

# Density and Viscosity Calculation of a Quaternary System of Amine Absorbents before and after Carbon Dioxide Absorption

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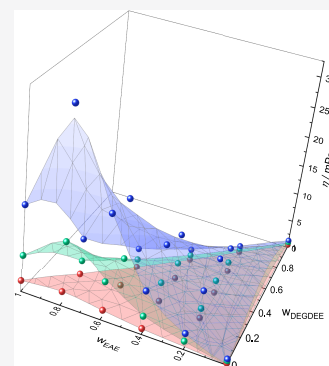


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**ABSTRACT:** Viscosity and density of amine absorbents affect directly their flow, which is involved in the process design and simulation of carbon dioxide capture. A mixture of 2-(ethyl amino) ethanol (EAE), diethylene glycol diethyl ether (DEGDDE), and water changes its phase from homogeneous to two-liquid ones on CO<sub>2</sub> absorption. It is difficult to calculate the viscosity and density of this phase separation solution, especially those of quaternary-component phases. In this research, models to calculate the density and viscosity of the quaternary-component system of EAE/DEGDDE/water/carbamate were suggested based on nonrandom two-liquid (NRTL)-DVOL and NRTL-DVIS models. Given the component concentrations, these models can replicate well the viscosity and density of the solutions. A good calculation result with a few numbers of parameters makes the models simple and easy to use.

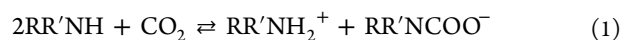


## 1. INTRODUCTION

Carbon dioxide capture using amine is the most mature technology in mitigating the greenhouse gas. However, energy consumption is a disadvantage of this method, especially in regeneration of the amine solution. Recently, the use of phase change amine absorbents has been of great interest in energy saving as well as the improvement in the amount of CO<sub>2</sub> captured.<sup>1–4</sup> The solution separates into solid–liquid or liquid–liquid phases after absorption. Regeneration of only the CO<sub>2</sub>-rich phase can save energy, which helps to overcome the energy penalty of this chemical absorption method.<sup>5</sup> Our group has also suggested a mixture of amine, ether, and water as an energy-saving solution for carbon dioxide capture,<sup>6–8</sup> which is composed of amine (2-(ethyl amino) ethanol, EAE), ether (diethylene glycol diethyl ether, DEGDDE), and water at a 30/60/10 weight basis. The CO<sub>2</sub>-unloaded solution is homogeneous. However, after CO<sub>2</sub> absorption, the high polarity of carbamate products leads to the formation of a new phase, a CO<sub>2</sub>-rich phase. As the absorption proceeds, the CO<sub>2</sub> as well as water amounts increase in this phase. The CO<sub>2</sub>-lean phase mainly contains ether. In the regeneration process, CO<sub>2</sub> is released when both phases of the solution are heated together up to 90 °C. The freed amine with small polarity then dissolves into the ether phase again. In other words, the extraction of amine by ether boosts the regeneration process, and the regeneration of this phase separation solution can thereby be carried out at a lower temperature (90 °C) than the conventional amine solution (120 °C). The combination of a heat pump to recover the absorption heat helps to decrease energy consumption of

this phase separation solution process down to 1.6 GJ/ton of CO<sub>2</sub>.<sup>8</sup>

EAE in its aqueous solution reacts with CO<sub>2</sub> as in reactions 1 or 2. R and R' are C<sub>2</sub>H<sub>5</sub>– and –CH<sub>2</sub>CH<sub>2</sub>OH, respectively.



The carbamate formation in reaction 1 requires two amines, while the bicarbonate formation in reaction 2 requires only one amine to capture a carbon dioxide. In a phase separation solution, EAE reacts with CO<sub>2</sub> to form carbamate anions, EAE cations, and a negligible amount of bicarbonate,<sup>7</sup> that is, reaction 1 is predominant over reaction 2. As a result, the solution in equilibrium contains two phases: the CO<sub>2</sub>-lean phase with dominant ether and the CO<sub>2</sub>-rich phase with unreacted EAE, water, and CO<sub>2</sub> in a carbamate form. In other words, the solution after absorption contains four components partitioned unequally into two phases.

The physical properties of absorbents such as density and viscosity are important in designing and simulating processes. Those properties have a great influence on mass transfer rates in absorbers and regenerators, as well as pump and heat exchanger

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Table 1. Chemical Sample Table

component	formula	CAS number	fraction purity	purity determination	source
2-(ethylamino) ethanol (EAE)	$C_4H_{11}NO$	110-73-6	98% <sup>a</sup>	GC <sup>b</sup>	TCI <sup>c</sup>
diethylene glycol diethyl ether (DEGDDE)	$C_8H_{18}O_3$	112-36-7	98% <sup>a</sup>	GC <sup>b</sup>	TCI <sup>c</sup>
carbon dioxide	$CO_2$	124-38-9	99.5% <sup>d</sup>	Orsat analysis	Nagoya Nissan, Ltd.

<sup>a</sup>Mass fraction. <sup>b</sup>Gas chromatography. <sup>c</sup>Tokyo Chemical Industry Co., Ltd. (TCI). <sup>d</sup>Mole fraction.

decisions. Therefore, they need to be accurately calculated/predicted, and studies on the correlation of these physical properties of amine mixtures with experimental data are necessary.

Many researchers have reported empirical models of viscosity and density for common absorbents with  $CO_2$ -unloaded or/and  $CO_2$ -loaded solutions such as monoethanolamine (MEA), N-methyldiethanolamine (MDEA), diethanolamine (DEA), etc.<sup>9–17</sup> Pinto et al. suggested the NRTL-DVIS (for viscosity) and NRTL-DVOL (for density) models for amine solutions.<sup>18–20</sup> They modeled viscosity and density using non-random two-liquid (NRTL)-based models. The NRTL-DVIS model was used to calculate the viscosity of multicomponent liquid mixtures of amine (ternary systems of  $H_2O$ /MEA/MDEA,  $H_2O$ /MEA/2-amino-2-methyl-1-propanol (AMP), and  $H_2O$ /MDEA/DEA).<sup>18</sup> Furthermore, Pinto et al. also reported the good replication of this NRTL-DVIS model to unloaded and loaded aqueous solutions of MDEA, dimethylethanolamine (DMEA), diethylethanolamine (DEEA), and 3-(methylamino)-propylamine (MAPA).<sup>19</sup> For density modeling, Pinto and Knuutila<sup>20</sup> demonstrated good agreement between the densities calculated from the NRTL-DVOL model and those of experimental data for amine aqueous solutions or amine/amine/water mixtures. Then, Skylogianni et al.<sup>21</sup> reported the ability of NRTL-DVIS and NRTL-DVOL models to accurately correlate the viscosities and densities in their amine/glycol/water systems, a ternary system similar to ours. The results in density modeling for binary and ternary systems are less than 0.4 and 0.3%, respectively. In viscosity, Skylogianni et al. gained a deviation lower than 3.0% for both binary and ternary systems using the same equations for aqueous solutions of MDEA, that of monoethylene glycol (MEG), and ternary systems of MDEA/MEG/water. However, those amine solutions are homogeneous during absorption, that is, they do not change their phase before and after reacting with  $CO_2$ . The estimation of viscosity and density of our phase separation solution is thus challenging, especially in building a simple yet high-accuracy one that can be easily used. To the best of our knowledge, there have been no reports on viscosity and density estimation of the phase change solution. In this work, we examined the  $CO_2$ -loaded solution consisting of unreacted amine (EAE), inert DEGDDE, water, and carbamate. The viscosities and densities of the loaded and unloaded amine solutions, especially the quaternary-component solution, were comprehensively investigated. Two models were applied in each physical property, and their accuracy was evaluated. The NRTL-DVOL and NRTL-DVIS models of Pinto et al., as mentioned above, successfully correlate not only the amine/amine/water mixture but also the mixture of amine/water/glycol. Therefore, we chose these models to calculate the viscosity of our four-component systems. Moreover, in density estimation, we tested the Hartono model, which has been applied successfully to the density of amine aqueous solutions.<sup>22,23</sup> In viscosity estimation, the Grunberg–Nissan model was also tested and compared to our results.<sup>16,24,25</sup> In general, the homogeneous solutions of ternary systems were

used to build the viscosity and density models, which were then applied to calculate the viscosities and densities of the quaternary systems. In addition, the influence of temperature on density and viscosity was examined in the temperature range of 293.15–363.15 K. This range covers the absorption temperature (313.15 K) and the regeneration temperature (363.15 K) of our proposed process.<sup>7</sup>

## 2. EXPERIMENTS

**2.1. Materials.** EAE (>98.0%,  $C_4H_{11}NO$ ,  $M_w = 89.14$ , TCI) and DEGDDE (>98.0%,  $C_8H_{18}O_3$ ,  $M_w = 162.23$ , TCI) were used as purchased (Table 1). Ultrafine water (Simplicity UV, Merck Millipore) was used in all experiments to eliminate the influence of  $CO_2$  from other sources.  $CO_2$  (>99.5%) and  $N_2$  (>99.99%) were supplied from Nagoya Nissan, Ltd.

The loading ( $\alpha$  (mol·mol<sup>-1</sup>)) measured by the moles of  $CO_2$  absorbed into the solution over the moles of total amine in solution was used to describe the amount of  $CO_2$  in the amine solution.

Through modeling of density and viscosity, there are two concentration bases used: the mole fraction basis for density modeling and the weight fraction basis for viscosity modeling. The solutions in discussion are hereafter referred to as EAE/DEGDDE/water  $x/y/z$  solutions where  $x$ ,  $y$ , and  $z$  indicate the weight percent of EAE, DEGDDE, and water before carbon dioxide absorption, respectively.

**2.2. Solution Classification.** In this paper, the models were built based on the calibration solutions (i.e., ternary systems). Then, they were applied to the calculation ones (i.e., quaternary systems) to calculate the viscosities and densities of these solutions. Therefore, the solutions can be classified into two: the calibration solutions that were used to determine the parameters of models and the calculation ones that were used to test the model accuracy.

