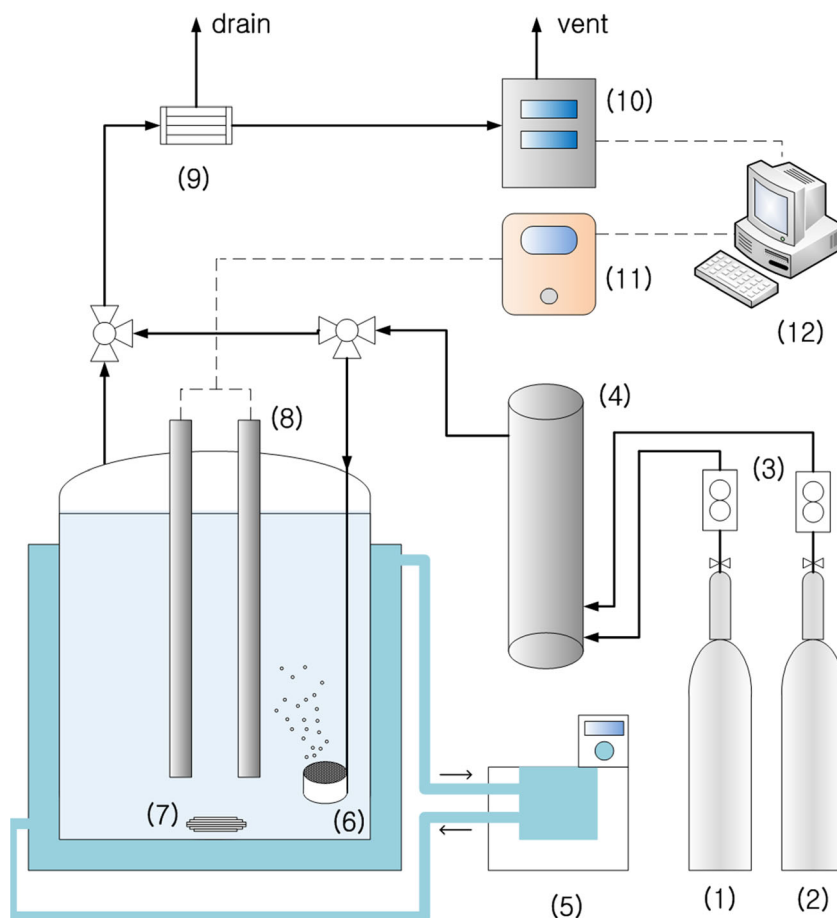


Table 2 Molar concentration ranges of solution in MEA, DEA, and TEA systems

Results	Molar concentration ranges of amine in solution applied to obtain results (M)						Remarks
	MEA		DEA		TEA		
	Low	High	Low	High	Low	High	
Chemical CO ₂ absorption capacity	0.1–0.5 (0.6–3.1)	1.0–5.0 (6.1–30.4)	0.1–1.0 (1.1–10.4)	2.0–5.0 (20.6–50.4)	0.1–0.5 (1.5–7.4)	1.0–2.1 (15.0–30.0)	Table 3 Fig. 4
Absorption completion time	0.1–0.5 (0.6–3.1)	1.0–5.0 (6.1–30.4)	0.1–1.0 (1.1–10.4)	1.0–5.0 (10.4–50.4)	–	–	Fig. 5
Overall absorption rate	0.1–1.0 (0.6–6.1)	1.0–5.0 (6.1–30.4)	0.1–1.0 (1.1–10.4)	1.0–5.0 (10.4–50.4)	–	–	Table 7 Fig. 6
Ionic activity coefficient	0.1–0.5 (0.6–3.1)	1.0–5.0 (6.1–30.4)	0.1–0.5 (1.1–5.2)	1.0–5.0 (10.4–50.4)	0.01–0.05 (0.15–0.75)	0.1–2.1 (1.5–30.0)	Fig. 9

In parenthesis, corresponding mass-based concentration ranges (wt%)

Chemically absorbed CO₂ capacity of MEA, DEA, and TEA systems

The CAC_{chem} and amine utilization (mol CO₂/mol amine) according to mass concentrations of TEA in the TEA system are shown in Fig. 4a and b, respectively, compared to the results involving the MEA and DEA systems (Han and Wee 2013, 2016, 2017). Here, the CAC_{chem} can be determined by subtracting the amount of CO₂ absorbed physically from the total CAC, which is obtained experimentally. The amount of CO₂ absorbed physically is calculated based on the water concentration of each aqueous solution, i.e., it is decreased, from 0.52 g CO₂/500 mL of water, proportionally to water concentration in amine aqueous solution. For example, the amount was assumed to 0.36 g CO₂/500 mL solution in 30 wt% amine solutions.

Although the CAC_{chem} of all amine systems increased according to the amine concentration as shown in Fig. 4a, the CAC_{chem} of TEA aqueous solution was lower than that of MEA and DEA aqueous solutions at the same concentration. In addition, they are divided into two ranges according to the slope in all systems as shown in Fig. 4a, which indicates the increasing ratio of CAC_{chem} (slope) according to the amine concentration. The increasing ratios of CAC_{chem} in each concentration range of the three systems are summarized in Table 3.

In all systems, the increasing ratio of CAC_{chem} was higher at low rather than high concentration ranges. It was the largest at low concentration ranges of the MEA system followed by the DEA and TEA systems. However, at the high concentration range, the increasing ratio of CAC_{chem} was large in the following order: MEA > TEA > DEA system. This phenomenon might be because the dominant reaction in the two ranges and the molecular weight of each amine are different. At low concentrations, because of the weak interaction to interfering each amine molecule, the molar ratio of CO₂ reacting with MEA, DEA, and TEA is 1 (CO₂):1 (amine), and the dominant reactions of the three amines are represented by Eqs. (9)–(11), respectively. Therefore, in this case, the increasing ratio of CAC_{chem} in the MEA system is the largest because the molar concentration of MEA in solution is the largest at similar mass concentrations in all amine aqueous solutions. However, at high concentration ranges, the dominant reaction of MEA and DEA systems was characterized by a molar ratio of 1:2 for CO₂ to the amine according to Eqs. (5) and (6). Therefore, the increasing ratios of CAC_{chem} to the amine concentration of the two systems were theoretically decreased by 50% in high concentration ranges. The ratio of amine molecules participating in the absorption was decreased and the interaction between the molecules was further increased in high concentration solution, which significantly reduced the increasing ratio of CAC_{chem} . Therefore, the increasing ratio of CAC_{chem} was decreased most in the DEA

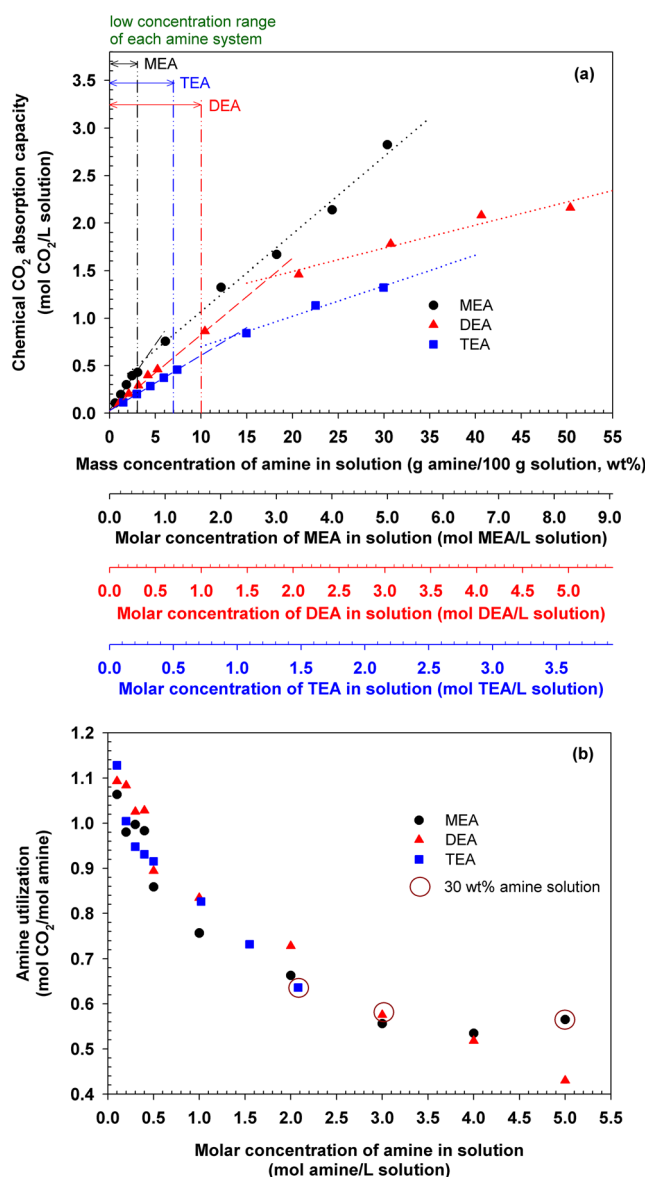


Fig. 4 **a** Chemical CO₂ absorption capacity and **b** amine utilization according to mass (and molar) concentrations of amine in MEA, DEA, and TEA systems

