Thermal Decomposition and Nonisothermal Kinetics of Monoethanolamine Mixed with Various Metal Ions

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Ethanolamine is a critical chemical for petrochemical enterprises. When corrosion occurs in pipelines, equipment, and containers in petrochemical enterprises, minute amounts of metal ions are released. In this study, the thermal decomposition and nonisothermal kinetics of monoethanolamine (MEA) and MEA mixed with copper and zinc ions were analyzed using thermogravimetry (TG) and differential scanning calorimetry (DSC). The TG tests revealed that MEA mixed with copper (II) and zinc (II) began thermal decomposition at 75.2 and 60.3 °C, respectively, whereas pure MEA began thermal decomposition at 89.7 °C. Two exothermic peaks were observed in the DSC curves for MEA mixed with copper (II) and zinc (II), and thermokinetic parameters were obtained from DSC data. The apparent activation energy ($E_a$) of each stage was calculated using several nonisothermal kinetic methods, namely the ASTM E698, Kissinger–Akahira–Sunose, Starink, and Flynn–Wall–Ozawa methods. The $E_a$ of pure MEA was $28.7 \pm 2.5$ kJ/mol, whereas that of the copper and zinc mixtures were $80.5 \pm 1.1$ and $46.8 \pm 1.7$ kJ/mol, respectively. The results can be used to improve the intrinsic safety of storage tanks and petrochemical plants.

As a derivative of ethylene oxide, ethanolamine is a valuable product of amino alcohol consisting of monoethanolamine (MEA), diethanolamine (DEA), and triethanolamine (TEA). Ethanolamine may be used for a variety of applications, including use in the intermediates of pesticides1, medicines2, detergent emulsifiers, resins3, and rubber4. Ethanolamine may also be used in desulfurization processes to remove acid gas and in the decarburization designs of refineries5. Ethanolamine is colorless, viscous, volatile, unstable, easily oxidized, corrosive6, and may cause fire or explosions when exposed to potent oxidants, such as hydrogen peroxide in a heated container7. Thermal decomposition and combustion may occur during the preparation, transportation, or storage of ethanolamine because of temperature imbalance and heat accumulation. At a company in Taoyuan, Taiwan in 2007, a fire and explosion occurred in a storage tank area containing 17 tanks of chemicals. The raw chemical materials involved in the accident primarily comprised glacial acetic acid, propylene glycol methyl ether, diethylene glycol butyl ether, and MEA.

The petrochemical sector has begun to expand, and petrochemical facilities are connected by a multitude of pipelines. Common metal pipeline materials include copper, zinc, and iron8. Pipeline corrosion is a critical concern for petrochemical enterprises; long-term corrosion of pipelines may lead to leaks and ruptures. In such cases, fires or explosions will occur if a transported material is inflammable or explosive and encounters an effective ignition source. Additionally, pipeline corrosion releases metal ions with free radicals9, which causes catalytic decomposition reactions that play a critical role in chain reactions and result in exothermic events. Corroded pipelines have caused leakages, fires, and explosion accidents worldwide, resulting in considerable economic losses, negative social aftermath, and environmental hazards. The Kaohsiung gas explosion and Chevron refinery fire incident were caused by corroded pipelines and led to extensive economic, social, and environmental damages10.
Table 1. Kinetic methods used in this study.

| Method | Expression | Plot | References |
|--------|------------|------|------------|
| ASTM E698 | \( \ln \left( \frac{\beta}{\beta_p} \right) = \text{Const} - \frac{T_p - T}{\Delta H_p} \) | \( \ln \left( \frac{\beta}{\beta_p} \right) \) against \( \frac{1}{T} \) | 36 |
| KAS | \( \ln \left( \frac{\beta}{\beta_p} \right) = \ln \left( \frac{A \alpha}{f_{\alpha}(\alpha)} \right) - \frac{E}{RT} \) | \( \ln \left( \frac{\beta}{\beta_p} \right) \) against \( \frac{1}{T} \) | 36,37 |
| Starink | \( \ln \left( \frac{\beta}{\beta_p} \right) = C_{\alpha} - 1.0037 \ln \left( \frac{\beta}{\beta_p} \right) \) | \( \ln \left( \frac{\beta}{\beta_p} \right) \) against \( \frac{1}{T} \) | 36 |
| FWO | \( \log \beta = \ln \left( \frac{A \alpha}{f_{\alpha}(\alpha)} \right) - 2.315 - 0.4567 \ln \left( \frac{\beta}{\beta_p} \right) \) | \( \log \beta \) against \( \frac{1}{T} \) | 37 |