The EAE concentrations in all solutions were labeled as the concentrations before absorption. The absorption temperature was at 313.15 K. The rich and lean phases were separated at this temperature as well. The solutions/phases were sampled at 313.15 K to examine their  $CO_2$ -absorbed amount.

**2.2.1. Calibration Solutions.** Solutions of EAE/DEGDDE/water and  $CO_2$ -absorbed solutions for building models are listed in Table 2. Density and viscosity of each solution were measured in the 293.15–363.15 K temperature range. Table 2 presents the  $CO_2$ -unloaded solutions (i.e., the EAE/DEGDDE/water mixtures). There are 131 data points in this group. The densities and viscosities of pure EAE and DEGDDE were measured in this work. The data of pure water were adopted from NIST.<sup>26</sup> Table 3 contains solutions of  $CO_2$ -unloaded and  $CO_2$ -loaded aqueous solutions of EAE with 96 data points (the EAE/water/carbamate mixtures). Solutions in Table 4 are the 108  $CO_2$ -unloaded and  $CO_2$ -loaded ones of EAE in the organic solution DEGDDE at 30–70 wt % (the EAE/DEGDDE/carbamate mixtures). As the loadings of solutions were different, the loading range was used to group the solutions with approximate

**Table 2. Ternary Systems of CO<sub>2</sub>-Unloaded Solutions (EAE/DEGDEE/Water) for Calibration**

DEGDEE / wt%	EAE / wt%					
	0	20	40	60	80	100
0	NIST <sup>26</sup>	(293.15–323.15)	(293.15–353.15)	(293.15–363.15)	(293.15–363.15)	(293.15–363.15)
20		(293.15–363.15)	(293.15–363.15)	(293.15–363.15)	(293.15–363.15)	
40		(293.15–363.15)	(293.15–363.15)	(293.15–363.15)		
60		(293.15–363.15)	(293.15–363.15)			
80		(293.15–363.15)				
100	(293.15–363.15)					

loadings in this table. The total data points for calibration are 335 points.

In the above three systems, only CO<sub>2</sub>-loaded EAE/DEGDEE solutions can exhibit phase separation when loadings exceed certain values.<sup>27</sup> In order not to complicate the calibration step, solutions of EAE/DEGDEE were adjusted to the loadings lower than the phase separation values to keep the solutions for calibration of the EAE/DEGDEE/carbamate mixture the homogeneous ones.

**2.2.2. Calculation Solutions.** Samples of CO<sub>2</sub>-unloaded solutions for calculation are listed in Table 5 (32 data points). For CO<sub>2</sub>-loaded mixtures, there were 13 sets of quaternary systems of EAE/DEGDEE/water/carbamate for calculation (Table 6, 161 data points). There were solutions that separated into two phases, which were marked as a set of a lean phase and a rich phase. There were solutions whose loadings were too low for the solution to separate into two phases. In other words, they were homogeneous before and after carbon dioxide absorption. They were denoted as *x*. The investigated temperature range for calculation solutions was 293.15–363.15 K. Experimental data of density and viscosity of all samples are listed in the Supporting Information (Tables S1–S8).

**2.3. Solution Preparation.** The preparation of CO<sub>2</sub>-unloaded samples was carried out with a Mettler Toledo ML204T/00 scale with an accuracy of 0.1 mg. Solutions without CO<sub>2</sub> were prepared at various concentrations of EAE, DEGDEE, and water by gravimetrically mixing these components, and the

concentrations were expressed in a weight basis of components. EAE in those solutions was the unreacted EAE.

The loaded solutions were prepared as follows: a fresh solution at a given concentration of amine was bubbled with CO<sub>2</sub> until full loading at 313.15 K; then, the loaded solution was diluted with the fresh amine solution to desired loadings at the given concentrations of amine. It is noticed that the solutions in Tables 3 and 4 are homogeneous ones. The phase separation occurs only in the presence of ether and only when the loading exceeds a certain value as mentioned above.

The amounts of absorbed CO<sub>2</sub> in all solutions were evaluated by TOC measurement (which is mentioned later in Section 2.4). The CO<sub>2</sub> form in these solutions can be estimated to be mainly carbamate for the following reasons:

- Loaded aqueous solutions of EAE (solutions in Table 3): In our previous work, the aqueous solution of EAE with a concentration of EAE higher than 80 wt % showed that its main product after CO<sub>2</sub> absorption—carbamate—is similar to that of phase separation solutions after CO<sub>2</sub> absorption.<sup>7</sup> The dominance of the carbamate product is due to the deficiency of water for reaction 2 to occur.
- Loaded solutions of EAE and DEGDEE (solutions in Table 4): Without water, reaction 2 cannot occur; therefore, carbamate is the only product of the reaction between EAE and CO<sub>2</sub>.
- The mixture of quaternary-component solutions (Table 6): In phase separation solutions, carbamate is the main product.<sup>7</sup>

In summary, CO<sub>2</sub> in all CO<sub>2</sub>-loaded solutions in our experiments was in a carbamate form, which means that EAE reacted with CO<sub>2</sub> as in eq 1. Reaction 1 was thus applied in calculating the concentration of EAE after absorption: 2 mol of EAE reacts with 1 mol of CO<sub>2</sub> to form 1 mol of carbamate. The unreacted EAE in solutions was therefore obtained by subtracting the reacted EAE as estimated above from the total amine amount in solution. In general, this work handled the concentrations of carbamate, unreacted EAE, water, and inert DEGDEE of all groups in calibration and calculation of density and viscosity. In contrast, the concentrations of EAE in all groups (except those in Table 2) are presented on the basis without CO<sub>2</sub> (before absorption). In calibration/calculation, its concentrations were converted into unreacted ones. In other words, the concentrations of EAE in calibration and calculation are those of unreacted ones after absorption. On the other hand, the concentrations of EAE used in discussion are those of EAE before absorption.

**2.4. Component Analysis.** The amounts of EAE, DEGDEE, and CO<sub>2</sub> (i.e., carbamate) in solutions after CO<sub>2</sub> absorption and dilutions as well as in each phase were determined using a TOC analyzer (TOC-L, Shimadzu). The

**Table 3. Ternary Systems of CO<sub>2</sub>-Unloaded and CO<sub>2</sub>-Loaded Aqueous Solutions of EAE (EAE/Water/Carbamate) for Calibration**

$\alpha$ (mol·mol <sup>-1</sup> )	EAE (wt %)		
	80	90	100
0	Table 2	(293.15–363.15)	Table 2
0.1	(293.15–363.15)	(293.15–363.15)	(293.15–363.15)
0.2	(293.15–363.15)	(293.15–363.15)	(293.15–363.15)
0.3	(293.15–353.15)	(293.15–353.15)	(293.15–353.15)
0.4	(293.15–353.15)	(293.15–343.15)	(293.15–343.15)

**Table 4. Ternary Systems of CO<sub>2</sub>-Unloaded and CO<sub>2</sub>-Loaded Organic Solutions of EAE (EAE/DEGDDE/Carbamate) for Calibration**

$\alpha$ (mol·mol <sup>-1</sup> )	EAE/DEGDDE ( $x/y$ ) <sup>a</sup>		
	30/70	50/50	70/30
0	(293.15–363.15)	(293.15–363.15)	(293.15–363.15)
0.03–0.04	(293.15–363.15)	(293.15–363.15)	(293.15–363.15)
0.12–0.17	(293.15–353.15)	(293.15–363.15)	(293.15–363.15)
0.21–0.31	(293.15–343.15)	(293.15–343.15)	(293.15–353.15)
0.25–0.35	(293.15–343.15)	(293.15–343.15)	(293.15–343.15)

<sup>a</sup> $x/y$  stands for the weight concentrations of EAE and DEGDDE, respectively.

**Table 5. CO<sub>2</sub>-Unloaded Solutions for Calculation**

CO <sub>2</sub> -unloaded	wt %
EAE/DEGDDE	40/60
EAE/DEGDDE/water	30/60/10
	30/50/20
	30/40/30

**Table 6. Quaternary Systems for Calculation: CO<sub>2</sub>-Loaded Solutions of EAE/DEGDDE/Water at Various Weight Bases**

30/60/10 ( $\alpha$ )	30/50/20 ( $\alpha$ )	30/40/30 ( $\alpha$ )	30/70 ( $\alpha$ )
A1/ Lean (0.183)	B6/ Lean (0.065)	C9/ Lean (0.331)	D11/ Lean (0.158)
A1/ Rich (0.472)	B6/ Rich (0.391)	C9/ Rich (0.399)	D11/ Rich (0.491)
A2/ Lean (0.246)	B7/ Lean (0.249)	C10/ Lean (0.086)	D12/ $x$ (0.117)
A2/ Rich (0.398)	B7/ Rich (0.388)	C10/ Rich (0.224)	
A3/ Lean (0.139)	B8/ Lean (0.076)		D13/ $x$ (0.049)
A3/ Rich (0.284)	B8/ Rich (0.144)		
A4/ Lean (0.098)			
A4/ Rich (0.156)			
A5/ $x$ (0.07)			

inorganic carbon (IC) and total nitrogen (TN) indicate the amount of carbon in CO<sub>2</sub> and that of nitrogen in amine, respectively. The concentrations of EAE and CO<sub>2</sub> were obtained from those two indexes. Total organic carbon (TOC) presents the amount of organic carbon in both amine and ether. Consequently, the carbon in DEGDDE is the difference between the TOC and the amount of organic carbon in EAE.

The water content in solutions was evaluated using a Karl Fischer moisture titrator (MKV-710, Kyoto Electronics Manufacturing Co., Ltd.).