system because the theoretical CAC_{chem} value decreased by half according to Eq. (6) as well as the DEA molecular size is relatively large compared to MEA. In the TEA system, the increasing ratio of CAC_{chem} was expected to be the lowest at

high concentration ranges due to its largest molecular size. However, the molar ratio of CO₂ to the amine was maintained at 1:1 in the dominant reaction. This effect reduced the decrease of CAC_{chem} with increased molecular size. Therefore, at high concentration ranges, the increasing ratio of CAC_{chem} in the TEA system was larger than in the DEA system.

When CO₂ is absorbed in 30 wt% MEA (5.0 M) and TEA (2.1 M) aqueous solutions, reactions (9) and (11) occur in the solutions, respectively, and thus, the ratio of theoretical CAC_{chem} between the two solutions is 2.40, which is the same value of molar ratio of amine concentration in the two solutions. However, the experimental CAC_{chem} values of 30 wt% MEA and TEA aqueous solutions were 2.82 and 1.32 mol CO₂/L solution, respectively, and thus, the molar ratio of CAC_{chem} was 2.13, which was smaller than the theoretical value. This result indicates that the proportion of available TEA molecules participating in the 1:1 reaction (effective TEA molecules) among the total amines in the solution was larger than that of the effective MEA. The proportion of effective MEA and TEA was 56.5% and 63.6%, respectively. Thus, in order to quantify the proportion of the effective amine, the ratio of the number of CO₂ moles chemically absorbed to the total number of amine moles in each solution was used to determine amine utilization and shown in Fig. 4b.

As shown in Fig. 4b, at low concentration ranges of all amine aqueous solutions (0.1–0.5 M), all the amine utilizations were close to 1.0. For example, TEA utilization at 0.1 M TEA aqueous solution was 1.13, which means that the experimental CAC_{chem} was 0.013 mol CO₂/L solution higher than the theoretical value of 0.1 M TEA aqueous solution according to Eq. (11). The additional CO₂ absorbed might be attributed to the unique structural characteristics of TEA comprising three C₂H₄OH groups (R). In other words, CO₂ might be absorbed slightly higher and, thus, isolated within the free space between TEA and water molecules. This result may be generated between the two substances due to the complex and irregular structure of TEA molecules in the solution at very low amine concentrations. On the other hand, the free space might disappear over 0.2 M TEA aqueous solution, and the CO₂ absorption occurring according to Eq. (11) resulted in TEA utilization of 1.00 in 0.2 M TEA aqueous solution.

In addition, the utilization of all amine systems was decreased as the amine concentration increased, and the

Table 3 Increasing ratio of chemical CO₂ absorption capacity (CAC_{chem}) of MEA, DEA, and TEA systems at low and high amine concentrations

	MEA	DEA	TEA
Increasing ratio of CAC_{chem} (mmol CO ₂ /g amine L solution)	13.81	8.02	5.83
Low concentration ranges (wt%)	0.6–3.1 (0.1–0.5)	1.1–10.4 (0.1–1.0)	1.5–7.4 (0.1–0.5)
Increasing ratio of CAC_{chem} (mmol CO ₂ /g amine L solution)	8.15	2.43	3.20
High concentration ranges (wt%)	6.1–30.4 (1.0–5.0)	20.6–50.4 (2.0–5.0)	15.0–30.0 (1.0–2.1)

In parenthesis, corresponding molar-based concentration ranges (M)

decreasing ratios to the amine concentration were similar in all systems. In the MEA and DEA systems, when the water concentration of the solution decreases (i.e., as amine concentration increases), the hydrolysis of carbamate is inhibited, and thus, the utilization is decreased. However, in the TEA system, hydrolysis rarely occurs since the reaction mechanism basically differs from the other two systems. Therefore, the decreased utilization in the TEA system was significantly attributed to low water concentration, which hinders Eq. (11) and intensifies the physical and chemical interactions among the molecules inhibiting the absorption, thereby reducing the activity of TEA molecules.

The amine utilization in approximately 30 wt% MEA (5.0 M) and DEA (3.0 M) aqueous solution was 0.564 and 0.576 mol CO₂/mol amine, respectively, and in 30 wt% TEA (2.1 M) aqueous solution, it was 0.633 mol CO₂/mol amine, which was slightly higher than in MEA and DEA. The utilization of MEA and DEA was strongly dependent on the extent of hydrolysis reaction of carbamate, which was further intensified as the mole ratio of water increased. Therefore, the DEA utilization was higher than that of the MEA system because the hydrolysis reaction occurred easily in the DEA aqueous solution, where the molar ratio of water is relatively higher.

However, although TEA utilization was decreased according to the concentration due to the lowered concentration of the effective amine caused by the diminished activity of TEA molecules at high concentration ranges, the utilization of 30 wt% TEA aqueous solution was the highest among those of all 30 wt% amine aqueous solutions. This result is because the decreasing utilization effects due to the increased amine concentration in the TEA system are relatively weaker than the effects caused by the inhibition of hydrolysis at high concentration range in MEA and DEA aqueous solutions.

Absorption completion time and overall absorption rate in MEA, DEA, and TEA systems

Figure 5 shows the CO₂ absorption completion time in MEA, DEA, and TEA systems according to the molar concentrations of amine in the solution.

The absorption completion time of all amine systems was similar at low concentration ranges and increased linearly according to amine concentration with the different slopes. In the high concentration range, the slope, which is the increasing ratio of absorption completion time to the amine concentration of MEA and DEA systems, was significantly lower than that of the previous range. However, in the TEA system, the absorption completion time increased linearly at all molar concentration ranges, and the absorption completion time of TEA at 2.0 M was significantly larger than that of the MEA and DEA systems. Considering the weight percent-based composition, the absorption completion time of the 30-wt%

TEA aqueous solution was 194 min, which was 2.0 and 1.7 times longer than those of the MEA and DEA aqueous solutions, the points indicated in circle, respectively.

In the MEA and DEA systems, the increasing ratio of absorption completion time varied significantly from the boundary dividing low and high concentration ranges, which strongly suggest that the dominant reactions were substantially different at two ranges in the two systems. That is, since the hydrolysis of carbamate significantly occurred in the low concentration range in the two systems, reactions (9) and (10) were dominant, which substantially increased the overall reaction time according to the amine concentration. However, at 1.0 M and higher concentration ranges, the low water concentration and the decreased extent of the hydrolysis reaction caused the dominance of reactions (5) and (6), decreasing the dependence of the concentration on reaction rate. Therefore, the increasing ratio of absorption completion time to the amine concentration was substantially lower than that at the low concentration range in the MEA and DEA systems. However, in the TEA system where solely single reaction (11) occurred at all concentration ranges, the absorption completion time was directly proportional to TEA concentration in the solution.

In addition, using the CAC_{chem} (Fig. 4a) and the absorption completion time (Fig. 5), the CAC_{chem} per time, i.e., the OAR, is shown in Fig. 6.