Generally, if corroded pipelines ethanolamine, the content of metal ions in the ethanolamine will increase gradually; the excess metal content then causes ethanolamine to foam and become unusable as a cleaning gas. Thus, the metal content of ethanolamine directly affects its quality and cost. More critically, this metal content provokes an incompatibility reaction, which induces advanced catalyzation of the material; consequently, the subsequent reaction cannot be controlled. Ávila6 investigated the thermal decomposition of MEA, DEA, TEA, and methyldiethanolamine (MDEA) and concluded that MEA exhibited the lowest thermal stability. In other studies, scholars11,22 have examined ethanolamine complexities using numerous methods, such as mixing ethanolamine with various oxidation states of vanadium. However, the thermal behavior of ethanolamine combined with metal ions has not been addressed in the literature; hence, the mechanism of metal ions in the thermal decomposition of ethanolamine should be determined.

The present study observed changes in the caloric value of MEA with the addition of various metal ions, namely copper (II) and zinc (II), by using thermogravimetry (TG), differential scanning calorimetry (DSC), and thermokinetic parameters, such as heat of decomposition (\( \Delta H_p \)), exothermic onset temperature (\( T_o \)), and peak temperature (\( T_m \))15–15, were obtained. The results revealed that the decomposition of MEA mixed with copper (II) and zinc (II) exhibited a reaction earlier than did the pure MEA. The apparent activation energy (\( E_a \)) of each stage was calculated using various thermokinetic models. The \( E_a \) of pure MEA was 28.7 \( \pm \) 2.5 kJ/mol, whereas that of the copper and zinc mixtures were 80.5 \( \pm \) 1.1 and 46.8 \( \pm \) 1.7 kJ/mol, respectively. The results of this study may serve as a reference for the preparation, application, usage, storage, and disposal of MEA, and could be used to minimize thermal risk and enhance the intrinsic safety of storage tanks in petrochemical plants.

**Experimental and Methods**

**Sample preparations.** MEA of 99 mass% purity was purchased from Acros Organics (Thermo Fisher Scientific Ltd., New Jersey, USA). The chemical formula of MEA is C2H7NO, and its Chemical Abstracts Service number is 141-43-5. Copper and zinc ions, which are common metallic materials used in pipelines, were separated from CuBr2 and ZnBr2 (provided by Alfa Aesar Ltd., Haverhill, MA, USA). To prevent deterioration, all samples were stored in a dry and dark place.

**TG experiments.** TG experiments were performed using a Perkin Elmer Pyris 1 thermogravimetric analyzer (Waltham, Massachusetts, USA) with a balanced furnace and vertical design. TG and differential TG (DTG) curves revealed variations in the mass loss and its derivative when the temperature was increased16,17. For pure MEA samples, the experimental temperature ranged from 30.0 to 300.0 °C and heating rates of 5.0, 10.0, 15.0, 20.0, and 25.0 °C/min were applied. In total, 10.0 mg of samples were used. Experiments using MEA mixed with CuBr2 and ZnBr2 were conducted at a heating rate of 10.0 °C/min within the temperature range of 30.0–650.0 °C. All samples were placed in a platinum crucible. Tests proceeded under an air atmosphere with 20.0 mL/min flow. Three sets of experiment were performed to ensure the reliability of the results and experimental methodology.

