Mixing hazard evaluation using small-scale Dewar vessels

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Abstract In mixing hazard evaluations, a smaller scale is preferred for safety reasons and in order to conserve the samples. We have developed a small-scale Dewar vessel test (SDVT) that measures the amount of heat from a temperature change upon the mixing of two chemicals. In general, the accuracy of small-scale tests is negatively impacted by heat loss. The purpose of this study is to establish experimental conditions and to validate the reproducibility and accuracy of our small-scale test. The adjustable experimental parameters for SDVT are: position of sample injection, amount of sample, stirring speed, and surrounding temperature. These conditions were optimized for the measurement of the heat of neutralization of hydrochloric acid and sodium hydroxide. Under the optimized experimental conditions, the reproducibility was validated by measurement of the heat of hydration between acetic acid anhydride and water. The relative standard deviation of the maximum temperature change was 3.1%. To validate the accuracy, the heat of reaction between the neutralization reaction and hydration reaction was calculated. The heat of reaction was in good agreement with the theoretical value. Thus, the SDVT has sufficient accuracy and reproducibility to serve as a screening method for the mixing hazard of chemicals.

Keywords: Mixing hazard evaluation, Screening method, Small-scale Dewar vessel test

Introduction

Unexpected chemical reactions triggered by the mixing of chemicals may occur in chemical processes [1]. Such mixing may cause runaway reactions leading to the destruction of equipment [2]. In order to prevent such accidents, it is necessary to understand the hazards of mixing chemicals using the mixing hazard evaluation method. In general, thermal hazard is usually evaluated with milligram or gram scale sample using heat flow calorimeter [3, 4] or accelerating rate calorimeter [5]. In mixing hazard evaluation, screening tests are conducted by observing bubble generation and measuring the temperature rise using a test-tube or beaker [6]. The feasibility of mixing is determined by criteria such as bubble generation, temperature rise and heat value. These tests may underestimate mixing hazards due to adiabatic heat loss. In typical mixing hazard evaluations, reaction calorimeters (RC-1) or small reaction calorimeters (Super CRC) are used [7-11]. RC-1 and Super CRC are often utilized for safety predictions and the determination of the optimal conditions of chemical processes [12-14]. The mixing hazard is evaluated by measuring the heat value. However, these methods are relatively expensive and require complicated operations.

Despite its simple structure, the Dewar vessel is a strong tool to investigate mixing hazards due to its high adiabaticity. The Dewar vessel test is specified in the United Nations Recommendations on the transport of dangerous goods [15]. It is also used for thermal hazard evaluations such as to determine self-accelerating decomposition temperature [16-24]. In addition, Dewar vessels are used for various thermal hazard evaluations [25-29]. Since the current Dewar vessel test uses a large volume vessel (500 mL-1.5 L), there are risks of toxic gas release along with thermal runaway during measurement. Furthermore, when the amount of sample is large, it becomes prohibitive to measure expensive samples. Thus, we have developed a small-scale Dewar vessel test (SDVT) with the same volume as the test-tube test (40 mL). The use of the SDVT must be helpful for reducing the cost and thermal risk compared to use of UN Dewar vessel, because the SDVT needs much less sample-size than the UN Dewar vessel. The simpler method is the more desirable for safety measurement for the mixing hazard. The test-tube test and the beaker test are known and widely used as the simplest test for mixing hazard. However, due to poor heat-insulation, they may not be adequate to assess the heat of reaction from the temperature change upon the mixing of two chemicals. The SDVT has an advantage in the heat-insulation comparing the test-tube test and the beaker test. Thus, the SDVT has great potential to alternate the UN Dewar vessel test, the test-tube test, and the beaker test. For wide use of the SDVT, the optimal experimental conditions and accuracy of SDVT must be demonstrated.