As mentioned above, the CO₂ absorption using MEA and DEA aqueous solutions occurs according to Eqs. (5) and (7) and Eqs. (6) and (8), respectively. Therefore, their OAR is represented by the sum of the two reaction rates and the OAR can be determined based on the dominant reaction. The concentration at which the two predominant reactions critically change was 1.0 M because the absorption rate was altered significantly at this point, as shown in Fig. 6.

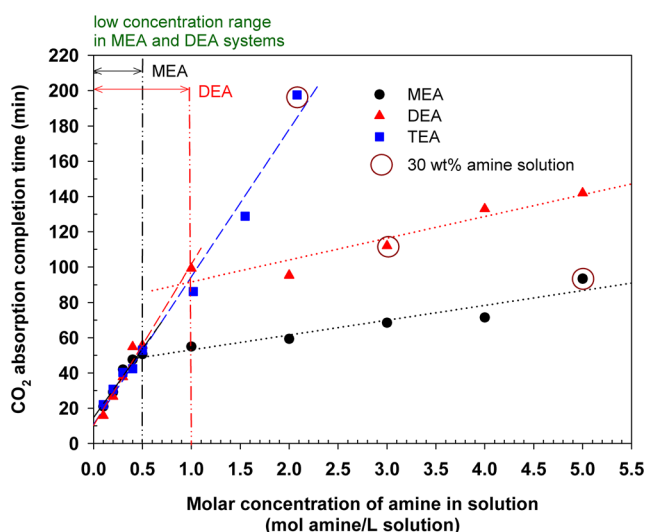


Fig. 5 CO₂ absorption completion time according to molar concentrations of amine in MEA, DEA, and TEA systems

Meanwhile, the OAR in the two systems was increased as amine concentration increased. However, the slope between 0.1 and 1.0 M was 9.18 mmol CO₂/mol amine min for MEA and 6.24 mmol CO₂/mol amine min for DEA, which were larger than between 1.0 and 5.0 M (3.64 and 0.27 mmol CO₂/mol amine min) for MEA and DEA systems, respectively. This phenomenon is attributed to the rate of reactions (9) and (10), which were predominant at low concentrations, and larger than those of reactions (5) and (6), which were dominant at high concentrations at which hydrolysis was inhibited.

However, in the TEA system, the OAR up to 1.0 M (15.0 wt%) increased proportionally with the concentration, with a maximum value of 9.8 mmol CO₂/L solution min, followed by a decline to 6.7 mmol CO₂/L solution min at 2.1 M (30.0 wt%). This phenomenon might be attributed to the base-catalyzed reactions involving CO₂ chemical absorption in TEA. As shown in Fig. 2, it is necessary to maintain an appropriate ratio between TEA and water molecules to maximize the overall reaction rate in the TEA system. Thus, the optimal concentration of TEA in the solution for CO₂ absorption is 1.0 M (15.0 wt%) in terms of OAR.

Ionic conductivity of R₃NH⁺

The IC of carbamic acid in the TEA system calculated in this study is summarized in Table 4 together with the IC of carbamic acid and carbamate in the MEA and DEA systems reported in previous studies. The table indicates the concentration ranges of the aqueous solutions used to estimate these values, and the electric charge of each ion (Han and Wee 2013, 2017; Patnaik 2017).

In the MEA and DEA systems, the IC of four ions such as RNH₃⁺, R₂NH₂⁺, RNHCOO[−], and R₂NCOO[−] was determined by the data obtained at the low amine concentration

range of 0.1–0.5 M. In addition, since the initial electrical conductivity measured (EC_m) of the two systems increased linearly within the concentration range, it was appropriate to use the dissociation constant (pK_a) value to calculate the concentration of dissociated ions (RNH₃⁺, R₂NH₂⁺, and OH[−]) in the initial state. However, in the same concentration range, the variation of initial EC_m of TEA aqueous solutions was not linear, and the increasing ratio of initial EC_m gradually decreased with increasing concentration because the interaction between TEA molecules in the solution was relatively stronger due to larger molecular weight and size compared to those of MEA and DEA. Therefore, it was incorrect to calculate the initial ionic concentrations in the TEA aqueous solution using the pK_a value of TEA. Thus, even at a lower concentration range of 0.01–0.05 M TEA in the solution, where the interaction between TEA molecules was substantially weaker, the IC of R₃NH⁺ was calculated.

Before CO₂ absorption in the three amine aqueous solutions, the amines reacted with water to generate carbamic acid and OH[−] as indicated in Eqs. (1)–(3). The pK_a values of MEA, DEA, and TEA are summarized in Table 5 (van Westrenen et al. 1990; Talebi et al. 2013; Rayer et al. 2014).

In the MEA and DEA systems, the IC of the RNH₃⁺ and R₂NH₂⁺ was calculated using the EC_m of the solution before CO₂ absorption and that of the solution saturated with absorbed CO₂. Subsequently, the IC of the RNHCOO[−] and R₂NCOO[−] was calculated using the EC_m variation measured in situ according to the amount of CO₂ absorbed in the overall range of amine concentrations.

In the TEA system, however, only R₃NH⁺ and HCO₃[−] were generated as shown in Eq. (11) throughout the concentration ranges of CO₂ absorption. In addition, the concentration of the ions generated can be calculated from the CAC_{chem} measured every second via Eq. (11). Therefore, the concentration of OH[−], HCO₃[−], and R₃NH⁺ in the TEA aqueous solution at all reaction states can be determined, and thus, the EC_c values in the TEA reaction system can be calculated via Eqs. (12)–(16) using the already known IC of OH[−] and HCO₃[−] and the IC of R₃NH⁺ guessed previously. Thereafter, the guessed IC of R₃NH⁺ was replaced by the final estimated value based on the practical value of R₃NH⁺, when the error between the EC_m and EC_c was reduced to a minimum. As a result, the final IC of R₃NH⁺ was calculated as 37.60 S cm²/mol z under the minimum calculation error of 14.73%.

The variations of EC_m and EC_c of 0.01–0.05 M TEA aqueous solutions, of which the concentration range was employed to determine the IC of R₃NH⁺, and the differences between the two ECs according to the reaction time during CO₂ absorption period are shown in Fig. 7.

As mentioned above, the ionic concentrations were calculated based on the CAC_{chem}. The CAC_{chem} used to estimate the ionic concentrations was calculated by subtracting the

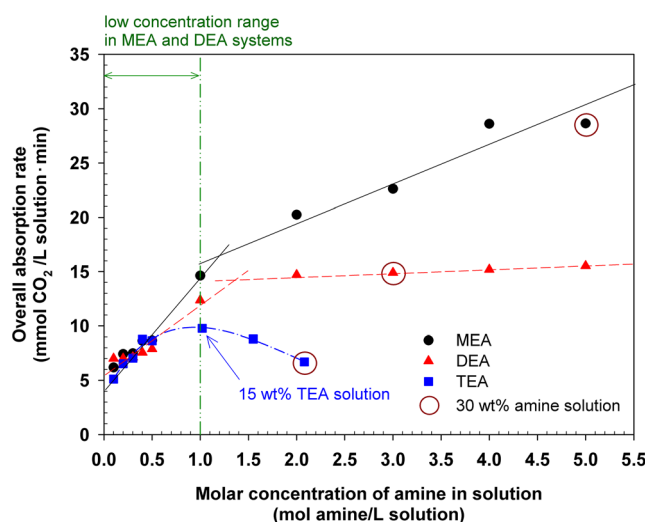


Fig. 6 Overall absorption rate according to molar concentrations of amine in MEA, DEA, and TEA systems

Table 4 Electric charge and ionic conductivity of ions generated by CO₂ absorption in MEA, DEA, and TEA systems and molar concentration range of aqueous solutions used to estimate ionic conductivity

Ions	Electric charge (z)	Ionic conductivity (S cm ² /mol z)	Molar concentration range of aqueous solution used to estimate ionic conductivity (M)
OH [−]	− 1	198.6 ^a	—
HCO ₃ [−]	− 1	44.50 ^a	—
RNH ₃ ⁺ (MEA)	+ 1	62.20 ^b	0.1–0.5
RNHCOO [−] (MEA)	− 1	25.80 ^b	0.1–0.5
R ₂ NH ₂ ⁺ (DEA)	+ 1	38.46 ^b	0.1–0.5
R ₂ NCOO [−] (DEA)	− 1	20.01 ^b	0.1–0.5
R ₃ NH ⁺ (TEA)	+ 1	37.60 ^c	0.01–0.05

^a Known value (Patnaik 2017)^b Estimated in previous works (Han and Wee 2013, 2017).^c Estimated in the present work

physical absorption capacity from the total CAC assuming a constant ratio of the physical absorption capacity at all reaction times.