**DSC experiments.** Thermal analysis tests were performed using a Mettler Toledo DSC-821 (Mettler Toledo International Inc., Columbus, OH, USA). Because of its ease and efficiency of operation, DSC is the standard instrument used in conventional thermoanalysis18. A DSC analysis was conducted to generate thermal curves denoting the temperature ranges of exothermic and endothermic reactions. Heat-flow data could be obtained from the area of the reactions19. The DSC-821 has been calibrated of heating rate at 4.0 °C/min before the experiment. In this study, DSC experiments were performed at heating rates of 2.0, 4.0, 6.0, 8.0, and 10.0 °C/min, and the test temperature range was set at 30.0–400.0 °C. STAR software was used to establish thermokinetic models and obtain kinetic parameters20,21. The sample sizes of MEA, MEA mixed with CuBr2, and MEA mixed with ZnBr2 were approximately 7.0 mg in each experiment. The sample ratio was approximately 2:1.

**Nonisothermal kinetic methods.** The dynamic parameter \( E_a \) was calculated in the nonisothermal experiment, which was performed in a growing environment. Kinetic analysis generally involves model-free and model-fitting methods22. The model-free method, also termed the isoconversional method, enhances analysis accuracy by excluding kinetic model functions23–25. In this method, the reaction rate is assumed to be only a function of temperature, and \( E_a \) values are compared at different conversions to corroborate the consistency of the reaction mechanism throughout the process26. Kinetic methods are divided into differential and integral methods27. In this study, the ASTM E698, Kissinger–Akahira–Sunose (KAS), Starink, and Flynn–Wall–Ozawa (FWO) methods were selected as representative methods for dynamic analysis. Table 1 presents the nonisothermal
kinetic methods used for the present study and obtained from TG–DTG and DSC analysis to estimate the $E_a$. All of these methods were transformed using the nonisothermal kinetic equation, as presented in Eq. (1):

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right) \beta(\alpha)$$

The value of $E_a$ was calculated with the slope of a line respectively by using the equations of these four methods. In terms of Starink method, $\ln(\beta/T^{1.8})$ was plotted against $1/T$ with a slope of $-1.0037 E_a/RT$ to obtain $E_a$.

Results and Discussion

Thermogravimetric analysis through TG testing. Figure 1 illustrates the TG and DTG curves of MEA at 5.0, 10.0, 15.0, 20.0, and 25.0 °C/min heating rates in an air atmosphere. The TG curves revealed that a single stage mass loss was observed within the temperature range of 50.0–200.0 °C, and decomposition was initially quick compared with other substances because of the volatility of MEA. The TG and DTG curves exhibited sufficient consistency. By increasing the heating rate, the reaction of mass loss became more intense; furthermore, the initial decomposition temperature ($T_i$), maximum decomposition temperature ($T_m$), and final decomposition temperature ($T_f$) all increased, as did the rate of mass loss, which reached 7.4%/min at a heating rate of 25.0 °C/min. The decomposition of all heating rates was complete without residues before the temperature reached 200.0 °C.

The TG and DTG curves of MEA and MEA individually mixed with CuBr$_2$ and ZnBr$_2$ at a heating rate of 10.0 °C/min in an air atmosphere are presented in Fig. 2. As indicated in the diagram, the mass-loss process of MEA mixed with CuBr$_2$ consists of three stages. The first stage, which occurred between 50.0 and 230.0 °C with a mass loss of 78.3%, was attributed to the reaction of MEA and CuBr$_2$. The second stage, which occurred...
between 230.0 and 450.0 °C with a mass loss of 6.9%, represented the decomposition of the remaining CuBr₂.

The third stage, which occurred between 450.0 and 700.0 °C, resulted in the formation of 5.6% of residues and corresponded to the formation of CuO. For MEA mixed with ZnBr₂, the TG and DTG curves indicated two stages of mass loss. The first decomposition (30.0–200.0 °C) resulted in 60.0% mass loss and was caused by the reaction of MEA and ZnBr₂. The mass loss (40.0%) of the second decomposition (at 200.0–700.0 °C) was caused by the decomposition of the remaining ZnBr₂ without residues' formation.

The calculated values of TG and DTG for various stages of the three samples are presented in Table 2, including the characteristic temperature and mass loss of each stage. As evident in these data, the reaction rate of MEA increased after copper (II) and zinc (II) had been added, and $T_i$ and $T_m$ decreased in the first stage. As indicated in Table 2, the addition of zinc (II) ($T_i$ = 60.3 °C) catalyzed the reaction of MEA more quickly than did the addition of copper (II) ($T_i$ = 75.2 °C).