**2.5. Density and Viscosity Measurement.** The viscosity and density were measured using a Stabinger-type kinematic viscometer (SVM 3001, Anton Paar). The geometry of the viscometer was cocylindrical, composed of a rotating outer cylinder and a floating inner cylindrical rotor. The density-measuring part of the viscometer was a vibrating U-tube densitometer. The calibration of the viscometer was performed by the manufacturer using a calibration fluid APN26. The density and viscosity were measured from 293.15 to 363.15 K in a 10 K interval. At high temperature, release of gas bubbles from samples caused the measurement of some samples to be impossible. This viscometer would stop and give an alert if this happened. At least 3 measurements were carried out, and the

average was used. All the experiments were performed under the ambient pressure (101,300 kPa), and the standard uncertainty of the pressure was estimated from the weather record in Nagoya City.

The reproducibility of the apparatus was reported by the manufacturer at 0.35% (viscosity) and 0.0001 g·cm<sup>-3</sup> (density). It was discussed by Chirico et al.<sup>30</sup> that the uncertainty of density is often limited by the purity of the sample. In our case, because the purities of our chemicals were approximately 98% (Table 1),  $u_r(\rho)$  due to the impurity was estimated to be 0.002, which is much larger than that of the apparatus described above. We therefore employed  $u_r(\rho) = 0.002$  as the standard uncertainty for the density. As the differences of viscosities between CO<sub>2</sub>-loaded and CO<sub>2</sub>-unloaded solutions were large, the combined expanded uncertainties for the viscosities were estimated at  $U(\eta) = 0.10\eta$  (at a 0.95 level of confidence ( $k = 2$ )). The repeatability in our measurements was evaluated with two samples for three times measurement. The deviations for density and viscosity measurements of pure ether in the 293.15–363.15 K range were 0.004 and 0.21%, respectively. CO<sub>2</sub>-loaded EAE/DEGDDE 30/70 solutions had significantly high viscosity in comparison to other CO<sub>2</sub>-loaded solutions. The rich phase of this solution at a 0.42 loading in the 293.15–363.15 K range showed 0.11 and 1.22% deviations for density and viscosity measurements, respectively.

### 3. DENSITY AND VISCOSITY MODELS

**3.1. Density Models.** First of all, the densities of pure components were modeled based on

$$\rho/\text{kg}\cdot\text{m}^{-3} = p_1 + p_2(T/\text{K}) + p_3(T/\text{K})^2 \quad (3)$$

where  $\rho$  is the density,  $T$  is the absolute temperature, and  $p_1$ ,  $p_2$ , and  $p_3$  are coefficients.

The obtained densities will then be applied to the building of mixture density models.

The volume of the mixture ( $V_m$ ) deviates from the sum of volumes of pure components. Therefore, the excess molar volume ( $V_m^E$ ) is a common approach to adjust the deviation from the ideal mixing caused by the difference in shape, size of components, and physical and chemical interactions among the component molecules as in eq 4.<sup>11</sup> Moreover, the hydrogen bonding between molecules is also included in the intermolecular interactions, which makes the volume of the mixture deviate from the sum of partial molar volumes of pure components.

$$V_m/\text{m}^3\cdot\text{mol}^{-1} = \sum_{i=1}^{NC} x_i V_i + V_m^E \quad (4)$$



where  $x_i$  and  $V_i$  are the mole fraction and the partial volume of a pure component  $i$  in a mixture, respectively. NC is the number of components.

There are many reports on density modeling from single amine solutions to mixture of amines with various considerations via excess molar volume calculation. Among them, the Redlich–Kister model<sup>10,14,17,25</sup> has shown good agreement with experimental data. However, its big disadvantage is the requirement of a large number of parameters, especially in solutions with more than three components. The excess molar volume in the Redlich–Kister model for binary systems can be expressed as

$$V_m^E = x_i x_j \sum_{f=1} A_{RK,f} (x_i - x_j)^{f-1} \times 10^{-6} \quad (5)$$

The integer  $f$  varies from 1 to the degree of polynomial expansion.  $A_{RK,f}$  is the Redlich–Kister coefficient. It has polynomial temperature dependence with  $r_{ff'}$  parameters as

$$A_{RK,f} = \sum_{f'=1} r_{ff'} T^{f'-1} \quad (6)$$

For solutions with more than two components, the excess molar volumes between each pair are calculated and correlated to the excess molar volume of the whole mixture.

In order to reduce the number of parameters, Hartono et al. calculated the excess molar volume for binary solutions as below<sup>22,23</sup>

$$V_m^E = (l_1 + l_2 t + l_3 x_1 + l_4 x_1^2) x_1 x_2 \times 10^{-6} \quad (7)$$

$l_1$  to  $l_4$  are parameters, and  $t$  is temperature (in °C).

In the approach of Pinto and Knuutila (NRTL-DVOL model), the excess molar volume is approached via the NRTL model and expressed as below<sup>20</sup>

$$V_m^E = R \times T \times \sum_{i=1}^{NC} x_i \times \frac{\sum_{j=1}^{NC} \tau_{ji} H_{ji} x_j}{\sum_{k=1}^{NC} H_{ki} x_k} \quad (8)$$

$$H_{ij} = \exp(-0.2\tau_{ij}) \quad (9)$$

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} \quad (10)$$

where NC is the number of components. The fitting parameters are  $R$ ,  $a_{ij}$ , and  $b_{ij}$ , where  $a_{ii} = 0$  and  $b_{ii} = 0$ .

**3.2. Viscosity Models.** Similar to the density modeling of pure components, the viscosities of pure components were modeled to obtain the calculated data for modeling the mixture viscosity. There were two models applied in building the viscosity models for pure components in this work. Equation 11 was applied to model the viscosities of pure EAE, DEGDEE, and carbamate. Viscosities of pure EAE carbamate were obtained via extrapolation, which is explained later in Section 4.2.2. As for water, the deviation of eq 12 is an order of magnitude smaller than that of eq 11. Therefore, we used the former in modeling the viscosity of pure water.

$$\ln(\eta/\text{mPa}\cdot\text{s}) = q_1 + q_2/(T/K) + q_3/(T/K)^2 \quad (11)$$

$$\eta/\text{mPa}\cdot\text{s} = o_1 + o_2/\left(\left(\frac{T}{K}\right) - o_3\right) \quad (12)$$

where  $q_1$ ,  $q_2$ ,  $q_3$ ,  $o_1$ ,  $o_2$ , and  $o_3$  are parameters.

The Grunberg–Nissan model<sup>16,24,25</sup> modified the Arrhenius formulation with adjustable parameters for calculating the mixture viscosity. It estimates the viscosity from ideal mixing and the excess part of viscosity as in eq 13

$$\ln(\eta_m/\text{mPa}\cdot\text{s}) = x_i \ln \eta_i + x_j \ln \eta_j + x_i x_j G_{ij} \quad (13)$$

where  $\eta_m$ ,  $\eta_i$ , and  $\eta_j$  are viscosity of the mixture and those of pure components  $i$  and  $j$  (mPa s), respectively.  $G_{ij}$  is the temperature-dependent interaction parameter, which is expressed as

$$G_{ij} = u_{ij1} + u_{ij2}(T/K) + u_{ij3}(T/K)^2 \quad (14)$$

where  $u_{ij1}$ ,  $u_{ij2}$ , and  $u_{ij3}$  are adjustable parameters. Until now, this correlation has been extensively examined for liquid mixtures, including several aqueous amine solutions. However, it has been reported that this model does not work well in polar mixtures, particularly in aqueous solutions.<sup>19,31,32</sup> Moreover, the disadvantage of this model is on its number of parameters. A large number of parameters are required, which made it too complex to apply this model to our quaternary solution. However, a comparison was carried out in viscosity modeling in this work.

Pinto and Svendsen used a similar approach to the excess Gibbs energy function in viscosity estimation (NRTL-DVIS model). In this model, an excess viscosity term counts the deviation between the experiment and ideality upon mixing. Given that the NRTL equation can express the equilibrium phase behavior of our phase separation solvent,<sup>18</sup> it is expected to be applicable to the excess viscosity of our solutions. In the right-hand side of eq 15, the NRTL-DVIS model includes the ideal viscosity based on pure components in the first term and the excess viscosity, which is the deviation between ideality mixing viscosity and “true” viscosity, in the second term. The excess viscosity part ( $\ln \eta_m^E$ ) is expressed as in eq 16.

$$\ln(\eta_m) = \sum_{i=1}^{NC} w_i \times \ln(\eta_i) + \ln(\eta_m^E) \quad (15)$$

$$\ln(\eta_m^E) = R \times \sum_{i=1}^{NC} w_i \times \frac{\sum_{j=1}^{NC} \psi_{ji} S_{ji} w_j}{\sum_{k=1}^{NC} S_{ki} w_k} \quad (16)$$

$$S_{ij} = \exp(-0.2\psi_{ij}) \quad (17)$$

$$\psi_{ij} = c_{ij} + \frac{d_{ij}}{T} \quad (18)$$

where  $c_{ii} = 0$  and  $d_{ii} = 0$ . Similar to density correlation, parametrization was carried out with  $c_{ij}$ ,  $d_{ij}$ , and  $R$ . The model takes temperature into account as in eq 18, which is suitable to our purpose. Fitted parameters are listed in the Results and Discussion section. We also applied the suggestion of Song et al. to use weight fractions instead of mole fractions in viscosity modeling for practical and accuracy purposes.<sup>33</sup>

**3.3. Modeling Approach.** A consistent approach was applied in modeling of both density and viscosity: one- to three-component systems were used in determination and optimization of parameters. These calibration steps were carried out as follows:

- The density and viscosity of pure components (EAE, DEGDEE, water, and carbamate) were modeled. Then, those calculated densities and viscosities were applied into model building.