For all five TEA aqueous solutions, the EC_m increased rapidly during the initial CO₂ absorption and maintained almost constant until the end of the absorption. The EC_c also increased rapidly at the beginning of CO₂ absorption, although its increasing ratio decreased as depicted by the curved line, and finally resembled EC_m at the end of CO₂ absorption. During the initial CO₂ absorption, EC_c was slightly higher than EC_m, and as the slope of EC_c decreased, the EC_m was higher than the EC_c. This reversal of the two EC values can be explained by the different proportions of chemical and physical CAC to total CAC in real absorption situation at all absorption times unlike previously assumed that the proportion is constant throughout the process. For example, the total CAC measured at 40 s after the injection of CO₂ in 0.03 M TEA aqueous solution was 26.1 mmol CO₂/L solution, compared to the CAC_{chem} calculated according to the EC_c value (603 μS/cm) estimated at 9.20 mmol CO₂/L solution, which was 35.2% of the total CAC measured. However, the EC_m value at 40 s was read as 306 μS/cm in Fig. 7c, and thus, the real CAC_{chem} was 4.35 mmol CO₂/L solution, which was calculated by substituting the EC_m (306 μS/cm) for the EC in Eq. (12), and combining this with Eqs. (13)–(16), it was 16.7% of the total CAC of 26.1 mmol CO₂/L solution. Thus, at 40 s, the proportion of the real physical CAC was 83.3% of 21.7 mmol CO₂/L solution.

Table 5 Dissociation constant (pK_a) of MEA, DEA, and TEA at 25 °C and 101.3 kPa

Amines	Dissociation constant (pK _a)
MEA	4.58 (van Westrenen et al. 1990)
DEA	5.12 (Talebi et al. 2013)
TEA	6.27 (Rayer et al. 2014)

The EC_c and EC_m values were equivalent at 2 min and 40 s, where the proportion of theoretical and real CAC_{chem} values were the same, about 35.2%. Subsequently, as the increasing ratio of EC_c decreased, the EC_m was higher than EC_c, and the difference between the two values was maximized at approximately 4 min. At this point, the real CAC_{chem} value was 26.6 mmol CO₂/L solution, which was calculated via Eqs. (13), (14), (16), and (12) where EC was replaced with the EC_m of 1574 μS/cm at 4 min, and thus, its proportion to the total CAC (65.0 mmol CO₂/L solution) was 40.8%. Therefore, the proportion of real CAC_{chem} to the total CAC increased until 4 min from the start, which indicates the selectivity of the chemical absorption to physical absorption increased to that time. In the next period, the extent of real CAC_{chem} decreased again and was 35.2% (28.9 mmol CO₂/L solution) of the total CAC (82.1 mmol CO₂/L solution) at 9 min and 10 s near the end point of CO₂ absorption. Here, the real CAC_{chem} was calculated in the same way using Eqs. (13), (14), (16), and (12) with the EC_m of 1686 μS/cm measured at that time. Finally, the real proportion of physical and chemical absorption capacity varied continuously during the absorption, and the real proportion of CAC_{chem} in the total CAC was the largest at 4 min in 0.03 M TEA aqueous solution.

Ionic activity coefficient of highly concentrated TEA aqueous solution

In 0.1–0.5 M TEA aqueous solutions, EC_c was calculated using the IC of R₃NH⁺ determined in the concentration range of 0.01–0.05 M and the EC_c variations calculated in 0.1–0.5 M TEA aqueous solutions were compared to those of EC_m. Figure 8 shows the difference between EC_c and EC_m according to the CO₂ absorption time in 0.5 M TEA aqueous solution.

In Fig. 8, the EC_m was measured at an average 60% lower than the EC_c at all absorption times, which suggests that the real activity coefficient of R₃NH⁺ and HCO₃[−] generated

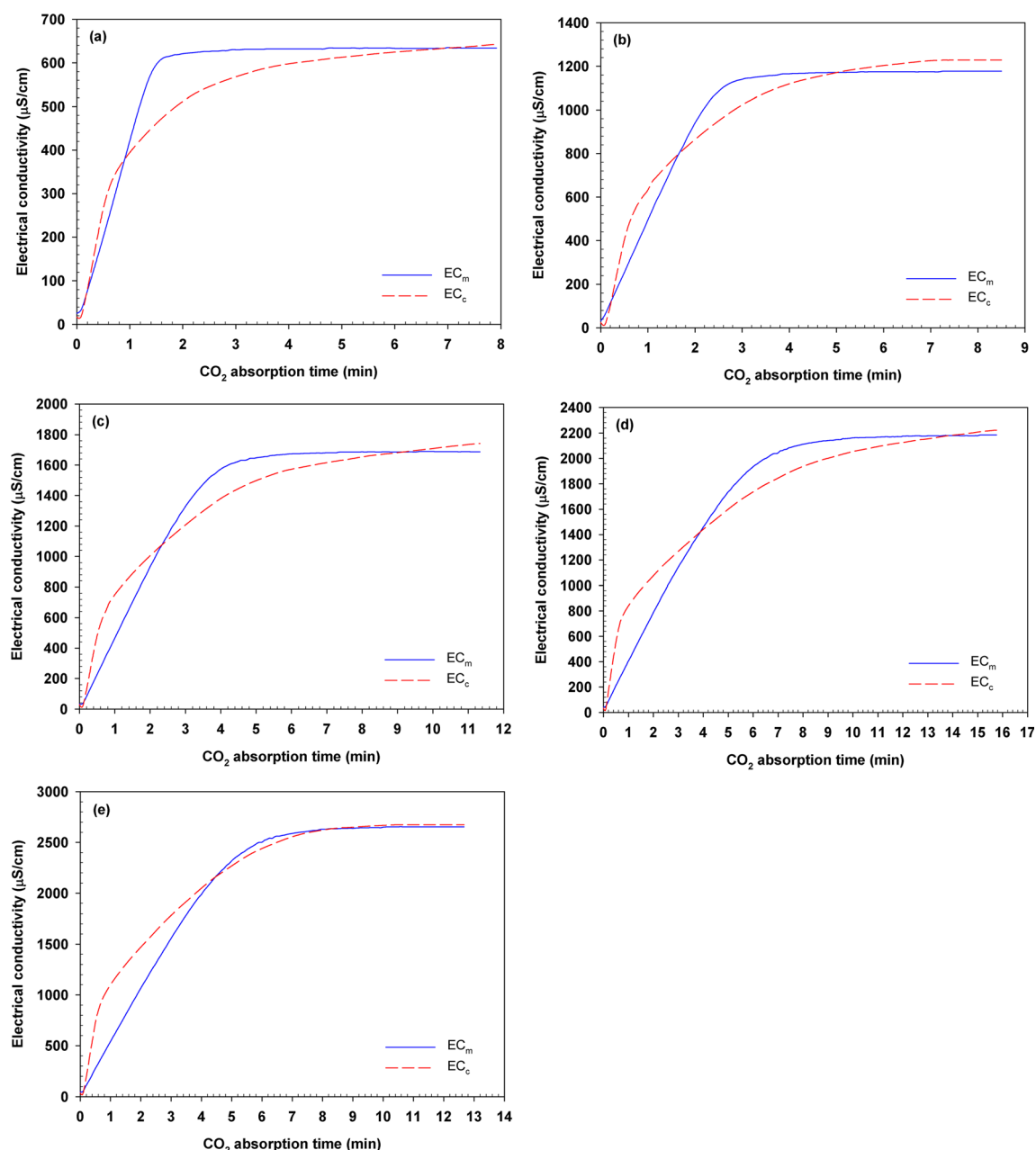


Fig. 7 Variations in measured (EC_m) and calculated electrical conductivity (EC_c) of 0.01–0.05 M TEA aqueous solutions according to reaction time during the absorption period: **a** 0.01, **b** 0.02, **c** 0.03, **d** 0.04, and **e** 0.05 M TEA solution

during the CO_2 absorption was lower than the theoretical activity coefficient calculated according to Eqs. (14)–(16). This phenomenon might be attributed to the relatively high concentration of R_3NH^+ , which results in stronger interaction between ions and molecules in the solution, as well as the R groups in the large R_3NH^+ could be entangled up together during the absorption.