**Table 2.** TG–DTG analysis results of MEA mixed with CuBr₂ and MEA mixed with ZnBr₂.

| Samples     | Stage | Temperature range (°C) | $T_i$ (°C) | $T_m$ (°C) | $T_f$ (°C) | W (%) |
|-------------|-------|------------------------|------------|------------|------------|-------|
| MEA         | I     | 30.0–200.0             | 89.7       | 133.0      | 148.3      | 100.0 |
| MEA + CuBr₂ | I     | 30.0–220.0             | 75.2       | 103.0      | 229.2      | 78.3  |
|             | II    | 220.0–450.0            | 290.3      | 333.0      | 392.5      | 6.9   |
| MEA + ZnBr₂ | I     | 30.0–200.0             | 60.3       | 74.0       | 138.0      | 60.0  |
|             | II    | 200.0–700.0            | 360.9      | 433.3      | 667.0      | 40.0  |

**Figure 3.** DSC curves for MEA, MEA mixed with CuBr₂, and MEA mixed with ZnBr₂ at a heating rate of 8.0 °C/min.

**Thermodynamics of DSC tests.** The DSC curves of the three samples at a heating rate of 8.0 °C/min are displayed in Fig. 3. For MEA, exothermic and endothermic peaks were observed at 120.0 and 320.0 °C, respectively. The exothermic onset temperature ($T_o$) and maximum decomposition temperature ($T_p$) were 89.5 and 130.3 °C, respectively. $T_o$ can be defined by the intersection of a line drawn tangent to the steepest slope of the curve with the baseline; moreover, $T_p$ is the maximum exothermic temperature that can be achieved in the exothermic interval. The curves of MEA mixed with CuBr₂ and MEA mixed with ZnBr₂ produced two exothermic peaks at approximately 120.0 and 320.0 °C, respectively. The first peak indicated that advanced canalization occurred after the addition of CuBr₂ and ZnBr₂ to MEA. $T_o$ decreased to 79.2 and 69.6 °C, respectively, which is consistent with the results of the TG test, and $T_p$ decreased to 117.6 and 110.5 °C, respectively. $\Delta H_o$ was similar in the first peak for all three samples, namely 185.4, 199.6, and 151.6 J/g, respectively. For the second exothermic peak of MEA mixed with CuBr₂ and ZnBr₂, the respective values of $T_p$ were 322.8 and 316.7 °C. The peak may be considered representative of the thermal decomposition of the remaining bromide. In this test, the influence of Br⁻ in the decomposition of MEA could be disregarded because both metallic compounds contained negative ions.

Figure 4 displays the temperature–heat flow curves of MEA mixed with (a) CuBr₂ and (b) ZnBr₂ at heating rates of 2.0, 4.0, 6.0, 8.0, and 10.0 °C/min. The DSC curves exhibited similar trends. The exothermic intervals of the first and second peaks were 50.0–180.0 and 200.0–380.0 °C, respectively, and $T_o$ and $T_p$ were delayed as the heating rates increased. For MEA mixed with ZnBr₂ in the DSC experiments, regularity among $T_o$, $T_p$, and $\Delta H_o$ with the increasing heating rates in the first peak could not be confirmed, as indicated in Fig. 4(b). These results can be attributed to the water adsorption of ZnBr₂, which rendered the initial reaction unstable. However, the values of $\Delta H_o$ in the second peak at different heating rates were between 99.5 and 124.7 J/g. For MEA mixed with CuBr₂, the $\Delta H_o$ results of the first and second peaks at five heating rates were 187.4–237.8 and 373.6–471.9 J/g, respectively. All thermokinetic parameter results are listed in Table 3.
Calculations and comparison of $E_a$. $E_a$ is a crucial kinetic parameter for evaluating the reactability of a substance. To further explore the effects of adding copper (II) and zinc (II) on the thermal stability of MEA, various nonisothermal kinetic methods were used to analyze the exothermic peaks in the DSC tests. $E_a$ results were calculated for MEA and MEA mixtures at each experimental stage.