- Pure water, EAE, DEGDEE, and their unloaded mixtures (the EAE/DEGDEE/water system, Table 2) were used to optimize their pair parameters (EAE-DEGDEE, EAE-water, and DEGDEE-water). The parameter  $R$  was also determined in this step.
- Then, those parameters were applied to determine the pair parameters of the next ternary system (EAE/carbamate/water, Table 3) (parameters for EAE-carbamate and carbamate-water).
- The last ternary system for calibration is EAE/DEGDEE/carbamate (Table 4), where the pair parameters of DEGDEE-carbamate were determined.

Those parameters were then applied to calculate the viscosity and density of the validation systems (solutions in Tables 5 and 6).

The optimization was carried out using the solver function of Excel from Microsoft. The optimization used the sum of the squared difference between calculated and experimental data as in the equation below

$$\Delta y^2 = (y_i^{\text{calc}} - y_i^{\text{exp}})^2 \quad (19)$$

where  $y_i^{\text{calc}}$  and  $y_i^{\text{exp}}$  are the densities/logarithm of viscosities obtained from modeling and experiments, respectively.

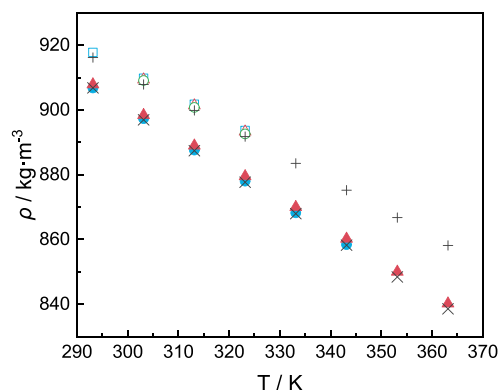
Average absolute relative deviation (AARD) was used to evaluate the quality of correlation

$$\text{AARD}[\%] = 100\% \frac{1}{n} \sum_{i=1}^n \left| \frac{y_i^{\text{exp}} - y_i^{\text{calc}}}{y_i^{\text{exp}}} \right| \quad (20)$$

where  $n$  stands for the total number of experiments used. In this equation,  $y_i^{\text{calc}}$  and  $y_i^{\text{exp}}$  stand for the densities/viscosities obtained from calculation and experiments, respectively.

## 4. RESULTS AND DISCUSSION

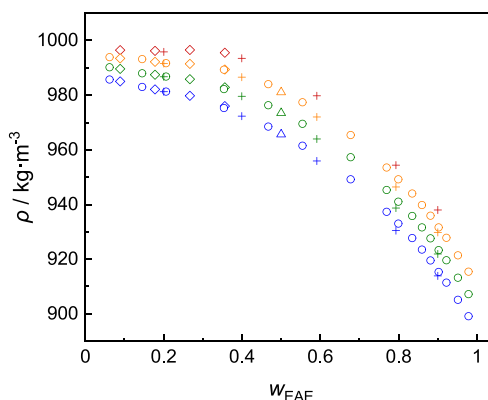
As density and viscosity modeling requires different concentration bases, in order not to confuse the readers, the plots in this



**Figure 1.** Densities of pure EAE and DEGDEE at different temperatures. Pure EAE: García-Abuín et al.<sup>16</sup> (open squares), Álvarez et al.<sup>24</sup> (open triangles), Chowdhury et al.<sup>34</sup> (open circles), and this work (+). Pure DEGDEE: Ku and Tu<sup>28</sup> (solid circles), Esteve et al.<sup>29</sup> (solid triangles), and this work (x).

work are presented in the weight fraction basis in case that the concentration is required.

Each section of density and viscosity modeling includes the confirmation of measurement validity, the modeling of pure components, and the application into quaternary systems.



**Figure 2.** Densities of CO<sub>2</sub>-unloaded aqueous solutions of EAE at various concentrations. Gao et al.<sup>17</sup> (diamonds), Álvarez et al.<sup>24</sup> (triangles), Chowdhury et al.<sup>34</sup> (circles), and this work (+). Explanation: 293.15 (dark red), 303.15 (orange), 313.15 (olive), and 323.15 K (blue).

**4.1. Density Model.** It is worthy reminding that the concentration basis in density modeling is the mole fraction.

**4.1.1. Density Measurement Uncertainty.** Densities of pure EAE and DEGDEE in our experiments in the  $T = 293.15$ – $363.15$  K range were compared with literature data (Tables S9 and S10).<sup>16,24,28,29,34</sup> A graphical comparison is shown in Figure 1. For pure EAE, the AARDs from García-Abuín et al.,<sup>16</sup> Álvarez et al.,<sup>24</sup> and Chowdhury et al.<sup>34</sup> are 0.20, 0.17, and 0.11%, respectively. In the case of DEGDEE, its densities were compared with literature data of Ku and Tu<sup>28</sup> and Esteve et al.<sup>29</sup> in the  $T = 293.15$ – $363.15$  K range. The deviations between this work and Ku and Tu and Esteve et al. are 0.02 and 0.19%, respectively. We consider that the overall AARDs for EAE (0.16%) and DEGDEE (0.12%) are acceptable.

The densities of EAE aqueous solutions at various weight fractions were also compared with the literature (Figure 2).<sup>17,24,34</sup> Even though the experimental densities are lower than those in the literature at concentrations larger than 0.6, the experimental densities in this work agree well with those in the literature. Therefore, Figures 1 and 2 confirm the high reliability of our density measurement.

**4.1.2. Calibration Process.** **4.1.2.1. Extrapolation of EAE Carbamate Density.** The viscosities and densities of pure EAE, DEGDEE, water, and carbamate are necessary in building the models. However, in CO<sub>2</sub> capture, the carbamate of EAE exists only in equilibrium, which means that it cannot be isolated. In this work, densities and viscosities at various loadings of CO<sub>2</sub>-loaded pure EAE were used to extrapolate these values of “pure” EAE carbamate at 293.15–363.15 K (Table 7). In a pure EAE solution, as there is no water for reaction 2 with a bicarbonate product to occur, EAE reacts with CO<sub>2</sub> as in reaction 1 to form carbamate. In the ideal condition, all EAE in a phase separation solution reacts to form EAE carbamate, and the solution can reach its highest loading of 0.50. Thus, all the CO<sub>2</sub> in solution is in a carbamate form, which means that the “pure” EAE carbamate is obtained at this loading. However, as the experimental conditions were not an ideal condition, the loading of solution is smaller than 0.5. The details of extrapolations are provided in the Supporting Information (Section III).

**4.1.2.2. Density Models for Pure Components.** The densities of pure components were modeled based on eq 3. The parameters and AARDs are listed in Table 8. The visualization of the models is presented in the Supporting Information

Table 7. Densities  $\rho$  of “Pure” EAE Carbamate Obtained via Extrapolation

	T (K)							
	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15
$\rho$ (kg·m <sup>-3</sup> )	1114.35	1106.98	1100.33	1093.40	1086.28	1078.73	1072.10	1063.50

Table 8. Parameters and AARDs in Density Calculation of Pure EAE, DEGDEE, Carbamate, and Water

parameters	EAE	DEGDEE	carbamate	water
$p_1$	1086	1106	1263	795.2
$p_2$	-0.3842	-0.4476	-0.3372	1.634
$p_3 \times 10^3$	-0.6729	-0.8006	-0.5780	-3.211
AARDs	0.01	0.03	0.02	0.01

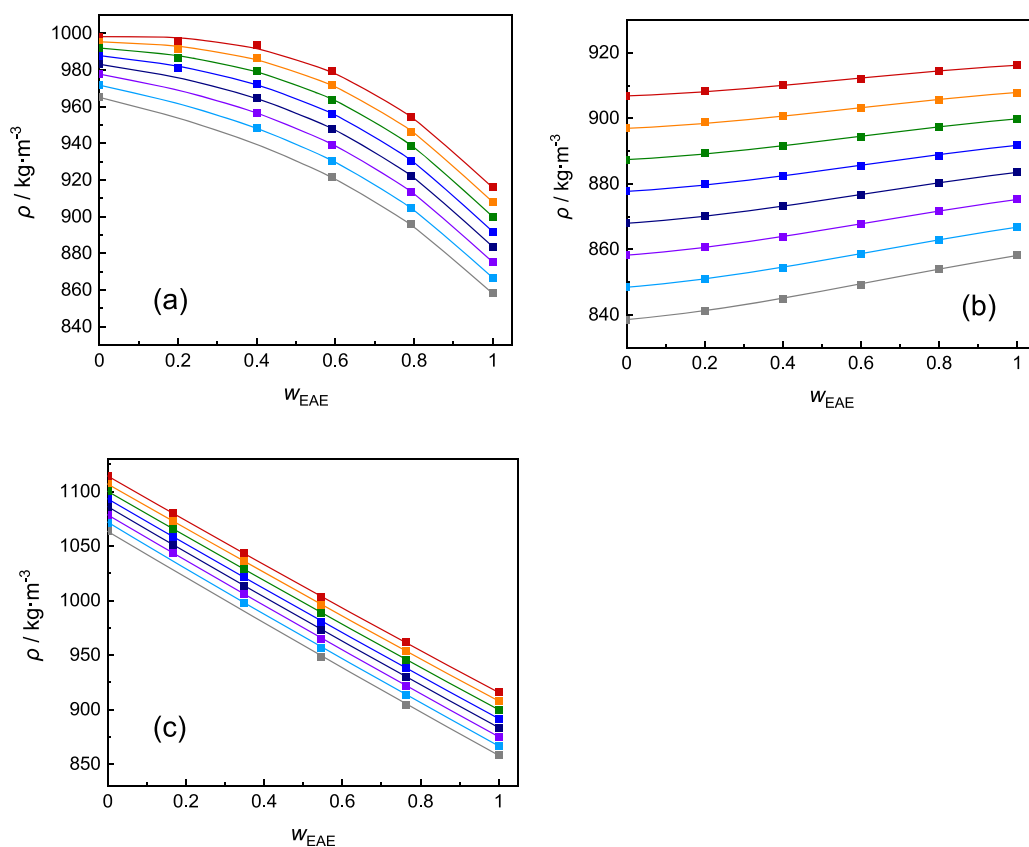
Table 9. Fitting Parameters for Density Modeling Using the NRTL-DVOL Equation