The purposes of this study are to optimize the experimental conditions, to validate the accuracy and reproducibility of SDVT, and to compare SDVT with the test-tube test. The experimentally adjustable parameters of SDVT are the position of the sample injection, the amount of sample, the stirring speed, and the surrounding temperature. These conditions are optimized using the temperature change of the heat of neutralization. To validate the reproducibility of SDVT, the relative standard deviation is determined by the maximum temperature change of the heat of the hydration reaction under the defined experimental conditions. To validate the accuracy of the SDVT, the measurement of the heat of neutralization and hydration is employed. The heat of reaction is calculated from the amount of heat dissipation. The heat dissipation is corrected by fitting using the least squares method and by a method of time integrating the difference between the temperatures of the sample and the air in the Dewar vessel. Finally, the utility of SDVT is validated by comparison with the results of the test-tube test.

Experimental

Materials

Commercially available hydrochloric acid (HCl, 0.5 mol L^{-1}) and sodium hydroxide (NaOH, 0.5 mol L^{-1}) were obtained from Wako Chemicals, and acetic acid anhydride ($(CH_3CO)_2O$, 97 %) was obtained from Kanto Chemical.

Experimental apparatus

The screening apparatus for mixing hazards using the small-scale Dewar vessel (volume: 40 mL; height: 190 mm; inner diameter: 17 mm) is shown in Fig. 1. The positions of the thermocouples for measuring the various temperatures are defined by the following measurements: 1. Liquid center (P_{Center}); 2. Liquid surface (P_{Surface}); 3. Upper liquid surface (P_{Upper}, distance: 10 mm); and 4. Out of Dewar vessel (P_{Out}). The temperature change (ΔT) by heat is measured by a K type SUS316 thermocouple located at P_{Center}. The temperature distribution of the sample is measured by a thermocouple at P_{Surface}. The temperature change of the air in the Dewar vessel is measured by a thermocouple at P_{Upper}. Room temperature is measured by a thermocouple at P_{Out}. The sample is injected along the wall of the Dewar vessel using a syringe. The temperature measurement starts before injecting the first sample, and the rate of stirring is 750 rpm. The mixture is stirred by a magnetic stirrer.

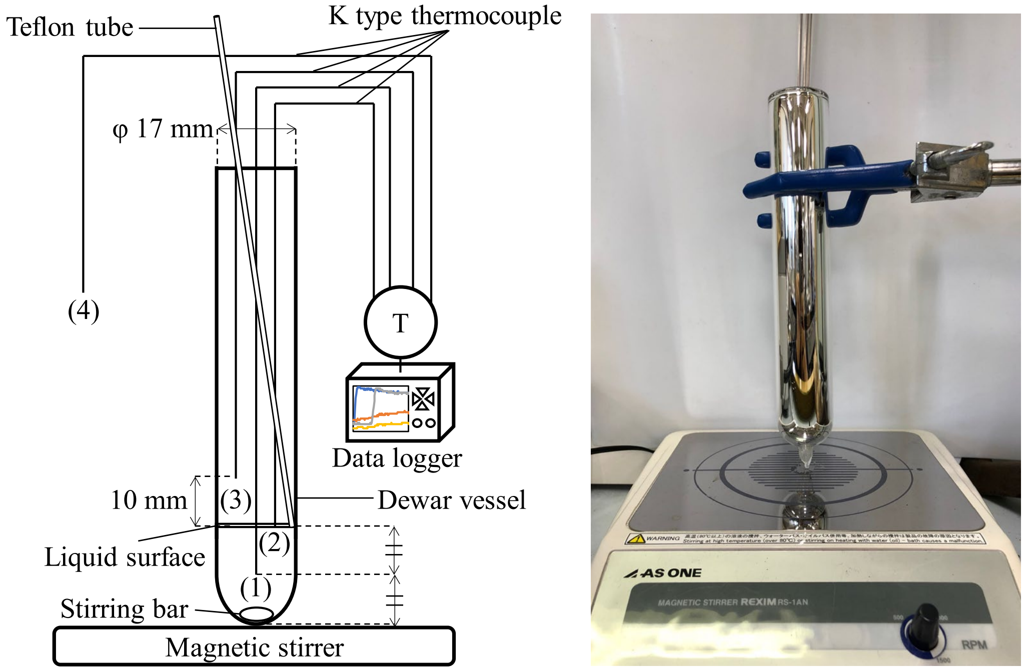

Fig. 1 Schematic drawing of small-scale Dewar vessel test (SDVT) apparatus

Optimization of test condition

In order to develop a method with high accuracy and reproducibility, it is necessary to optimize of the test conditions.