The ASTM E698 was first used to calculate the $E_a$ of each set of experiments. Figure 5 displays the plots of $\beta T$ versus $1/T_p$ for the four exothermic peaks according to the ASTM E698 method. The $E_a$ results for the first and second peaks of MEA mixed with CuBr$_2$ were 30.3 and 115.6 kJ/mol, and those for MEA mixed with ZnBr$_2$ were 31.5 and 113.7 kJ/mol.

Table 3. Thermodynamic data from the DSC curves of MEA mixed with CuBr$_2$ and MEA mixed with ZnBr$_2$ at heating rates of 2.0, 4.0, 6.0, 8.0, and 10.0 °C/min.

| Samples       | $\beta$ (°C/min) | Mass (mg) | $T_{01}$ (°C) | $T_{p1}$ (°C) | $\Delta H_{d1}$ (J/g) | $T_{02}$ (°C) | $T_{p2}$ (°C) | $\Delta H_{d2}$ (J/g) |
|---------------|------------------|-----------|----------------|----------------|-----------------------|----------------|----------------|------------------------|
| MEA + CuBr$_2$| 2.0              | 6.58      | 54.8           | 85.3           | 195.5                 | 273.0          | 291.0          | 406.0                  |
|               | 4.0              | 6.85      | 70.2           | 101.2          | 187.4                 | 278.0          | 308.6          | 471.9                  |
|               | 6.0              | 6.93      | 78.3           | 111.4          | 203.4                 | 281.0          | 315.3          | 373.6                  |
|               | 8.0              | 6.87      | 79.2           | 117.6          | 199.6                 | 285.1          | 322.1          | 419.2                  |
|               | 10.0             | 6.67      | 86.0           | 133.7          | 206.6                 | 287.3          | 326.8          | 419.6                  |
| MEA + ZnBr$_2$| 2.0              | 7.30      | 64.7           | 74.5           | 78.2                  | 263.0          | 289.0          | 99.5                   |
|               | 4.0              | 7.85      | 66.1           | 96.8           | 101.2                 | 272.5          | 301.7          | 124.76                |
|               | 6.0              | 7.41      | 68.6           | 96.5           | 117.2                 | 280.6          | 311.9          | 113.16                 |
|               | 8.0              | 7.52      | 69.6           | 110.4          | 151.5                 | 287.3          | 316.7          | 119.21                 |
|               | 10.0             | 7.21      | 71.5           | 106.5          | 97.1                  | 292.5          | 324.7          | 113.78                 |

Figure 4. DSC curves for MEA mixed with (a) CuBr$_2$ and (b) ZnBr$_2$ at heating rates of 2.0, 4.0, 6.0, 8.0, and 10.0 °C/min.
ZnBr$_2$ were 42.1 and 116.9 kJ/mol, respectively. However, the ASTM E698 method could not be used to reveal the overall trend of $E_a$ at each conversion. The values for $E_a$ acquired using the ASTM E698 method were slightly inaccurate for these experiments because of the basic assumptions of the method. Subsequently, the KAS, Starink, and FWO methods were used for different conversions. The DSC curve exhibited artificiality in baseline.

Figure 5. Plots of $\ln(\beta T^2)$ versus $1/T$ for MEA mixed CuBr$_2$ and MEA mixed with ZnBr$_2$ for four exothermal peaks calculated using the ASTM E698 method.

Figure 6. Plots of log$\beta$ versus $1/T$ for the first peak of MEA mixed with ZnBr$_2$ determined using the KAS, Starink, and FWO methods at different conversions.