NRTL-DVOL	1.DEGDEE		2.EAE		3.water		4.carbamate	
1.DEGDEE			$a_{12}$	-2.0188	$a_{13}$	-2.7362	$a_{14}$	-3.2326
			$b_{12}$	127.35	$b_{13}$	328.48	$b_{14}$	433.33
2.EAE	$a_{21}$	2.5966			$a_{23}$	-0.83030	$a_{24}$	4.4094
	$b_{21}$	-96.899			$b_{23}$	-75.258	$b_{24}$	-486.06
3.water	$a_{31}$	-1.2175	$a_{32}$	-0.81752			$a_{34}$	4.6855
	$b_{31}$	2377.6	$b_{32}$	1179.2			$b_{34}$	-200.58
4.carbamate	$a_{41}$	22.446	$a_{42}$	-1.6384	$a_{43}$	-2.3153		
	$b_{41}$	-4863.0	$b_{42}$	163.60	$b_{43}$	347.42		

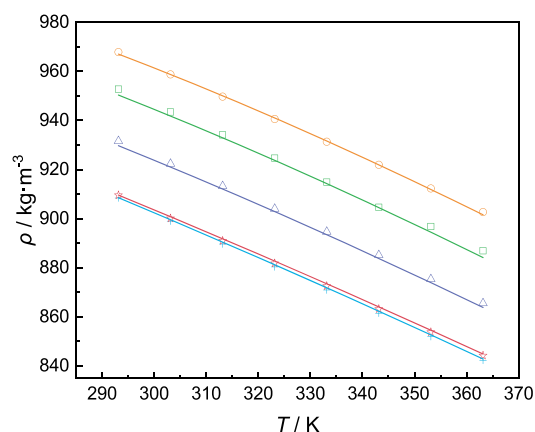
(Figure S4). The models well replicated the experimental data with reasonable AARDs.

**4.1.2.3. Densities of Binary Mixtures.** Experimental and calculated densities of binary mixtures (EAE/water, EAE/DEGDEE, and EAE/carbamate) are presented in Figure 3. Without ether (DEGDEE = 0), the increase in the amount of EAE decreases the densities in the EAE/water mixture (Figure 3a). This is attributed to the density order of pure solutions: carbamate > water > EAE > DEGDEE. Similarly, the solution without water has an elevated density as the concentration of EAE increases in the EAE/DEGDEE mixture (Figure 3b). In the mixture of EAE/carbamate, the increase in EAE concentration is followed by the decrease in density of the mixture. The higher density of carbamate than that of EAE is attributed to this

decrease. As mutual solubility of DEGDEE and water is low in our temperature range,<sup>35</sup> densities of the DEGDEE/water mixture cannot be obtained. It can be seen that the model replicates well the experimental data in binary mixtures.



**Figure 3.** Densities of binary systems at various loadings: (a) EAE/water, (b) EAE/DEGDEE, and (c) EAE/carbamate. Marks and lines indicate experimental and calculated densities, respectively. 293.15 (dark red), 303.15 (orange), 313.15 (olive), 323.15 (blue), 333.15 (navy), 343.15 (purple), 353.15 (light blue), and 363.15 K (gray).



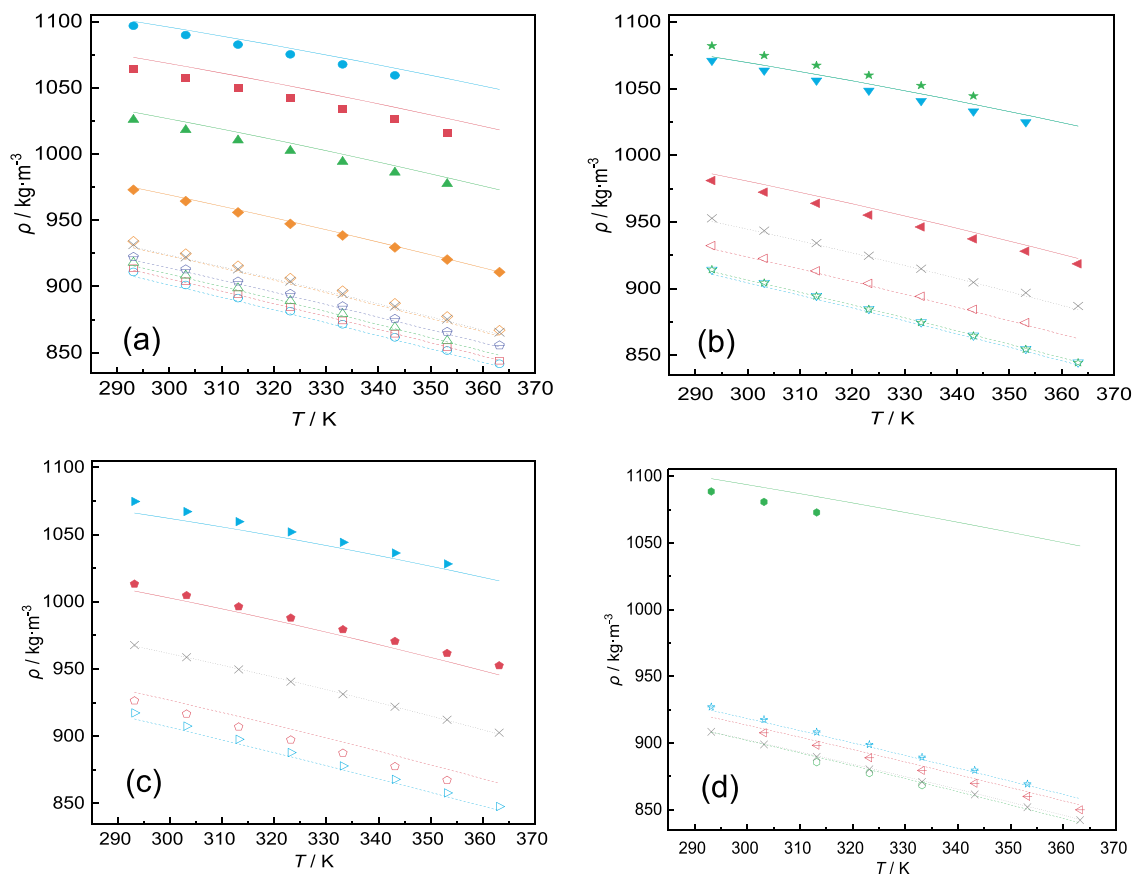
**Figure 4.** Experimental and calculated densities of CO<sub>2</sub>-unloaded mixtures of EAE/DEGDDEE/water (weight basis) at 30/40/30 (circles), 30/50/20 (squares), 30/60/10 (triangles), 40/60 (stars), and 30/70 (+). Marks and solid lines indicate experimental densities and calculated densities, respectively.

The fitting parameters for density modeling using the NRTL-DVOL equation are presented in Table 9. The *R* parameter was −0.01498. Those parameters are valid for estimating all the systems of EAE/DEGDDEE/water/carbamate as long as carbamate is the only product.

**Table 10.** AARDs and Numbers of Data in Density Modeling Using the NRTL-DVOL Equation for EAE/DEGDDEE/Water/Carbamate Mixtures

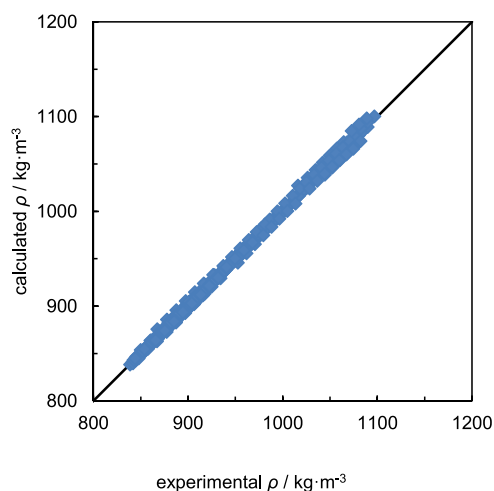
	<i>n</i>	AARD (%)
EAE/DEGDDEE/water	131	0.040
EAE/water/carbamate	96	0.083
EAE/DEGDDEE/carbamate	108	0.118
EAE/DEGDDEE/water/carbamate	193	0.350

**4.1.3. Calculation Process.** **4.1.3.1. CO<sub>2</sub>-Unloaded Solutions.** Figure 4 presents the experimental and calculated densities of CO<sub>2</sub>-unloaded mixtures of EAE/DEGDDEE/water. At the same temperature, the density of pure EAE is larger than that of DEGDDEE. As a result, the increase in EAE in the EAE/DEGDDEE mixture contributes to the increase in mixture density, though the degree of the increase is small. When there is water in solution, the increase in mixture density is significant. This is due to the higher density of water than those of EAE and DEGDDEE. There is a similarity in behavior of densities in relation with temperature in all solutions: an identical slope in density and temperature relation, i.e., the independence of the coefficient of thermal expansion on the solution. Even if the deviation between calculated and experimental data is large, this slope can be reproduced in general. There is a similarity in the way that calculated data deviates from the experimental one.

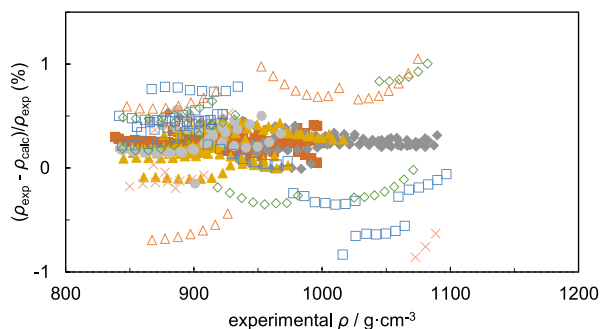


**Figure 5.** Densities of CO<sub>2</sub>-loaded mixtures of EAE/DEGDDEE/water (weight basis) at (a) 30/60/10, (b) 30/50/20, (c) 30/40/30, and (d) 30/70. Explanation: Marks and lines represent the experimental and calculated data, respectively. CO<sub>2</sub>-lean phases (empty marks and dashed lines), CO<sub>2</sub>-rich phases (filled marks and solid lines), and CO<sub>2</sub>-unloaded solutions (× and dotted lines). The rich phase and the lean phase of the same data set have similar marks.