The position of the sample injection, the amount of sample, the stirring speed, and the surrounding temperature were selected as experimental conditions in this study. A suitable experimental condition was determined by measuring the heat of neutralization using hydrochloric acid (HCl) and sodium hydroxide (NaOH). The samples, which were HCl and NaOH, were preheated using a water bath, and the temperature range was about 10 ℃ to 40 ℃. After both temperatures of HCl and NaOH stabilized, NaOH (5.0 mL) was injected into the Dewar vessel containing HCl (5.0 mL).

Fig. 2 shows the positions of sample injection: the top of the Dewar vessel (I_{Top}), 10 mm below the top of the Dewar vessel (I_{10}), and the liquid surface of the sample ($I_{\mathrm{Sur.}}$). The ΔT of liquid center ($\Delta T_{\mathrm{Center}}$) and ΔT of liquid surface ($\Delta T_{\mathrm{Surface}}$) were measured for the neutralization reaction. In examining the position of the sample injection, the amount of sample, and the stirring speed, it was decided that the optimal conditions occurred by matching $\Delta T_{\mathrm{Center}}$ and $\Delta T_{\mathrm{Surface}}$, because the distribution of temperature becomes more even. In examining the surrounding temperature, the correlation coefficient was calculated by the effect of the difference between room temperature (T_{a}) and start temperature of the sample (T_{i}) on the maximum temperature change (ΔT_{max}). T_{a} was not changed, and T_{i} was adjusted about 10 ℃ to 40 ℃ using water bath. The condition with the highest correlation coefficient was determined to be the optimal condition.

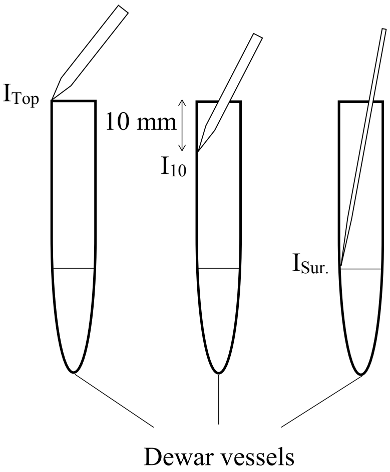

Fig. 2 Position of sample injection

Validation of reproducibility and accuracy

The reproducibility of SDVT was validated by measuring the temperature change under the defined test conditions. The accuracy of SDVT was validated by calculating the heat of reaction.

To validate the reproducibility, the relative standard deviation (RSD) from the standard deviation (SD) of ΔT_{max} was used with the criterion that the RSD be within ±5.0%. Measurement was carried out by the heat of the hydration reaction: 9.0 mL of H_2O was injected into the Dewar vessel containing 1.0 mL of $(CH_3CO)_2O$.

To validate the accuracy, the difference between the experimental value and the theoretical value of the heat of reaction was calculated, with the criterion of difference being within ±5.0%. Measurement was carried out by the heat of neutralization with a high reaction rate and the heat of hydration with a low reaction rate. The theoretical value of the heat of neutralization reaction is 55.9 kJ mol^{-1} [30], and the heat of hydration reaction is 58.6 ± 0.4 kJ mol^{-1} [31]. In the neutralization reaction, 5.0 mL of NaOH is injected into the Dewar vessel containing 5.0 mL of HCl. In the hydration reaction, 9.0 mL of H_2O is injected into the Dewar vessel containing 1.0 mL of $(CH_3CO)_2O$.

Validation of utility of SDVT

By using a test-tube of the same volume as the small-scale Dewar vessel, the utility of SDVT was validated by comparing the results of these two measurements under the same conditions.