| Conversion ($\alpha$) | 1st Peak |          |          | 2nd Peak |          |          |
|----------------------|----------|----------|----------|----------|----------|----------|
|                      | KAS      | Starink  | FWO      | KAS      | Starink  | FWO      |
|                      | $E_a$ (kJ/mol) | $R^2$ | $E_a$ (kJ/mol) | $R^2$ | $E_a$ (kJ/mol) | $R^2$ | $E_a$ (kJ/mol) | $R^2$ |
| 0.1                  | 50.9     | 0.689    | 51.3     | 0.694    | 54.0     | 0.737    | 143.4    | 0.978    | 143.7    | 0.978    | 144.7    | 0.980    |
| 0.2                  | 50.7     | 0.748    | 51.1     | 0.753    | 54.0     | 0.791    | 127.0    | 0.998    | 127.5    | 0.997    | 129.5    | 0.998    |
| 0.3                  | 56.7     | 0.810    | 57.1     | 0.814    | 59.7     | 0.842    | 122.1    | 0.994    | 122.6    | 0.994    | 125.0    | 0.995    |
| 0.4                  | 64.4     | 0.805    | 64.8     | 0.809    | 67.2     | 0.834    | 121.2    | 0.992    | 121.7    | 0.993    | 124.3    | 0.994    |
| 0.5                  | 72.6     | 0.748    | 73.4     | 0.758    | 75.6     | 0.787    | 123.0    | 0.992    | 123.5    | 0.992    | 126.1    | 0.993    |
| 0.6                  | 86.7     | 0.733    | 87.0     | 0.736    | 88.6     | 0.762    | 125.6    | 0.992    | 126.1    | 0.992    | 128.6    | 0.993    |
| 0.7                  | 116.4    | 0.788    | 116.5    | 0.790    | 116.9    | 0.807    | 130.2    | 0.991    | 130.7    | 0.991    | 133.1    | 0.992    |
| 0.8                  | 172.8    | 0.842    | 172.9    | 0.844    | 170.8    | 0.853    | 142.8    | 0.984    | 143.7    | 0.984    | 145.3    | 0.986    |
| 0.9                  | 190.7    | 0.897    | 190.7    | 0.898    | 188.0    | 0.904    | 167.7    | 0.963    | 168.1    | 0.963    | 169.2    | 0.967    |
| Mean                 | 79.4     | 0.777    | 79.8     | 0.781    | 81.6     | 0.806    | 124.4    | 0.992    | 124.9    | 0.992    | 127.4    | 0.993    |
| Standard deviation   | 21.0     | 0.031    | 20.9     | 0.030    | 20.1     | 0.030    | 3.2      | 0.001    | 3.2      | 0.001    | 3.2      | 0.001    |

Table 4. $E_a$ for MEA mixed with CuBr$_2$, calculated using the KAS, Starink, and FWO methods at different conversions.
Therefore, the conversion at the interval of \( \alpha \) between 0.1 and 0.9 was selected for the kinetic analysis.

For the KAS, Starink, and FWO methods, general trends in \( E_a \) values can be identified at different conversions.

Plots for the first peak of MEA mixed with ZnBr\(_2\) obtained using these three methods at different conversions are displayed in Fig. 6; the fitting plots deviated substantially at the conversions of 0.1–0.2 and 0.8–0.9.

**Table 5.** \( E_a \) for MEA mixed with ZnBr\(_2\), calculated using the KAS, Starink, and FWO methods at different conversions.

| Conversion (\( \alpha \)) | KAS \( E_a \) (kJ/mol) | \( R^2 \) | KAS \( E_a \) (kJ/mol) | \( R^2 \) | KAS \( E_a \) (kJ/mol) | \( R^2 \) |
|--------------------------|-------------------------|---------|-------------------------|---------|-------------------------|---------|
| 0.1                      | 51.6                    | 0.903   | 52.1                    | 0.905   | 54.5                    | 0.920   |
| 0.2                      | 47.7                    | 0.939   | 46.6                    | 0.941   | 50.8                    | 0.951   |
| 0.3                      | 47.3                    | 0.936   | 47.8                    | 0.937   | 50.6                    | 0.949   |
| 0.4                      | 46.3                    | 0.948   | 46.7                    | 0.950   | 49.7                    | 0.959   |
| 0.5                      | 45.6                    | 0.971   | 45.5                    | 0.965   | 48.6                    | 0.972   |
| 0.6                      | 43.4                    | 0.978   | 43.9                    | 0.979   | 47.2                    | 0.983   |
| 0.7                      | 42.7                    | 0.989   | 43.2                    | 0.989   | 46.6                    | 0.992   |
| 0.8                      | 47.8                    | 0.955   | 46.8                    | 0.956   | 51.6                    | 0.965   |
| 0.9                      | 41.4                    | 0.358   | 40.6                    | 0.369   | 45.8                    | 0.456   |
| Mean                     | 45.1                    | 0.964   | 45.4                    | 0.964   | 48.5                    | 0.971   |