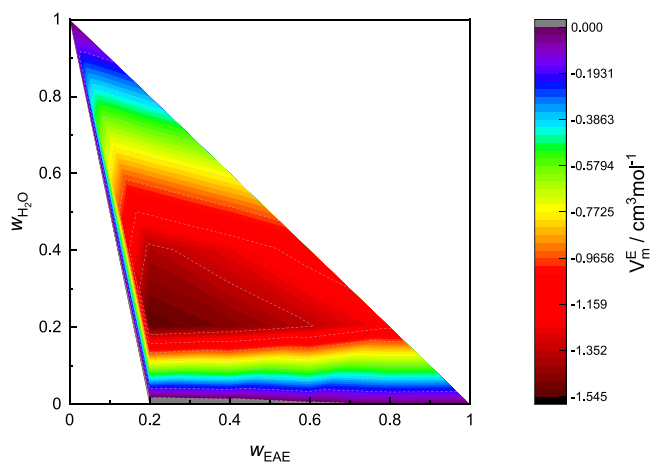




**Figure 6.** Comparison between experimental and calculated densities of all systems.

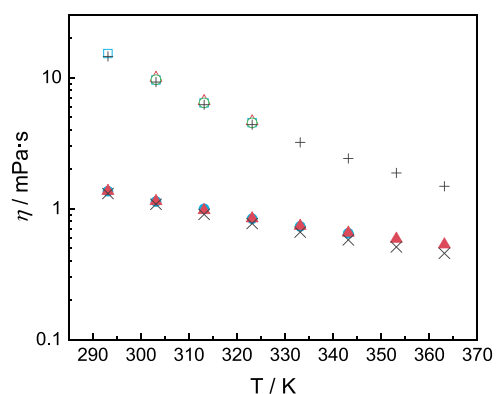


**Figure 7.** Deviations  $(\rho_{\text{exp}} - \rho_{\text{calc}})/\rho_{\text{exp}}$  of experimental and calculated densities in relation with experimental densities of all solutions. EAE/DEGDEE/water (solid squares), EAE/water/carbamate (solid diamonds), EAE/DEGDEE/carbamate (solid triangles), CO<sub>2</sub>-unloaded mixtures of EAE/DEGDEE/water (solid circles), and CO<sub>2</sub>-loaded mixtures of EAE/DEGDEE/water (30/60/10 (open squares), 30/50/20 (open diamonds), 30/40/30 (open triangles), 30/70(x)).

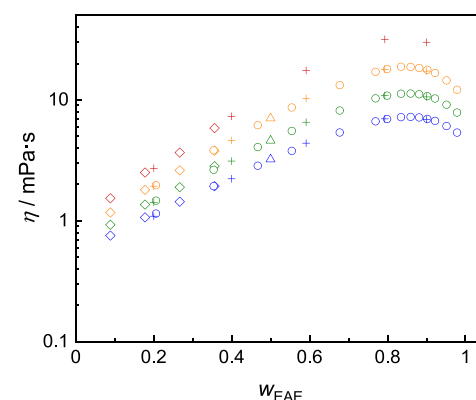


**Figure 8.** Excess molar volume  $V_m^E$  of CO<sub>2</sub>-unloaded EAE/DEGDEE/water mixtures at 313.15 K.

**4.1.3.2. CO<sub>2</sub>-Loaded Solutions.** When CO<sub>2</sub> is absorbed into the solution, the increase in the mixture volume is negligible while its weight increases. As a result, the density of the mixture increases when the loading increases. As mentioned above, the rich phase contains amine, carbamate, and water, while



**Figure 9.** Viscosities of pure EAE and DEGDEE at different temperatures. Pure EAE: García-Abuín et al.<sup>16</sup> (open squares), Álvarez et al.<sup>24</sup> (open triangles), Chowdhury et al.<sup>34</sup> (open circles), and this work (+). Pure DEGDEE: Ku and Tu<sup>28</sup> (solid circles), Esteve et al.<sup>29</sup> (solid triangles), and this work (x).



**Figure 10.** Viscosities for aqueous solutions of EAE at various concentrations: Gao et al.<sup>17</sup> (diamonds), Alvarez et al.<sup>24</sup> (triangles), Chowdhury et al.<sup>34</sup> (circles), and this work (+). Explanation: 293.15 (dark red), 303.15 (orange), 313.15 (olive), and 323.15 K (blue).

DEGDEE is the main component of the lean phase. Consequently, densities of the rich phases are higher than those of the lean phases, and their density order is rich phase > unloaded solution > lean phase. The experimental and calculated values for CO<sub>2</sub>-loaded mixtures of EAE/DEGDEE/water at various weight bases are presented in Figure 5. The calculated densities of the lean phase, the rich phase, and homogeneous solutions match well with experimental data within 0.350% AARD. In other words, the model was able to replicate the experimental data with reasonable accuracy. It is noticed that the B6 and B7 samples (both are rich phases) of EAE/DEGDEE/water 30/50/20 solutions have similar component concentrations (Supporting Information Table S4). Therefore, their measured and calculated viscosities were superimposed to each other in Figure 5b (solid inverted triangle and solid star marks).

The deviations between experimental and calculated densities in all systems are listed in Table 10. The deviations of all systems are below 0.5%. The accuracy of the NRTL-DVOL model is good enough for simulations and engineering calculation purposes.

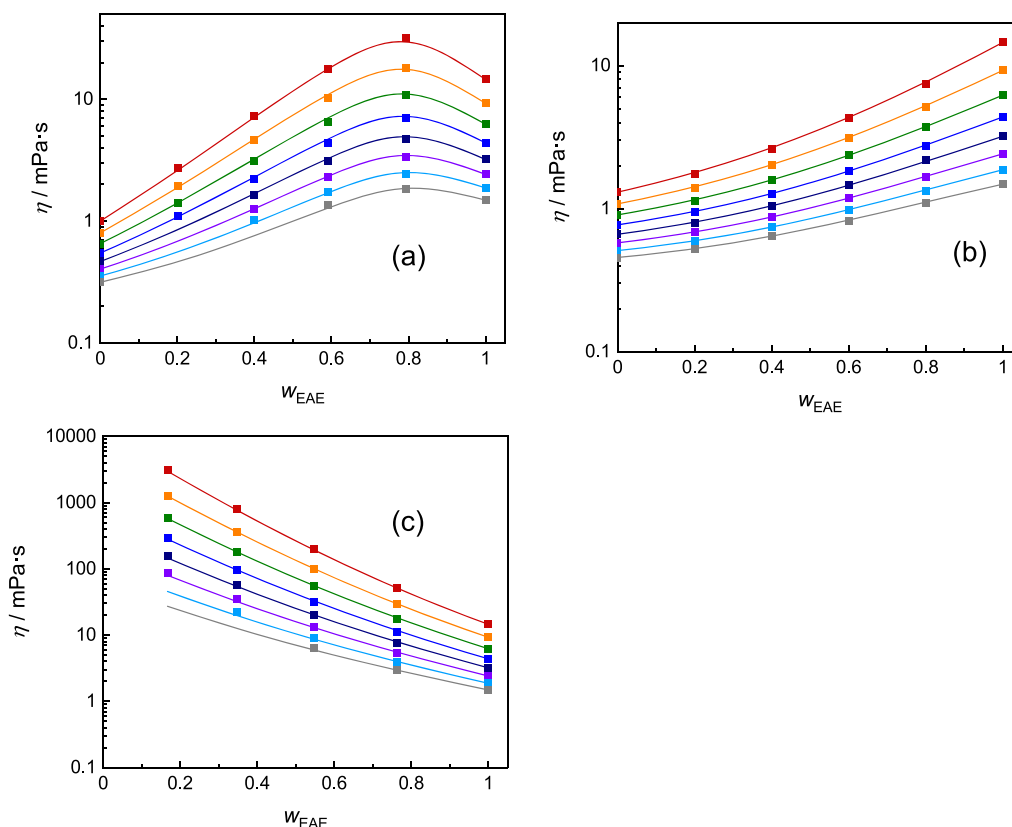
The parity plot of all systems (Figure 6) shows good agreement between experimental and calculated densities. The deviations between calculated and experimental data are presented in Figure 7. The solutions for calibration (filled

Table 11. Viscosities  $\eta$  of “Pure” EAE Carbamate Obtained via Extrapolation

	$T$ (K)							
	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15
$\eta$ (mPa·s)	11566.96	4274.0	1765.6	804.1	396.4	208.3	111.1	56.7

Table 12. Parameters and AARD Values in Viscosity Modeling of Pure EAE, DEGDEE, Carbamate, and Water

parameters	EAE	DEGDEE	carbamate	parameters	water
$q_1$	−4.3869	−3.8631	−11.410	$o_1$	−1.9066
$q_2$	1036.8	841.20	4293.3	$o_2$	−925.60
$q_3$	146.36	89.517	86.168	$o_3$	435,183
AARDs	0.11	0.21	2.86		0.13



**Figure 11.** Viscosities of binary systems at various loadings: (a) EAE/water, (b) EAE/DEGDEE, and (c) EAE/carbamate. Marks and lines: experimental and calculated viscosities, respectively. 293.15 (dark red), 303.15 (orange), 313.15 (olive), 323.15 (blue), 333.15 (navy), 343.15 (purple), 353.15 (light blue), and 363.15 K (gray).

marks) show good agreement, while the solutions for calculation (empty and  $\times$  marks) have large deviation. However, the deviations are acceptable.