The test-tube test and SDVT were compared by measuring the heat of hydration using water (H_2O) and acetic acid anhydride ($(CH_3CO)_2O$), for which the reaction rate and heat value are low and high, respectively. H_2O (9.0 mL) was injected into the Dewar vessel containing $(CH_3CO)_2O$ (1.0 mL). The test-tube test and SDVT were measured at the same time and results of the measurements were compared.

In the test for these validations, the initial difference between room temperature and the start temperature of the sample (T_a -T_i) was controlled. The number of tests was 10 times, and the T_a - T_i at that time was 0.0 K to 1.6 K.

Results and discussion

In this study, we optimized the test conditions, validated the accuracy and reproducibility, and validated the utility of SDVT by comparison with the test-tube test.

Optimization of test conditions

Position of sample injection

The amount of sample was used 10 mL, and the stirring speed was 750 rpm. Three positions were measured in the neutralization reaction as shown in Table 1.

In the case of I_{Top} and I_{10}, there was a difference in the distribution of temperature. It is assumed that part of the sample adhered on the wall the surface of the Dewar vessel, because a distance separates the sample injection position and the liquid surface. Thus, the entire amount of sample was not mixed in the Dewar vessel. In the case of $I_{Sur.}$, since ΔT_{Center} and $\Delta T_{Surface}$ coincided, the temperature of the sample was constant. Therefore, the suitable condition for the position of sample injection is $I_{Sur.}$.

Table 1 Results of ΔT at each sample injection position

Position of sample injection	ΔT_{Center} / K	$\Delta T_{Surface}$ / K
I_{Top}	3.1	1.9
I_{10}	2.8	2.6
$I_{Sur.}$	3.3	3.3

Amount of sample and stirring speed

Figs. 3, 4, 5, and Table 2 show the measurement results for different amounts of sample with and without stirring. Figs. 3 and 4 show the results using 10 mL of sample with and without stirring, respectively. Fig. 5 shows the results using 5 mL of sample without stirring. With only 5 mL of sample, the thermocouple at the center of the liquid touched the stirring bar, thus the measurement was not conducted with the sample stirring.

In the results shown in Fig. 3, ΔT_{Center} and $\Delta T_{Surface}$ do not change much after about 20 seconds. In the results shown in Fig. 4, the temperatures do not coincide. In the results shown in Fig. 5, although ΔT_{Center} and $\Delta T_{Surface}$ coincide immediately after the start of the measurement, the temperature does not become even. Table 2 shows that only when the amount of sample is 10 mL and the sample is stirred at 750 rpm do ΔT_{Center} and $\Delta T_{Surface}$ agree, at 3.2 K. Therefore, the optimal amount of sample is 10 mL and stirring is necessary.

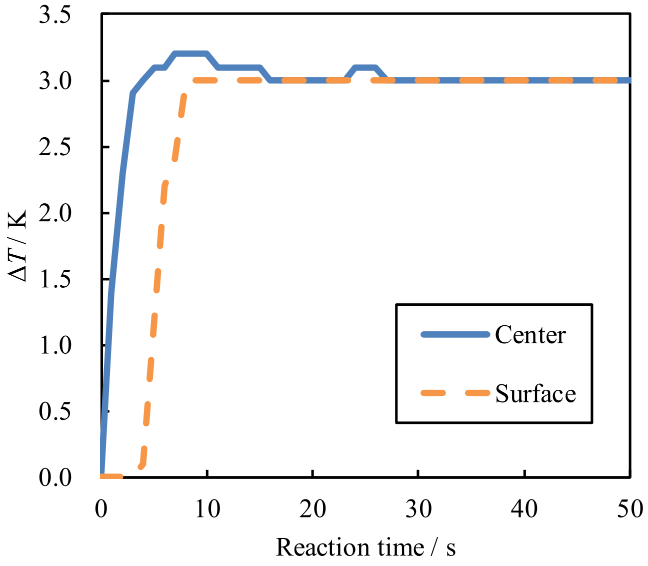

Fig. 3 Relationship between ΔT and reaction time for heat of neutralization using 10 mL of sample while stirring

