

Estimation on Autocatalytic Reaction for Ethanolamine – A Green Approach

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ABSTRACT

Ethanolamine, which is a derivative of ethylene oxide, is not only a major material in organic chemicals but is also the most valued product among amino alcohols. However, ethanolamine might catch fire automatically when mixed with peroxide or nitrocellulose due to its thermal instability and high sensitivity to thermal sources. Runaway reactions because of ethanolamine will lead to severe damage to equipment, people, the environment, and create a social impact. Therefore, it is necessary to provide thermal safety information regarding the decomposed mechanism and thermal hazard characteristics by using thermal analysis technology. As a green approach, our aim was to determine thermal safety parameters, such as apparent exothermic onset temperature, maximum temperature, heat of decomposition, self-heating rate, pressure rise rate, maximum pressure, by differential scanning calorimetry. The results can be used to calculate the optimal parameters for processing a safer design and establish the database of ethanolamine for proactive loss prevention protocol.

Keywords: derivative of ethylene oxide; organic chemicals; thermal safety information; decomposed mechanism; thermal analysis technology

1 Introduction

Ethanolamine is the most common product of ethylene oxide derivative which is widely used in the chemical industry, such as insecticides, intermediates of medicine, softening agent of synthetic fiber, dye stuff of dispersant and resin in recent decades. On a worldwide scale, ethanolamine is produced as approximately 1.3 million metric tons per year, and the output keeps increasing yearly [1]. Without a doubt, ethanolamine instability property and detrimental effects do still exist in usage, storage, and transporting of ethanolamine. Ethanolamine will have an obvious reaction with fire automatically when combined with peroxide [2].

In a chemical reaction, a catalyst is a substance that can keep its composition and quality but alter the rate of reaction. Autocatalysis is the product of a reaction that can increase its rate of reaction: the product of a reaction can play a catalytic role [3]. The typical graph of an autocatalysis reaction shows double bend curve. Since there

is very little catalyst at the beginning, the reaction carries on very slowly. As catalyst increases, the rate of reaction increases until the density of reactant decreases. The classic autocatalytic system is shown as the following:

$$\frac{du(t)}{dt} = a - u(t)v^p(t), \quad t > 0 \quad (1)$$

$$\frac{dv(t)}{dt} = u(t)v^p(t) - v(t), \quad t > 0 \quad (2)$$

$$u(0) = u_0 > 0, \quad v(0) = v_0 > 0 \quad (3)$$

where a is original concentration of the reaction precursor, u is the densities of the reactant, v is autocatalyst [4].

There are two sides to every question. Despite the fact that ethanolamine was thought of as a kind of most common material to be used, the thermal hazard risk needs to be considered when it is used. Thus, to stress safety concerns, our task was to estimate the autocatalytic reaction for ethanolamine. To determine the possible potential hazard of ethanolamine, metal ion was added with ethanolamine in the experiment.

In this study, we used differential scanning calorimetry (DSC) to determine the thermokinetic model and DSC curve of ethanolamine and ethanolamine with metal ion. DSC is a highly trustworthy option as a powerful thermoanalytical technique for determining the thermokinetic data [5,6]. The primary questions that we addressed are as follows: enthalpy (ΔH_d), exothermic onset temperature (T_0), and peak temperature (T_{max}). The goal is to contribute to the decrease of hazard from the usage, storage, and transportation of ethanolamine as much as possible.

2 Experiments and methods

2.1 Material

Ethanolamine (99 mass%), which was used for testing analysis and without further purification, was purchased from Acros Organics, Thermo Fisher Scientific, New Jersey, USA. With regard to incompatibility trials, FeO_2 (98 mass%) and CuO_2 (99 mass%), that were offered from Showa Kako Corporation, Suita-shi, Osaka, Japan, were used together with ethanolamine separately. All chemicals were stored in medicine cabinets which are shady and cool [1,7]. The structure of ethanolamine is shown in Figure 1.



Figure 1: Structure of ethanolamine [1,7].