Our calibration data were used to build the Hartono model<sup>22,23</sup> as well (the details are presented in the [Supporting Information, Section V](#)). This model, which shows good performance on MEA aqueous solutions, showed 0.60% AARD for our CO<sub>2</sub>-loaded quaternary solutions. With a significantly lower value of AARD, the NRTL-DVOL model gives better calculation to our quaternary systems than that of Hartono.

**4.1.4. Excess Molar Volume.** In the excess molar volume approach of the EAE/DEGDEE/water mixture (Figure 8), the excess molar volume in the organic solution of EAE (water = 0) is positive at 313.15 K. In the mixtures of EAE, DEGDEE, and water, the sign of the excess molar volume is opposite (negative), which means that there is a contracting behavior in the mixture.

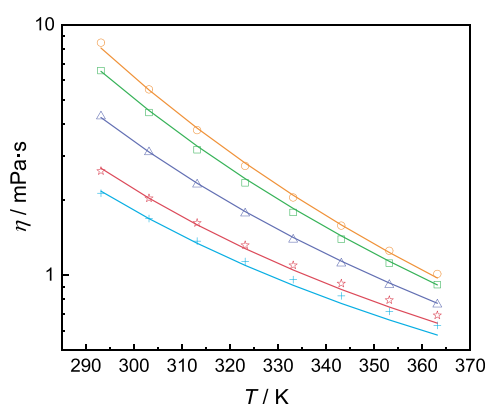
The excess molar volume is a consequence of the structure and interactions between molecules. The interactions between molecules, for example, hydrogen bond formation between EAE and water molecules, might cause the negative sign of the excess molar volume, or this negative excess molar volume can also be explained by the partial accommodation of EAE and DEGDEE molecules within the void space of structured water.

The minimum values in the excess molar volume of water-containing mixtures lie in vicinity of the 0.2 weight fraction range of water. The negative minima of the excess molar volume shift to the lower concentration range of EAE. A similar behavior of the excess molar volume was observed at other temperatures as well. The contributions of these factors should be further examined in future works.

**4.2. Viscosity Model.** The concentration basis in viscosity modeling is the weight fraction.

**Table 13.** Fitting Parameters for Viscosity Modeling Using the NRTL-DVIS Equation

NRTL-DVIS	1.DEGDEE		2.EAE		3.water		4.carbamate	
1.DEGDEE			$c_{12}$	-1.0561	$c_{13}$	-0.72518	$c_{14}$	0.084774
			$d_{12}$	-159.67	$d_{13}$	864.59	$d_{14}$	591.66
2.EAE	$c_{21}$	1.9941			$c_{23}$	0.037530	$c_{24}$	3.6416
	$d_{21}$	-7.6658			$d_{23}$	1441.6	$d_{24}$	-475.86
3.water	$c_{31}$	-2.1800	$c_{32}$	-3.6098			$c_{34}$	0.19168
	$d_{31}$	578.07	$d_{32}$	664.15			$d_{34}$	-625.78
4.carbamate	$c_{41}$	0.35131	$c_{42}$	-1.9047	$c_{43}$	463.38		
	$d_{41}$	-749.49	$d_{42}$	43.235	$d_{43}$	-596.17		

**Figure 12.** Experimental and calculated viscosities of CO<sub>2</sub>-unloaded mixtures of EAE/DEGDEE/water (weight basis) at 30/40/30 (circles), 30/50/20 (squares), 30/60/10 (triangles), 40/60 (stars), and 30/70 (+). Marks and solid lines indicate experimental data and calculated data, respectively.

**4.2.1. Viscosity Measurement Uncertainty.** In order to validate our measurement methodology, the viscosities of pure EAE and DEGDEE in comparison with literature data are presented in Figure 9. In EAE viscosity measurement, our work deviates from literature data at 3.60, 5.94, and 3.34% (García-Abuín et al.,<sup>16</sup> Álvarez et al.,<sup>24</sup> and Chowdhury et al.,<sup>34</sup> respectively) in  $T = 293.15\text{--}323.15$  K. Deviations from the literature of pure DEGDEE in viscosity measurement are 7.71 and 9.27% (Ku and Tu<sup>28</sup> and Esteve et al.,<sup>29</sup> respectively) in  $T = 293.15\text{--}363.15$  K. The viscosity of DEGDEE of this work is in good agreement with the literature in the temperature range 293.15–315.15 K. At a higher temperature range, our values are lower than those of the literature because these low viscosities deviate from the suitable application range of our Stabinger viscometer. Therefore, a higher AARD in the DEGDEE pure solution was obtained. The overall AARDs for EAE and DEGDEE are 4.22 and 8.60%, respectively.

Furthermore, the viscosities of EAE aqueous solutions at various weight fractions were calculated and compared with literature data (Figure 10).<sup>17,24,34</sup> Our data agree well with those of the literature. The acceptable deviation proves that the viscosity measurement in this work is reliable.

**4.2.2. Calibration Process.** **4.2.2.1. Carbamate Extrapolation.** As viscosities of pure components are necessary in building

viscosity models and EAE carbamate is not commercially available, its viscosity is obtained in a similar method to that in density (Section 4.1.2). The  $\ln \eta$  was used in extrapolation. The viscosities of “pure” EAE carbamate are presented in Table 11. The details of the extrapolation are listed in the Supporting Information, Section III.

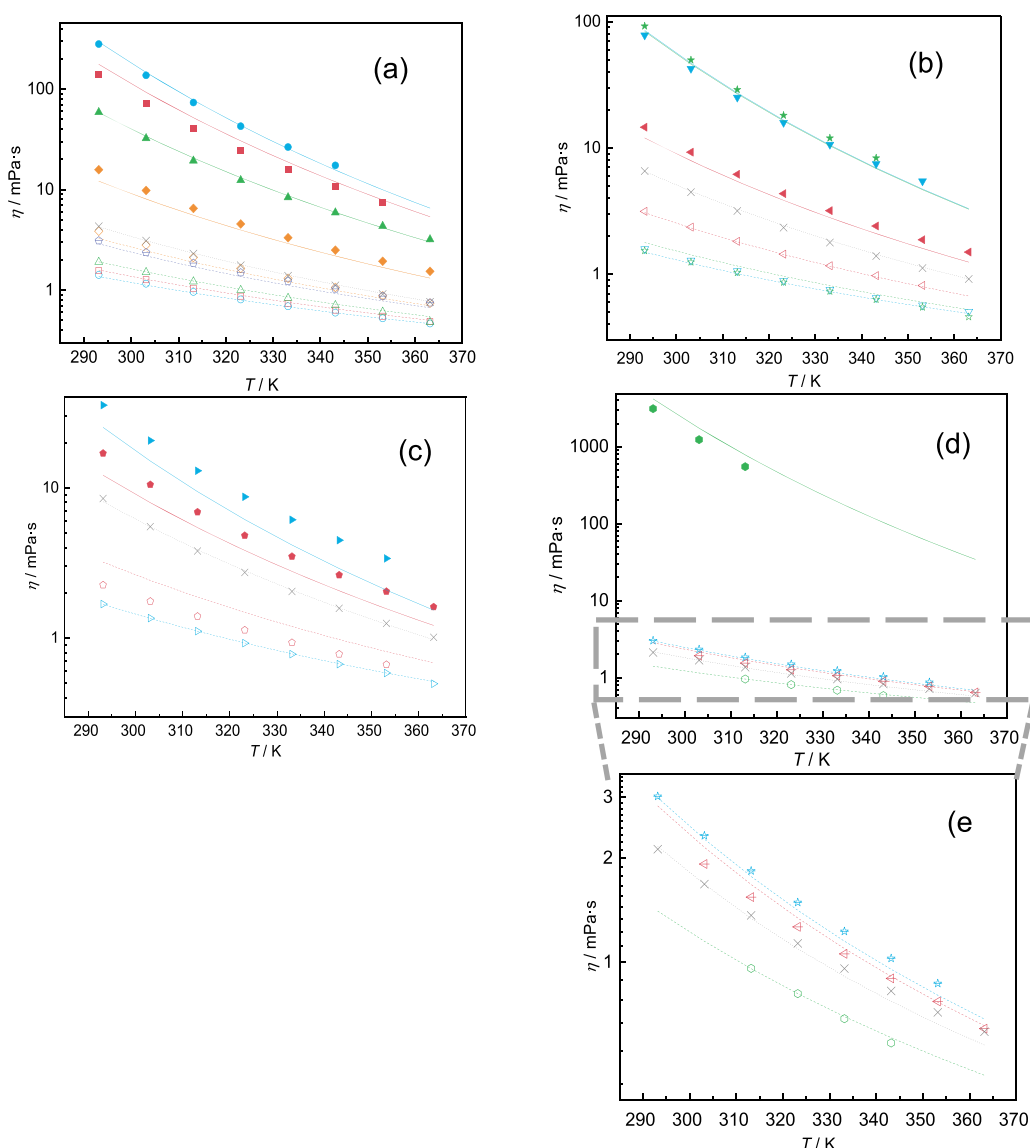
**4.2.2.2. Modeling of Pure Components.** As mentioned in Section 2.2, viscosities of pure EAE, DEGDEE, and carbamate were modeled based on eq 11, and that of pure water was modeled based on eq 12. The parameters and AARD values of these models are listed in Table 12.