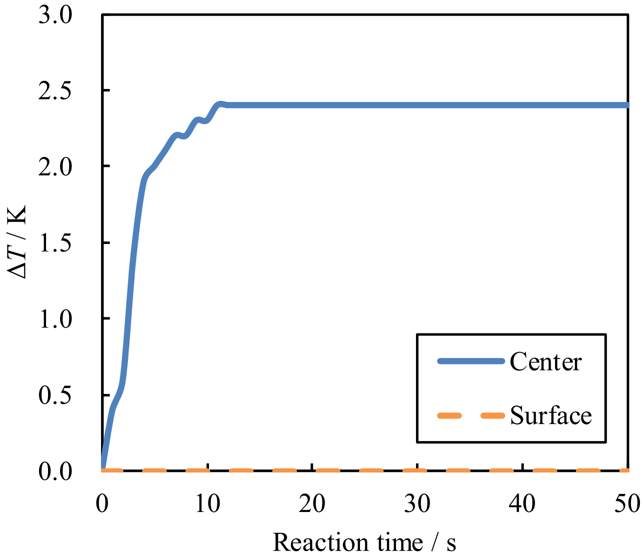

Fig. 4 Relationship between ΔT and reaction time for heat of neutralization using 10 mL of sample without stirring

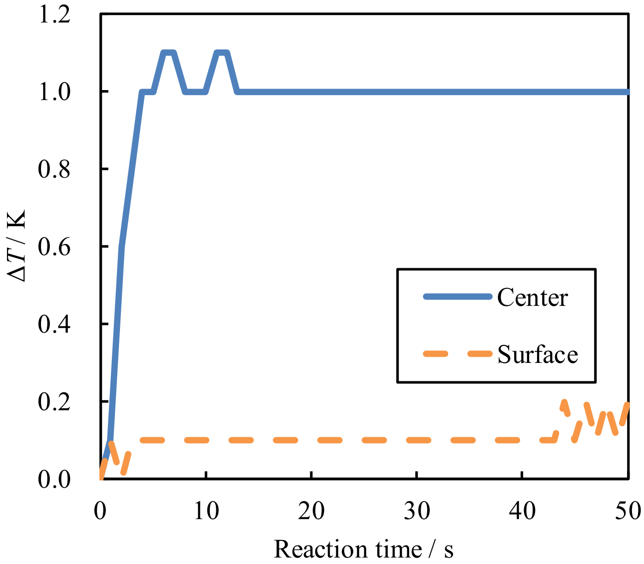

Fig. 5 Relationship between ΔT and reaction time for heat of neutralization using 5 mL of sample without stirring

Table 2 Results of ΔT at each position of sample injection

Amount of sample / mL	$\Delta T_{\mathrm{Center}}$ / K	$\Delta T_{\mathrm{Surface}}$ / K
10 (stirring)	3.2	3.2
10 (without stirring)	2.4	0.0
5.0 (without stirring)	1.0	0.4

Surrounding temperature

Fig. 6 shows the results of measurements of the surrounding temperature. ΔT_{max} versus the difference between T_a and T_i in the neutralization reaction was measured of 150 times. The difference between T_a and T_i has an effect on ΔT_{max}.

The overall coefficient of correction is 0.53. When T_i is higher than T_a ($T_i > T_a$), the variability of ΔT_{max} is large, as illustrated by the correlation coefficient of ΔT_{max} of 0.16. When T_a is higher than T_i ($T_a > T_i$), the variability of ΔT_{max} is small, with a correlation coefficient for ΔT_{max} is 0.64. Therefore, the suitable experimental condition for the surrounding temperature is ($T_a > T_i$).

However, when T_a and T_i are the same, an error of about 1-2 K occurs. Considering measurement error due to (T_a-T_i), there was error of 1-2K in measurement of ΔT_{max}. In mixing hazard evaluation, we should avoid underestimating the thermal hazard by adding the error to ΔT_{max}.