2.2 DSC

The thermal analysis data were measured by using a Mettler Toledo DSC-821 with nitrogen-gas atmosphere. All experiment samples were encapsulated in stainless steel aluminum pans which were placed in a test crucible that can sustain temperature up to 720.0 °C. The system of this model was tested to be capable of experiments under pressures of 100 bar [8]. Analysis of experiments was carried out by Thermal Analysis System Software to obtain thermokinetic data. The scanning rates, which were used to detect significant difference among samples, were selected for analyzing programmed ramp consisting 0.5, 1.0, 2.0, 4.0, and 8.0 °C min⁻¹. All samples, which were placed in airtight aluminum pans, were heated from 30.0 to 300.0 °C. The selected temperature range was determined by a thermal cracking test from Thermogravimetry (TG) which has the ability to investigate the thermal cracking of materials [9]. Three times of reproducibility were represented by each experiment to reconfirm the authenticity of samples.

2.3 Thermokinetic analysis

To determine the thermokinetic parameters of ethanolamine by non-isothermal kinetic model, the type of reaction must be checked and examined. Two reaction types were found regularly: Autocatalysis and *n*th order reactions. In general, an *n*th order reaction is one where a reactant reaches maximum heat flow in the initial stage or in few minutes. At this time, the exothermic output is not only the maximum but also the most dangerous moment. From another aspect, autocatalysis means the runaway reaction was suddenly brought out by the stage that the reactant received a term of calorific capacity. An *n*th order can be calculated by Arrhenius equation as shown in Eq (4).

$$k = Ae^{-E_a/RT} \quad (4)$$

where k_0 is frequency factor of reactant, E_a is activation energy, R is gas constant, T is absolute temperature. According to the Arrhenius equation, activation energy can be determined and expressed as in Eq (5).

$$k = k_0 \exp\left(\frac{-E_a}{RT}\right) \quad (5)$$

When the relation between logarithm of k combine and T^{-1} is relatively a straight line, it shows that this function fits Arrhenius behavior. The slope of this line is $-E_a R^{-1}$.

$$\frac{d\alpha}{dt} = k_0 \exp\left(\frac{-E_a}{RT}\right) (1 - \alpha)^n \quad (6)$$

Autocatalysis reaction can be expressed in Eq (6).

$$f(\alpha) = (1 - \alpha)^{n_1} (\alpha^{n_2} + z) \quad (7)$$

To acquire the E_a and k_0 of autocatalysis reaction, the autocatalysis reaction equation and Arrhenius equation are combined.

3 Results and discussion

Thermal analysis of ethanolamine with different metal oxides was carried out in DSC. Random sampling was adopted in all experiments to determine the sequence of all samples to avoid unexpected factors that may cause inaccuracy. To discriminate between the exothermic reactions of ethanolamine, ethanolamine with Fe₂O₃, and ethanolamine with CuO, experiments were designed for pure substance and substances with metal ions. The DSC tests involved ethanolamine, ethanolamine with Fe₂O₃, and ethanolamine with CuO at a heating rate of 4.0 °C min⁻¹. Of the three experiments, ethanolamine with CuO had a protruding curve compared to the exothermic reaction test of ethanolamine and ethanolamine with Fe₂O₃, as shown in Figure 2.

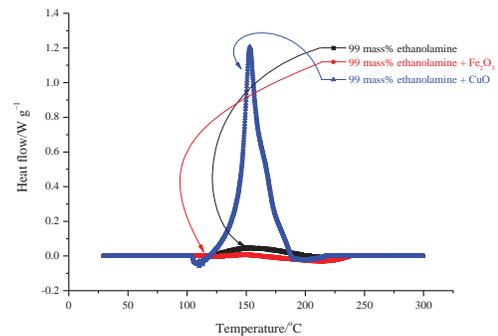


Figure 2: DSC thermal curve of temperature versus heat flow for 99 mass% ethanolamine and ethanolamine mixed with Fe₂O₃ and CuO at heating rate of 4.0 °C min⁻¹.