**4.2.2.3. Viscosities of Binary Mixtures.** Figure 11 presents the experimental and calculated viscosities of binary systems. The models well replicate the viscosities of binary mixtures of EAE/water, EAE/DEGDEE, and EAE/carbamate. For mixtures of EAE and water (without DEGDEE), viscosities at all temperatures have the maxima at an approximately 0.8 weight fraction of EAE. According to Chowdhury et al.,<sup>34</sup> the more hydrophobic a compound is, the greater the viscosity maxima shift to the water-rich region. Comparing the viscosity maxima of MEA, EAE, and DMEA in aqueous solutions, they found that the viscosity peak of DMEA shifts more to the water-rich region than those of MEA and EAE. It is attributed to the dynamic characteristic of hydrophobic hydration.<sup>36</sup> Accompanied with the increase in the amount of the hydrophobic solute, the molecular mobility of water decreases. As a result, the viscosity of the solution increases. Therefore, the hydrophobic compounds have viscosity maxima shifted to the water-rich region. In our EAE aqueous solutions, since EAE is not so hydrophobic, the viscosity peaks were found at an approximately 0.8 weight fraction of EAE.

Table 13 lists parameters determined in viscosity modeling using the NRTL-DVIS equation for quaternary systems. The value of the  $R$  parameter is 3.808.

**4.2.3. Calculation Process.** **4.2.3.1. CO<sub>2</sub>-Unloaded Solutions.** Viscosities of CO<sub>2</sub>-unloaded EAE/DEGDEE/water mixtures at various weight bases were calculated and compared to experimental data (Figure 12). At the same temperature, the viscosity of pure solutions is EAE > DEGDEE > water. As a result, the increase of amine increases the viscosity of the mixture in solutions without water (mixtures of EAE/DEGDEE at 30/70 and 40/60 (weight basis)). This increase is more significant than the density increase of the same solutions. However, viscosities of solutions without water are lower than those with water. For EAE/DEGDEE/water mixtures at 30/40/30, 30/50/20, and 30/60/10 weight bases, the substitution of DEGDEE by water increases the viscosity of solution when the amount of EAE is kept constant. This is due to the formation of hydrogen bonds in solution. The AARDs for these CO<sub>2</sub>-unloaded solutions are 2.43%. Pinto et al. used this NRTL-DVIS model with their parameters to fit the water–amine–amine systems. Their average AARDs varied from 2.90 to 4.59%. Therefore, our AARD value is acceptable, which means that the NRTL-DVIS model is able to replicate well the viscosity of the CO<sub>2</sub>-unloaded solutions.

**4.2.3.2. CO<sub>2</sub>-Loaded Solutions.** The experimental and calculated viscosities of CO<sub>2</sub>-loaded mixtures of EAE/DEGDEE/water are presented in Figure 13. There is a decreasing tendency in viscosity as the loading decreases. Similarly to the density, the viscosity order is as rich phase > unloaded solutions > lean phase. However, the rich-phase viscosities increase remarkably as compared to those of the lean phase and unloaded solutions. Moreover, the increase in rich-

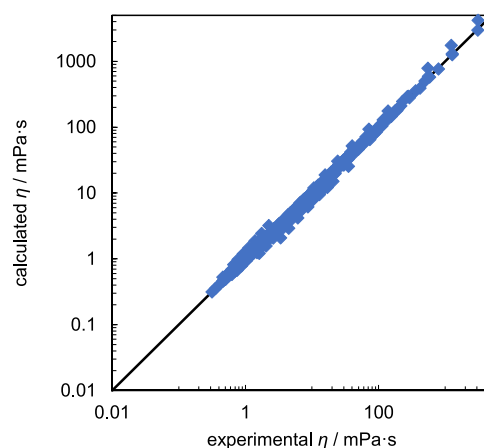


**Figure 13.** Viscosities of CO<sub>2</sub>-loaded mixtures of EAE/DEGDDE/water (weight basis): (a) 30/60/10, (b) 30/50/20, (c) 30/40/30, (d) 30/70, and (e) magnified viscosity plot of the lean phase of 30/70. Explanation: Marks and lines represent the experimental and calculated data, respectively. CO<sub>2</sub>-lean phases (empty marks and dashed lines), CO<sub>2</sub>-rich phases (filled marks and solid lines), and CO<sub>2</sub>-unloaded solutions (× and dotted lines). The rich phase and the lean phase of the same data set have similar marks.

**Table 14.** AARDs and Number of Data in NRTL-DVIS Modeling for Viscosities of EAE/DEGDDE/Water/Carbamate Mixtures

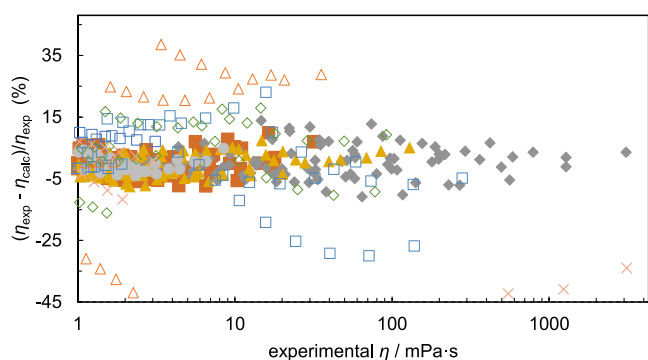
	<i>n</i>	AARD (%)
EAE/DEGDDE/water	131	2.04
EAE/water/carbamate	96	3.88
EAE/DEGDDE/carbamate	108	3.29
EAE/DEGDDE/water/carbamate	193	9.24

phase viscosity of mixtures without water (the rich phase in set D11 of the EAE/DEGDDE mixture, Figure 13d) is about 10 times of the rich phase at an approximate loading of water-containing solutions (the rich phase in set A1 of EAE/DEGDDE/water 30/60/10, Figure 13a). The higher weight fraction of carbamate in the former solution (0.913, compared to 0.728 of the latter) contributes to the increase in viscosity. However, water in the latter also reduces its viscosity. This observation is consistent with the conclusion of Machida et al.



**Figure 14.** Comparison between experimental and calculated viscosities for all systems.





**Figure 15.** Deviations  $(\eta_{\text{exp}} - \eta_{\text{calc}})/\eta_{\text{exp}}$  of experimental and calculated viscosities in relation with experimental viscosities in all solutions: EAE/DEGDDEE/water (solid squares), EAE/water/carbamate (solid diamonds), EAE/DEGDDEE/carbamate (solid triangles),  $\text{CO}_2$ -unloaded mixtures of EAE/DEGDDEE/water (solid circles), and  $\text{CO}_2$ -loaded mixtures of EAE/DEGDDEE/water (30/60/10 (open squares), 30/50/20 (open diamonds), 30/40/30 (open triangles), and 30/70 (x)).

that viscosity of  $\text{CO}_2$ -loaded amine/DEGDDEE mixtures was too high to mix the solution with a stirrer.<sup>7</sup> As water is present abundantly in 30/40/30 solutions, the bicarbonate product in eq 2 might be present, which causes the large deviation between calculation and experiments in this solution. However, the influence of water on viscosity is difficult to examine due to the difference in loadings of these solutions. As mentioned in Section 4.1.3, the B6 and B7 samples (both are rich phases) of EAE/DEGDDEE/water 30/50/20 solutions have similar component concentrations (Supporting Information Table S8). Therefore, their measured and calculated viscosities were superimposed to each other in Figure 13b (solid triangle and solid star marks).

The AARDs for all systems in viscosity modeling by using the NRTL-DVIS equation are listed in Table 14. Agreement between calculated and experimental viscosities is satisfactory in our model. This NRTL-DVIS viscosity model can be used to calculate the viscosity of quaternary systems as long as the concentrations of components are known.

The difference between experimental and calculated viscosity is visualized in Figure 14. Good agreement between calculated and experimental viscosity demonstrates the ability of the NRTL-DVIS model in calculating the viscosity of  $\text{CO}_2$ -unloaded and  $\text{CO}_2$ -loaded solutions within one equation with small numbers of parameters.

The deviation  $(\eta_{\text{exp}} - \eta_{\text{calc}})/\eta_{\text{exp}}$  (%) as a function of experimental viscosity was investigated and is presented in Figure 15. A large deviation appears at rich phases of EAE/DEGDDEE 30/70 (loading, 0.491) and EAE/DEGDDEE/water 30/40/30 (loading, 0.399) solutions. However, a reasonable deviation in other solutions confirms the feasibility of this model in viscosity calculation for quaternary systems.

As mentioned above, the model of Grunberg–Nissan is not recommended for aqueous solutions.<sup>18</sup> When applying the Grunberg–Nissan equation to our data, the ternary systems with water have AARD values of 19.08 (water/EAE/DEGDDEE mixture) and 24.08% (EAE/water/carbamate mixture) as compared to 5.46% of the ternary system without water (EAE/DEGDDEE/carbamate mixture). The AARD value in viscosity prediction for the quaternary solutions is 40.58%, which confirmed the conclusion of Poling et al.<sup>31</sup> The details on

the modeling of Grunberg–Nissan are provided in the Supporting Information (Section V).

## 5. CONCLUSIONS

Simple models in viscosity and density calculation for a phase separation solution before and after  $\text{CO}_2$  absorption were built based on ternary systems. These models can be applied to the mixture of EAE/DEGDDEE/water/carbamate with a given set of compositions as long as carbamate is the only product in the reaction between EAE and  $\text{CO}_2$ . The density model can replicate well the experimental data, and the deviation of the viscosity model is acceptable.

To our best knowledge, we have presented the first models to calculate viscosity and density for phase change solutions for carbon dioxide capture: the viscosity and density of solutions before and after absorption can be obtained within the same equation. The advantage of these models is that the calculations agree well with experimental data using a small number of parameters.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jced.1c00195>.

All data in this work used in calibration and calculation; viscosity and density comparison of pure EAE and DEGDDEE between those in the literature and those in this work; extrapolation of viscosity and density of pure carbamate; visualization of viscosity and density modeling of pure EAE, DEGDDEE, water, and carbamate; parity plots and AARDs of other viscosity and density models built based on our data (PDF)

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### Author Contributions

The manuscript was written with contributions of all authors. The final version of the manuscript was approved by all authors.

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## Notes

The authors declare no competing financial interest.

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