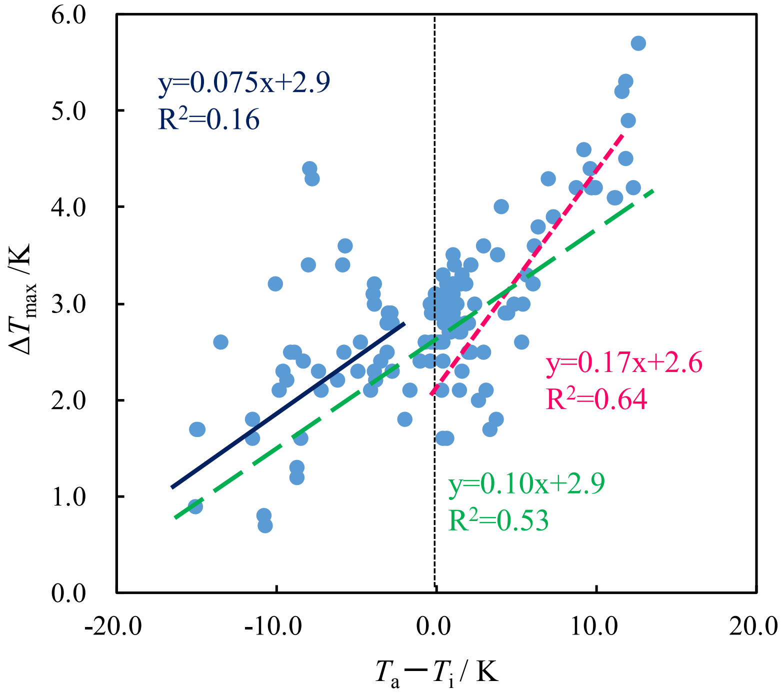

Fig. 6 Effects of difference between T_a and T_i on ΔT_{max}

Calculation method for heat of reaction

Although the Dewar vessel has high adiabaticity, the amount of heat dissipation must still be considered. Therefore, we examined the calculation method for the heat of reaction to consider the amount of heat dissipation.

A theoretical temperature change curve is obtained by combining the heat term and the dissipation term.

It is assumed that when temperature rises in a first-order reaction, the heat term is given by Eq. (1):

$$T(t) - T_a = (T_\infty - T_a)(1 - e^{-kt}) \qquad (1)$$

where T: sample temperature (°C); t: time (s); T_a: room temperature; k: kinetic constant (s^{-1}); and h: coefficient of heat transfer of Dewar vessel ($W\ m^{-2}\ K^{-1}$).

The amount of heat dissipation is assumed to be proportional to the difference between the sample temperature and room temperature as shown by Eq. (2):

$$\frac{d(T - T_0)}{dt} = h(T - T_a) \qquad (2)$$

For Eq. (1) and Eq. (2),

$$\alpha = T_\infty - T_0;\ x = T(t) - T_a$$

From Eq. (1) and Eq. (2), the following formula is obtained:

$$\frac{dx}{dt} = k\alpha \mathrm{e}^{-kt} - hx \qquad (3)$$

The general solution of Eq. (3) is shown by Eq. (4)

$$x(t) = \frac{\alpha k}{h-k}\mathrm{e}^{-kt} + C\mathrm{e}^{-ht} \qquad (4)$$

where C: constant of integration.

$$x\,(0) = 0;\ C = \frac{\alpha k}{k-h}$$

When $\beta = \frac{\alpha k}{k-\mathrm{h}} > 0$, from Eq. (4), the following formula is obtained:

$$x(t) = \beta(\mathrm{e}^{-ht} - \mathrm{e}^{-kt}) \qquad (5)$$

β, h, and k were obtained by fitting the temperature change curve according to experimental values based on the method of least squares using Eq. (5). The maximum temperature change under adiabatic conditions ($\Delta T_{\mathrm{corr.}}$) is obtained from β, h, and k. The heat of reaction is calculated using $\Delta T_{\mathrm{corr.}}$.