In this case, the reaction of ethanolamine mixed with CuO was not only presented in comparison to pure ethanolamine, but also the maximum heat flow displayed obviously. With regard to that there was no reaction in pure materials, CuO was confirmed as being an incompatible substance for ethanolamine. This may suggest that enormous heat will be generated when ethanolamine is mixed with CuO during process, usage, transportation, machining, or storage. Table 1 presents the onset temperature of ethanolamine mixed with CuO being higher than the other two groups of experiments, but the end set temperature was lower than others. The findings showed that when ethanolamine was mixed with CuO, the stage of amassing energy was accumulated in a longer period and released in a short time.

Table 1: Thermal stability data from the non-isothermal heating experiments with 99 mass% ethanolamine and ethanolamine mixed with Fe₂O₃ and CuO at a heating rate of 4.0 °C min⁻¹.

Sample	Mass/mg	$T_0/^\circ\text{C}$	$T_p/^\circ\text{C}$	$T_f/^\circ\text{C}$	$\Delta H_d / \text{J g}^{-1}$
Ethanolamine	3.93	134.05	150.95	229.78	31.40
Ethanolamine + Fe ₂ O ₃	4.62	135.11	146.08	178.92	4.99

Ethanolamine + CuO	3.59	143.81	153.02	165.89	395.19
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Table 2: Thermal stability data from the non-isothermal heating experiments with 99 mass% ethanolamine mixed with CuO of heating rate at 0.5, 1.0, 2.0, 4.0, and 8.0 °C min⁻¹.

Heating rate /°Cmin ⁻¹	T ₀ /°C	T _p /°C	T _f /°C	ΔH _d /J g ⁻¹
0.5	132.21	132.27	132.28	178.43
1.0	123.55	136.39	146.37	157.42
2.0	137.60	144.98	153.62	379.00
4.0	143.81	153.02	165.89	395.19
8.0	158.73	170.02	187.57	285.07

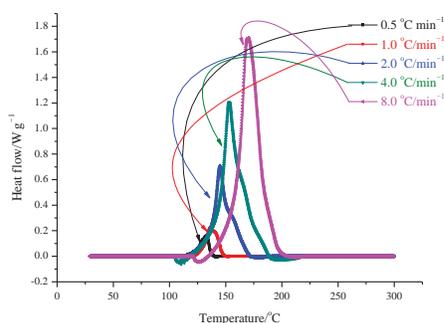


Figure 3: DSC thermal curve of temperature versus heat flow with 99 mass% ethanolamine and ethanolamine mixed with CuO at heating rates of 0.5, 1.0, 2.0, 4.0, and 8.0 °C min⁻¹.

Considering the different situations in reality, ethanolamine mixed with CuO was investigated at a heating rate of 0.5, 1.0, 2.0, 4.0, and 8.0 °C min⁻¹. With higher heating rate, the maximum temperature and end set temperature of reaction within ethanolamine mixed with CuO are also higher, as listed in Table 2. Figure 3 shows that heat flow is getting higher and exothermic onset temperature is getting later with higher heating rate on DSC. Most importantly, the maximum heat flow of 0.5 and 8.0 °C min⁻¹ is 1.71 W g⁻¹ and 0.16 W g⁻¹ respectively. That is, there is an approximately ten-fold gap between the heat flow reasonably at heating rates of 0.5 and 8.0 °C min⁻¹.

As mentioned above, E_a was calculated by taking test methods from the American Society for Testing and Materials E698-5 in this study [10]. This conversional rate equation is expressed in Eq (8).

$$\frac{d\alpha}{dt} = Ae^{-E_a/RT} f(\alpha) \quad (8)$$

To confirm the credibility of the thermokinetic model that we simulated, linear regression was adopted to provide R-square, as shown in Figure 4. The findings of Figure 4 show that there is an excellent relationship within the experiments. E_a and A are determined by the slope and intercept. E_a is 98.695 kJ mol⁻¹, and R-square is high to

0.933.