**Figure 7.** Variation of \( E_a \) at different conversions for (a) MEA mixed with CuBr\(_2\) and (b) MEA mixed with ZnBr\(_2\).
Conversion of 0.3–0.7, the fitting plots were nearly parallel. Accordingly, the average of $E_a$ was calculated within the interval of 0.3–0.7, as suggested in relevant studies [26, 29]. The plots of other peaks that are not displayed in Fig. 6 were similar to this figure after fitting. $E_a$ was readily calculated at different conversions using the slope of the curves in Fig. 6. Tables 4 and 5 list the $E_a$ of MEA mixed with CuBr$_2$ and ZnBr$_2$ at different conversions. The variation of $E_a$ at different conversions for these four exothermic peaks according to the KAS, Starink, and FWO methods is represented in Fig. 7. Similar results for $E_a$ were obtained with the KAS and Starink methods, whereas the FWO method yielded a slightly higher $E_a$ value.

Table 6 summarizes the calculated results of $E_a$ and $R^2$ for each nonisothermal method. The $E_a$ of pure MEA was 28.7 ± 2.5 kJ/mol, which is lower than the value indicated in related studies [6]. For MEA mixed with CuBr$_2$, the $E_a$ of the first peak was 80.5 ± 1.1 kJ/mol, suggesting that the $E_a$ of the mixture was higher than that of pure MEA. The data listed in Table 6, along with the curves delineated in Fig. 7, demonstrate that the $E_a$ increased with conversion; this was likely because of a chemical reaction and the formation of a copper-alkanolamine complex [30]. The calculated value of $E_a$ in the second stage was 125.9 ± 1.5 kJ/mol, which was slightly higher than the value reported in a relevant study [31]. This value may be attributable to the decomposition of the remaining CuBr$_2$. For MEA mixed with ZnBr$_2$, the $E_a$ values of the first and second peaks were 46.8 ± 1.7 and 113.6 ± 1.9 kJ/mol, respectively. As indicated by the $R^2$ values in Table 6, the FWO method was superior to other methods regarding the analysis of pure MEA and MEA mixtures and is widely used in thermokinetics analysis [32].

### Conclusions

In this study, the thermal decomposition and nonisothermal kinetics of pure MEA and MEA mixed with copper (II) and zinc (II) were illustrated using TG and DSC. In the TG tests, the thermal decomposition of MEA mixed with CuBr$_2$ and ZnBr$_2$ began at 75.2 and 60.3 °C, respectively; all mixtures produced prior decomposition reactions compared with pure MEA (89.7 °C).

In the DSC analysis, two exothermic peaks were observed after the addition of CuBr$_2$ and ZnBr$_2$ to MEA. Although no notable change in $\Delta H_2$ occurred, $T_c$, decomposed early at 79.2 and 69.6 °C in the copper and zinc mixtures, respectively. These results suggested that metal ions may provoke early reactions during the manufacturing process. These advanced reactions may lead to thermal decomposition of the material of interest at low temperatures, resulting in thermal hazards. Moreover, nonisothermal methods, namely the ASTM E698, KAS, Starink, and FWO methods, were used to analyze the decomposition kinetics of MEA and MEA mixtures. The fitting was insufficient in a single conversion compared with the $R^2$ in different conversions. The $E_a$ of pure MEA was 28.7 ± 2.5 kJ/mol. The $E_a$ results of the copper and zinc mixtures were 80.5 ± 1.1 and 46.8 ± 1.7 kJ/mol, respectively. Chemical reactions caused by the addition of metal ions resulted in these results of higher $E_a$ for the mixtures.

Ethanolamine is widely used in petrochemical industries, and the operation of such enterprises involves numerous unsafe processes. Because of the advanced reactions of metal ions to ethanolamine, corroded pipelines and equipment should be promptly replaced to reduce the likelihood of chemical disasters and ensure plant safety.

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Author Contributions

Mengning Wei and An-Chi Huang performed the analysis, contributed the literature research, and wrote the paper; Chi-Min Shu and Lijing Zhang conceived the research theme and edited the paper.

Additional Information

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