The real ionic activity coefficients in highly concentrated aqueous solution (γ_c) saturated with absorbed CO_2 in 0.1–2.1 M TEA (1.5–30.0 wt%), 1.0–5.0 M MEA (6.1–30.4 wt%), and 1.0–5.0 M DEA (10.4–50.4 wt%) solutions were calculated using Eq. (18) and shown in Fig. 9. In addition,

their regression results were expressed as short dash lines. Meanwhile, the theoretical IAC in aqueous solution below 0.5 M of the systems was indicated by a single solid line because they are all the same for all systems according to Eqs. (16) and (17).

Although the γ and γ_c in the 0.1 M TEA aqueous solution saturated with absorbed CO_2 were 0.758 and 0.751, respectively, the γ_c further declined sharply with increased concentration compared to the theoretical value, and thus, the γ_c of the 0.5 M TEA aqueous solution was 0.547 which was 22% lower than the γ value of 0.697. On the other hand, in 0.1–0.5 M MEA and DEA aqueous solutions at which the

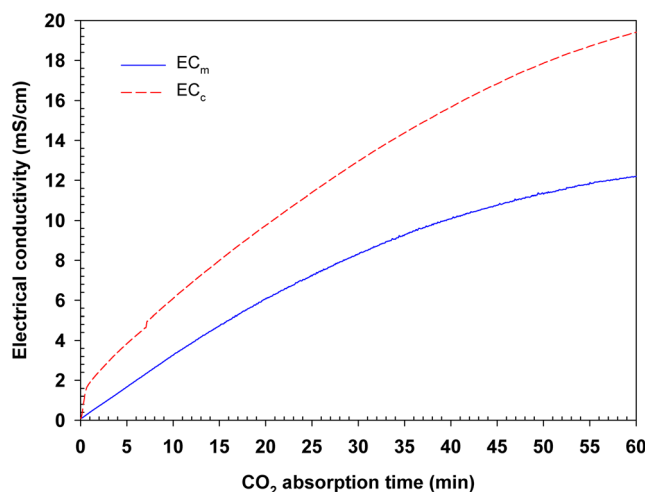


Fig. 8 Difference between measured (EC_m) and calculated electrical conductivity (EC_c) of 0.5 M TEA aqueous solution according to absorption time until 1 h

concentration was low enough to ignore the molecular or ionic interaction, the theoretical γ values calculated using Eqs. (16) and (17) may be similar to real γ values in the solutions, and thus, the EC_c calculated using the theoretical γ was not significantly different from the EC_m .

In the concentration range of 1.0 M or higher, the γ_c decreased according to the concentration increase as shown in Fig. 9 in all three systems, and the decreasing ratio of the TEA system was the largest with 11.72×10^{-2} L solution/mol amine compared to the DEA (10.23×10^{-2} L solution/mol amine) and MEA (5.75×10^{-2} L solution/mol amine) systems. This phenomenon might be attributed to substantial differences in the distance between ions, as well as to different amounts of water presenting around the ions in the three systems, which is primarily caused by different molecular sizes, resulting in differences in intensity of interaction between ions

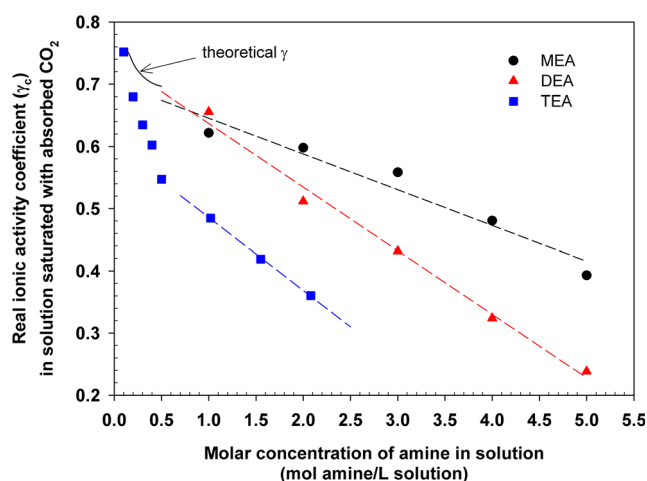


Fig. 9 Real ionic activity coefficients in highly amine concentrated aqueous solution (γ_c) saturated with absorbed CO_2 , their regression results, and theoretical ionic activity coefficient (γ) in 0.1–0.5 M MEA, DEA, and TEA aqueous solutions

or molecules among the systems. For example, the decreasing ratio of γ_c in the DEA system was larger than in the MEA system. This is because the interaction between ions or molecules in the DEA system was stronger, which is caused by the distance between the DEA molecules that was even closer compared to the MEA system under same increase in molar concentrations. However, at 1.0 M aqueous solutions where the concentration is relatively low at high concentration range, the γ_c of the DEA system was larger than that of the MEA. This phenomenon might be explained by the relatively high levels of zwitterions, which reduce γ_c , due to the relatively large density of electron dispersion of carbamic acid and carbamate in the MEA system. This effect is predominant compared to the two aforementioned effects contributing to a decrease in γ_c .

The γ_c of TEA aqueous solutions above 1.0 M was smaller than that of the MEA and DEA aqueous solutions at similar concentration. That is, the γ_c values decreased with the increase in molecular weight and the molar concentration of amine in solution. In the TEA system, water is a significant reactant, unlike in the MEA and DEA systems, and it does not reduce the γ_c of the systems. Thus, the γ_c of the TEA system in highly concentrated solution is relatively low, which is attributed to the sole interaction between R_3NH^+ and HCO_3^- , OH^- , or R_3NH^+ . In particular, the three R groups that constitute the basic structure of R_3NH^+ are physically linked with each other, and contribute to the stronger physical and chemical interactions between the molecules or ions. Accordingly, the γ_c was the lowest and its decreasing ratio was the highest in the TEA system.

Correlation between CAC_{chem} and EC_m in highly concentrated TEA aqueous solution

The variations in CAC_{chem} and EC_m according to CO_2 absorption time across all ranges of TEA aqueous solution (0.1–0.5 M and 15.0–30.0 wt%) are shown in Fig. 10a and b, respectively.