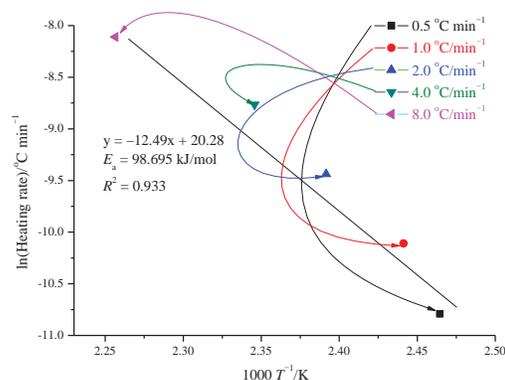


Figure 4: Apparent activation energy calculation with 99 mass% ethanolamine mixed with CuO.

In this study, we used differential isoconversional methods to assess thermokinetic parameters of reaction [10]. Equation 9 shows a differential isoconversional method, which is used to calculate E_a and A , is often seen.

$$\ln \frac{d\alpha}{dt} = \ln[A(\alpha)f(\alpha)] - \left(\frac{E(\alpha)}{RT(t)}\right) \quad (9)$$

The relationship between reaction progress versus $E(\alpha)$ and reaction progress versus $\ln[A(\alpha)f(\alpha)]$ is shown in Figure 5.

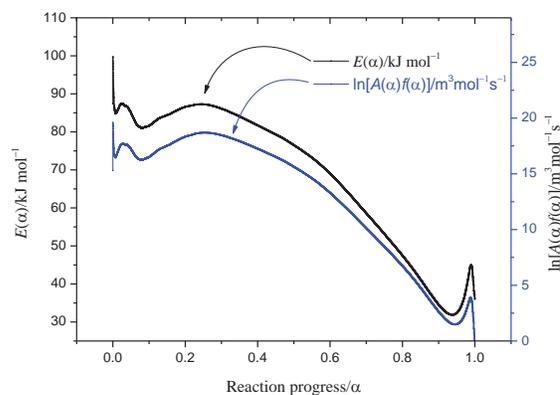


Figure 5: Apparent activation energy with degree of conversion and pre-exponential factor with degree of conversion with reaction progress from 99 mass% ethanolamine mixed with CuO.

For the reaction stage in this case, the active range of α presents decreasing curves mainly. It shows that autocatalytic reaction happening with $E(\alpha)$ is presenting a decreasing curve. According to observations, the curves of reaction progress versus with $E(\alpha)$ and reaction progress versus $\ln[A(\alpha)f(\alpha)]$ are almost perfectly coinciding.

Moreover, $SADT$ was investigated in this study in different mass. As observed, the curve of $SADT$ and mass of ethanolamine mixed with CuO presents an inverse ratio, as shown in Figure 6. That is, the thermal stability of a lower mass, such as 50.0 kg, is better than the higher one.

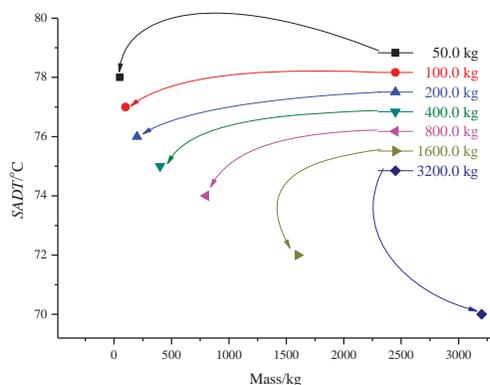


Figure 6: Simulation results on mass versus *SADT* of 99% mass% ethanolamine mixed with CuO.

4 Conclusions

This study showed that CuO is an incompatible metal material for ethanolamine. More specifically, ethanolamine is more likely to cause hazard when mixed with CuO which normally exists in industrial places. Therefore, it is necessary to choose a container or pipe with proper material of chemical property to avoid being rusty. To practice the process under upset scenarios, we can apply the thermokinetic data, which are ΔH_d , T_0 , T_{max} , and *SADT*, that were obtained by thermal calorimetric technology and thermokinetic technology. Estimation of autocatalytic reaction by using the thermal analysis technology is fast, safe, exact, and a highly trustworthy method for the thermal stability of substance. Hence, the findings of this study can provide a better way for managing safety procedures.

5 Acknowledgments

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