As shown in the Fig. 10, CAC_{chem} and EC_m of all the solutions are increased rapidly from the beginning of the absorption and increased slowly with time to remain constant upon completion of absorption. This phenomenon is explained by the rapid absorption rate of CO_2 initially when TEA concentration is relatively high, and the solutions are gradually saturated with CO_2 as the concentration of TEA decreases progressively with reaction. In addition, because the CAC_{chem} is directly related to ionic concentration, the EC_m variation according to the absorption time is similar to CAC_{chem} , and thus, the EC_m value converges to a specific value near the end point. However, the EC_m of the 1.0 M TEA aqueous solution at the end point of CO_2 saturation was 16.64 mS/cm, which was higher than that of 1.6 and 2.1 M solutions with higher CAC_{chem} . This effect might be

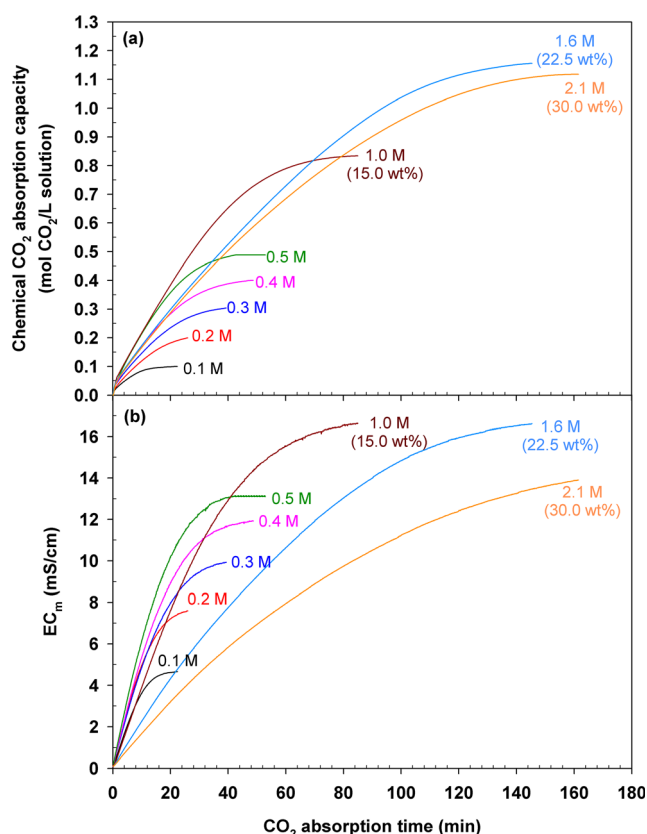


Fig. 10 **a** Variations in chemical CO_2 absorption capacity and **b** measured electrical conductivity (EC_m) according to absorption time in all TEA aqueous solutions

attributed to further decrease in the effective ionic concentration, which significantly influences the EC, in 1.6 and 2.1 M solutions than in 1.0 M solution due to their higher concentration. Thus, in the highly concentrated aqueous solution, although the CAC_{chem} and EC_m variation was not exactly similar, it was strongly consistent in each TEA aqueous solution. Therefore, the correlation could be derived that EC_m is generally proportional to CAC_{chem} . The values of EC_m and CAC_{chem} in the eight different TEA aqueous solutions are shown in Fig. 11 based on regression analysis using the least square method. In addition, the slope, y-intercept, and regression coefficient (r^2) are summarized in Table 6.

The slope of correlation equation (SCE) indicates the CAC_{chem} required to increase the EC of the solution by 1 mS/cm. In 0.1 M TEA aqueous solutions, 1.88 mol CO_2/L solution was absorbed to increase 1 mS/cm of EC. In contrast, in the 0.5 M solution, 1 mS/cm was increased when the CAC_{chem} was 3.79 mol CO_2/L solution, which is two-fold higher. As shown in Table 6, the SCE value increased as amine concentration in the solution increased, suggesting that higher CAC_{chem} is needed to raise the EC by 1 mS/cm when the amine concentration in the solution was higher, resulting in increased ionic concentration. This

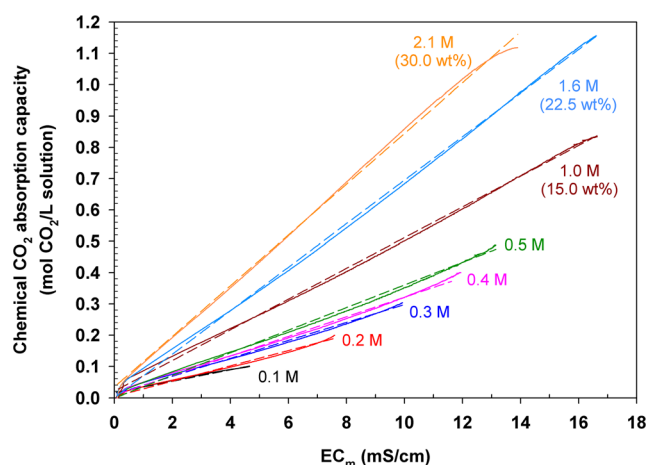


Fig. 11 Correlation between chemical CO_2 absorption capacity and measured electrical conductivity (EC_m) (solid line) and its regression results (dotted line) in all TEA aqueous solutions

phenomenon can be explained by the stronger interaction between the ions, such as R_3NH^+ and HCO_3^- under increased amine concentration, resulting in increased amounts of zwitterions such as $\text{R}_3\text{NH}^+\cdot\text{HCO}_3^-$, which decrease the EC in the solution.

The y-intercept of correlation equation (ICE) indicates the CAC_{chem} of the solution when the EC_m of the solution is zero. However, since the solutions always exhibit an infinite value of EC_m , the ICE is negligible in terms of CAC_{chem} , but is only of mathematical significance. As shown in Table 6, both the SCE and the ICE increase proportional to the TEA concentrations, and thus, they can correlate with the concentrations, as shown in Fig. 12.

The SCE and the logarithmic value of the ICE are directly proportional to the solution concentration. The regression analysis obtained using the least square method using these two values at eight solution concentrations are shown in Fig. 12, which are expressed by Eq. (19) for SCE and Eq. (20) for ICE for all TEA aqueous solutions.

$$\text{SCE} = 0.030 \cdot C + 0.022 \quad (19)$$

$$\text{ICE} = 10^{0.213 \cdot C + 0.997} \quad (20)$$

The values of r^2 in Eqs. (19) and (20) were 0.999 and 0.815, respectively. The SCE and ICE values represent the factors correlating the CAC_{chem} and the EC_m values. Therefore, the correlation equation can be expressed using the concentration of TEA as shown in Eq. (21). In addition, the MEA, DEA, and TEA systems were compared using the correlation equations of MEA and DEA expressed by Eqs. (22) and (23), respectively. Furthermore, these values according to amine concentrations in the solution in the concentration range of 0.1 to 5.0 M are represented as shown in Fig. 13.

Table 6 Slope (SCE), y -intercept (ICE), and regression coefficient (r^2) in correlation analysis of chemical CO_2 absorption capacity and measured electrical conductivity (EC_m) in TEA systems

	Molar concentration of TEA in solution (M of TEA)							
	0.1	0.2	0.3	0.4	0.5	1.0	1.6	2.1
SCE ($\times 10^2$) (mol CO_2 cm/mS L solution)	2.47	2.84	3.08	3.32	3.79	5.14	6.95	8.36
ICE ($\times 10^3$) (mol CO_2 /L solution)	10.0	11.2	11.4	12.3	13.9	17.5	14.7	34.1
Regression coefficient, r^2	0.987	0.994	0.996	0.996	0.996	0.996	0.998	0.998

$$\begin{aligned} \text{CAC}_{\text{chem TEA}} (\text{mol CO}_2/\text{L solution}) \\ = (0.030 \cdot C + 0.022) \cdot \text{EC}_m + 10^{0.213 \cdot C + 0.997} \end{aligned} \quad (21)$$

$$\begin{aligned} \text{CAC}_{\text{chem MEA}} (\text{mol CO}_2/\text{L solution}) \\ = (0.013 \cdot C + 0.0078) \cdot \text{EC}_m - 0.0793 \cdot C + 0.0755 \end{aligned} \quad (22)$$

$$\begin{aligned} \text{CAC}_{\text{chem DEA}} (\text{mol CO}_2/\text{L solution}) \\ = e^{0.558 \cdot C - 4.089} \cdot \text{EC}_m - 0.0612 \cdot C + 0.101 \end{aligned} \quad (23)$$

In Fig. 13a, while the SCE of the MEA and TEA systems were linearly increased according to the concentrations, that of DEA was increased exponentially. As mentioned above, a larger SCE value indicates that additional CAC_{chem} is required to increase the EC_m of 1 mS/cm, and the SCE is constant at the given initial concentration of amine in solution. Here, the slope of SCE is also an important variable to compare the sensitivity of EC_m and CAC_{chem} variation in the three systems. It is an intensive value expressed as the unit of mol CO_2 absorbed per EC_m and amine concentration, and it is a constant not affected by amine concentration in the MEA and TEA systems. However, the slope of SCE in the DEA system depends on the initial DEA concentration in solution and its value at specific amine concentrations, i.e., the slope of

tangential line, can be derived from Eq. (23). For example, the slope of SCE in 2.1 M DEA aqueous solution was 3.02×10^{-2} mol CO_2 cm/mS mol amine, which was larger than that of the TEA system (3.00×10^{-2} mol CO_2 cm/mS mol amine) as shown in Fig. 13. In the concentration range below 2.1 M, the slope of SCE in the TEA system was the largest and lower in the order of DEA and MEA systems.

The factors affecting the slope of SCE value include IC and effective ionic concentration of each aqueous solution. Thus, although the amount of CO_2 absorbed and the ions generated by the absorption is similar in the two systems, the slope of

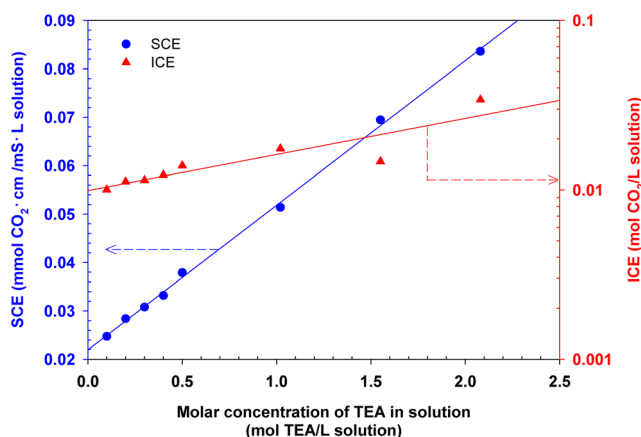


Fig. 12 Variations in slope (SCE) and y -intercept (ICE) of correlation equation between chemical CO_2 absorption capacity and measured electrical conductivity (EC_m) according to the molar concentration of TEA in solution

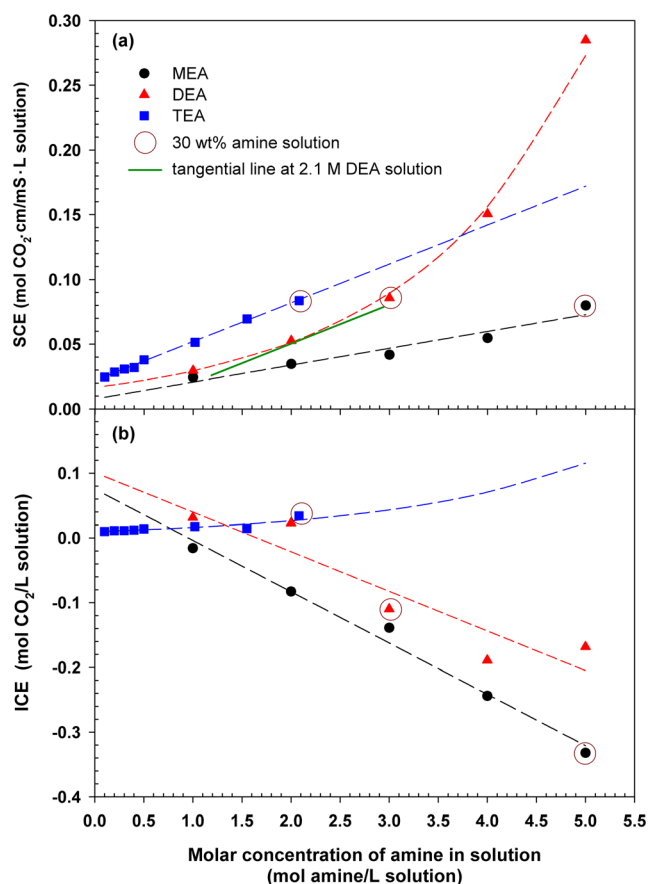


Fig. 13 Comparison of **a** slope (SCE) and **b** y -intercept (ICE) of correlation between chemical CO_2 absorption capacity and measured electrical conductivity (EC_m) according to molar concentrations of amine in MEA, DEA, and TEA systems

SCE in one system might increase further if the effective ionic concentration and the IC of the presenting ions are low, and the TEA system can be applied in this case.

The effective ionic concentration can be determined as the product of the total ionic concentration obtained using the CAC_{chem} (Fig. 4a) and the IAC (Fig. 9). Although the amine utilization and the CAC_{chem} of the three amine aqueous solutions were not significantly different, the γ_c in the TEA system was the lowest at all concentration ranges, and the γ_c in the MEA system was the highest except in the case of 1.0 M aqueous solution. For example, the CAC_{chem} of 2.0 M MEA and TEA aqueous solution was 1.20 and 1.34 mol CO_2/L solution, respectively, and the total concentration of ions generated according to Eqs. (7) and (11) was equal to the CAC_{chem} of each solution, i.e., the total concentration of ions generated in TEA aqueous solution was higher than in the MEA aqueous solution. However, the γ_c of MEA and TEA aqueous solutions were 0.598 and 0.360, respectively. Therefore, the effective ionic concentrations were 0.718 for MEA and 0.476 mol/L solution for the TEA system, i.e., the effective ionic concentration in TEA aqueous solution was smaller. Thus, the slope of SCE in the TEA system showed the highest value due to the lowest effective ionic concentration and relatively low IC.

However, at concentrations above 2.1 M, the slope of SCE in the DEA system showing an exponential increase was higher than that of TEA due to the lack of conversion of the R_2NCOO^- generated via CO_2 absorption in the solution to HCO_3^- . Hydrolysis rarely occurs in highly concentrated DEA aqueous solution, which reduces amine utilization. In addition, the IC of R_2NCOO^- is 20.01 S cm^2/mol z, which is lower than that of HCO_3^- (44.50 S cm^2/mol z). Therefore, although the amount of CO_2 absorbed is similar in solutions at concentrations exceeding 2.1 M in the three systems, the EC variation of the DEA aqueous solution was smaller (i.e., low sensitivity) and the slope of SCE is higher. However, the slope of SCE in the MEA system was the lowest at all concentration ranges, even though hydrolysis is rarely conducted in highly concentrated aqueous solutions as in the DEA system. This effect can be explained by the IC of RNH_3^+ (62.20 S cm^2/mol z), which is relatively larger than that of the other ions. That is, RNH_3^+ is the key factor explaining the low slope of SCE, which results in high EC sensitivity to the CAC_{chem} at all concentration ranges in the systems.

Comparison of MEA, DEA, and TEA aqueous solutions

Based on the overall results, the significant CO_2 absorption in the three amine systems characterized by increasing ratio of CAC_{chem} and maximum absorption rate was compared.

First, the CAC_{chem} of the three amine systems, as summarized in Table 3, was increased proportionate to amine concentration with varying increasing ratios at low and high

concentration ranges. In the low concentration range, where the interaction between molecules and ions is low, the increasing ratio of CAC_{chem} is primarily affected by molecular weight (and/or size) of amine because CO_2 absorption with amine occurs at 1:1 molar ratio in all amine systems. Therefore, in the specific range, the increasing ratio of CAC_{chem} was the largest in the MEA system (13.81 mmol CO_2/g amine L solution), which carried the lowest molecular weight. The ratio was the least with 5.83 mmol CO_2/g amine L solution in the TEA system. However, at high concentration ranges, because the molar ratio of CO_2 with the amine in the absorption reaction system was 1:2 in the MEA and DEA systems and 1:1 in the TEA system, the amount of DEA required to absorb 1 mol of CO_2 was larger than that of TEA, which reduced the increasing ratio of CAC_{chem} in the DEA (2.43 mmol CO_2/g amine L solution) compared to that of the TEA system.

Second, the maximum absorption rates of the three systems are summarized in Table 7.

The maximum absorption rates of the MEA and DEA systems were 28.6 and 16.1 mmol CO_2/L solution min, respectively, which were observed in the solution with the highest concentration (5.0 M). However, the absorption rate according to amine concentration increased with different increasing ratios in their two amine concentration ranges because the dominant reaction differed at low and high concentration ranges and the hydrolysis reaction was inhibited with the increase in amine concentration.

In the MEA and DEA systems, the dominant reaction was significantly changed at 1.0 M. However, in the TEA system, CO_2 was absorbed by a single base-catalytic reaction at all concentration ranges, and thus, the absorption rate according to amine concentration in the solution varied in the form of a parabolic curve. As a result, the absorption rate was the highest at 9.8 mmol CO_2/L solution min with 15 wt% (1.0 M) TEA aqueous solution.

Finally, the electrical properties, including the IC of carbamic acid and carbamate, as well as the decreasing ratio of γ_c , the SCE value, and its slope in the three amine systems, are compared in Table 8.

As previously mentioned, carbamate is generated via CO_2 absorption in the MEA and DEA systems, but not in the TEA system. However, carbamic acid is the final product in the three systems. The IC of carbamic acid in MEA, DEA, and TEA was 62.20, 38.46, and 37.60 S cm^2/mol z, respectively. The IC of carbamic acid in MEA was the largest and that of TEA the smallest in value. IC is known to be affected by ionic (or molecular) weight or size suggesting that larger size and ion weight with the same electric charge, charge density, and IC decreased further (Sauerheber and Heinz 2016). The relative ratio of IC of carbamic acid of MEA, DEA, and TEA was 1.00:0.62:0.61, while the reciprocal ratio of their molecular weights was 1.00:0.59:0.41. Therefore, the decreasing ratio

Table 7 Maximum absorption rate and its amine concentration point of MEA, DEA, and TEA systems

	MEA	DEA	TEA
Maximum absorption rate (mmol CO ₂ /L solution min)	28.6	16.1	9.8
Amine concentration point (M)	5.0 (30.4)	5.0 (50.4)	1.0 (15.0)

In parenthesis, corresponding mass-based concentration ranges (wt%)

of IC of R_3NH^+ was larger than that of its reciprocal molecular weight, which might be explained by the molecular size of the three carbamic acids. Thus, as the number of R groups increased in the molecule, the increasing ratio of the molecular size was lower than that of the molecular weight. The molecular size can be estimated via molar volume. The molar volume of MEA, DEA, and TEA was 60.48, 96.46, and 132.02 cm³/mol, and the relative ratio was 1.00:1.59:2.18. However, the relative ratio of molecular weight was 1.00:1.72:2.44, suggesting that the increasing ratio of molar volume was smaller than that of its molecular weight. Therefore, the molecular structure of DEA and TEA is characterized by adding one and two R groups to MEA, respectively, and the increase in molecular size is lower than the molecular weight, such that the charge density of $R_2NH_2^+$ and R_3NH^+ is relatively higher than that of RNH_3^+ .

In the three amine systems, the SCE value can be used to estimate CAC_{chem} according to EC_m variation of the solution at a given initial concentration of amine in solution. When the same amount of CO₂ is absorbed, the SCE is increased as the EC_m variation declines further and the initial concentration of amine in the solution increases. However, the slope of SCE is an intensive value that is not affected by amine concentration in the MEA and TEA systems. The slope of SCE is predominantly determined by the IC and the effective ionic concentration. In other words, the slope of SCE is increased as the IC and the effective ionic concentration are decreased. As a result, the slope of SCE in the TEA system, in which IC and effective ion concentration are the smallest, is the largest.

Unusually, however, the slope of SCE in the DEA system increased exponentially according to DEA concentration,

resulting in a rapid increase of slope of SCE higher than that of TEA at 2.1 M or higher solution concentrations. This phenomenon can be explained by the very low DEA utilization and limited hydrolysis over 2.1 M solution, and the CO₂ absorption is completed with the high concentration of R_2NCOO^- of which IC is the lowest. However, although the same phenomena occur in the MEA system, the slope of SCE is low due to even larger IC of RNH_3^+ .

Conclusions

In the present study, the overall performance of CO₂ absorption, the reaction characteristics, and the electrical properties of the three CO₂–amine absorption systems using MEA, DEA, and TEA aqueous solutions as absorbents were compared. The different results are mostly attributed to differences in molecular structure (or weight/size) and the unique reaction mechanism, and the following conclusions can be drawn:

1. The predominant factors affecting the increasing ratio of the chemical CO₂ absorption capacity at low and high concentration ranges of all three systems were amine molecular weight (and/or size) and molar ratio of CO₂ to amine in the reaction, respectively.
2. While CO₂ absorption completion time of the TEA system increased linearly at all concentration ranges, the increase fluctuated at low and high concentrations in the MEA and DEA systems. This phenomenon was attributed to absorption of CO₂ by a single base-catalyzed reaction in the TEA system regardless of the concentration range,

Table 8 Electrical properties including ionic conductivity of carbamic acid and carbamate, decreasing ratio of real ionic activity coefficient (γ_c), SCE calculated using amine concentrations, and its slope in MEA, DEA, and TEA systems

		MEA	DEA	TEA
Ionic conductivity (S cm ² /mol z)	Carbamic acid	62.20	38.46	37.60
	Carbamate	25.80	20.01	—
Decreasing ratio of γ_c above 1.0 M ($\times 10^2$) (L solution/mol amine)		− 5.75	− 10.23	− 11.72
SCE (mol CO ₂ cm/mS L solution)		0.013C* + 0.008	$e^{0.558C* - 4.089}$	0.030C* + 0.022
Slope of SCE ($\times 10^2$) (mol CO ₂ cm/mS mol amine)		1.30	1.63 (at 1.0 M)**	3.00
			3.02 (at 2.1 M)**	
			8.71 (at 4.0 M)**	

*C is the initial molar concentration of amine in solution before CO₂ absorption

** Slope of SCE in DEA system at specific concentrations calculated using the derivative equation of SCE: $0.558C(e^{0.558C - 4.089})$

whereas hydrolysis of carbamate in the other two systems was predominant at low concentration ranges (below 1.0 M).

3. The absorption rate of the MEA and DEA systems was proportional to amine concentration, and the maximum absorption rate was observed at 30.4 wt% MEA and 50.4 wt% DEA solution. On the other hand, the absorption rate of the TEA system according to amine concentration followed a parabolic curve and the maximum absorption rate was measured with 15.0 wt% solution.
4. The ionic conductivity (IC) of R_3NH^+ (R : C_2H_4OH) was smaller than that of RNH_3^+ and slightly lower than that of $R_2NH_2^+$. The decreasing ratio of IC of the three carbamic acids was larger than that of the reciprocal molecular weight of the three amines. This phenomenon might be attributed to relatively larger charge density of R_3NH^+ compared to RNH_3^+ and $R_2NH_2^+$ because the molar volume of TEA was not increased as much as the increase in molecular weight, due to substitution of hydrogen by C_2H_4OH group in ammonia molecule.
5. At relatively high amine concentrations in the solution (> 1.0 M) in all the three systems, the ionic activity coefficient (IAC) decreased as the molecular weight of amine and the molar concentration of the solution increased, and thus, the decreasing ratios were the largest in the TEA system and smallest in the MEA system. These results can be explained by the differential interaction in the three systems due to differences in molecular weight (or size) and water concentration. However, because water is one of the reactants in the TEA solution, which does not significantly affect the IAC, the decrease in the IAC of the TEA system is attributed to the chemical interactions and the physical entrapment of molecules by the three large R groups.
6. CAC_{chem} in the three systems was estimated in situ by the equations expressing EC_m variation during carbonation and initial amine concentration in the solution. The slope of the equations (SCE) is a function of initial amine concentration in all solutions. On the other hand, the slope of SCE to amine concentration in the MEA and TEA systems is constant; however, it depends on the amine concentration in the DEA system. The slope of SCE was strongly affected by the effective ionic concentration and their IC in each aqueous solution. The slope of SCE in the TEA system was the highest among the systems below 2.1 M. However, at concentrations above 2.1 M, the slope of SCE in the DEA system was the largest and that in the MEA system was the smallest. The results are explained by the fact that dominant reactions are different in the low and high concentration solutions of the three systems as well as the amine molecular structure and weight are different in the systems.

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