The heat of reaction can be represented by Eq. (6):

$$Q = mc\Delta T_{\mathrm{corr.}} / n \qquad (6)$$

where Q: heat of reaction (kJ mol^{-1}); m: mass of sample (g); c: specific heat (J g^{-1} K^{-1}) and n: amount of material (mol).

Validation of reproducibility and accuracy

Reproducibility

Under the defined experimental conditions, the reproducibility was validated by the hydration reaction.

Fig. 7 shows the reproducibility of the reaction. $\Delta T_{\max}$ versus the difference between T_a and the T_i is shown by the hydration reaction. The average of $\Delta T_{\max}$ was 12 K with a standard deviation (SD) of 0.36. The relative standard deviation (RSD) was calculated as 3.1%, which falls within the RSD criterion of ±5.0%. Therefore, it was shown that SDVT can perform measurements with high reproducibility.

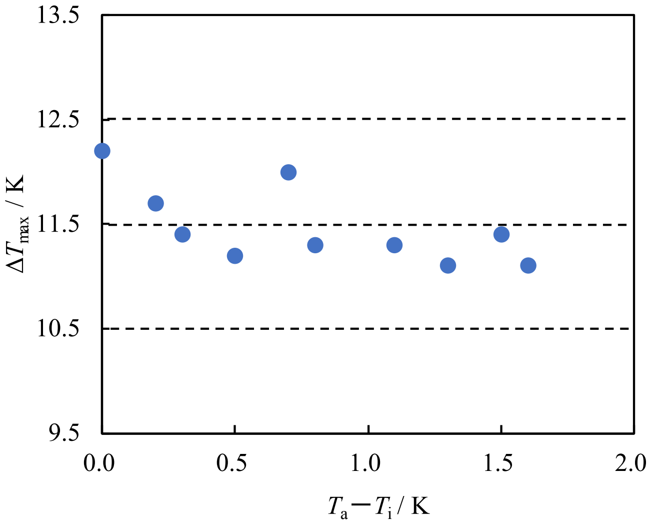

Fig. 7 Relationship between $\Delta T_{\max}$ and difference between T_a and T_i using the hydration reaction

Accuracy

Accuracy was validated by calculating the heats of the neutralization reaction and hydration reactions.

Fig. 8 shows temperature change curves of experimental values and correction values using the neutralization reaction, ΔT, versus reaction time. These curves were in good agreement. Therefore, there was no difference between the experimental and correction values of the maximum temperature change (3.20 K). The heat of reaction was calculated to be 54.0 kJ mol^{-1}, which was in good agreement with the theoretical value of 55.9 kJ mol^{-1}. The difference between the experimental and theoretical values for the heat of reaction was -3.4%, within the criterion of ±5.0%.

Fig. 9 shows temperature change curves of experimental values and correction values using the hydration reaction, ΔT, versus reaction time. The temperature change of the experimental and correction values did not coincide. It is assumed that heat dissipation occurs during the reaction in a system with a large temperature change and low reaction rate such as the hydration reaction. Table 3 shows ΔT_{max}, $\Delta T_{corr.}$, and heat of reaction using the hydration reaction. ΔT_{max} and heat of reaction are 12.2 K and 51.7 kJ mol^{-1}, respectively, and $\Delta T_{corr.}$ and heat of reaction are 13.9 K and 58.9 kJ mol^{-1}, respectively. The difference in heat of reaction between the experimental and correction values was approximately 7.0 kJ mol^{-1}. The correction value was in good agreement with the theoretical value of 58.6 ± 0.4 kJ mol^{-1}. Since there is almost no difference between the correction and theoretical values, the criterion of being within ±5.0% was satisfied.

Therefore, it is possible to correct for the heat dissipation in a first-order reaction, and SDVT can be used to calculate the heat of reaction equivalent to the theoretical value. In addition, if it is possible to calculate the heat dissipation rate in each test, a correction can be applied to the n-order reaction.

Thus, SDVT has enough accuracy and reproducibility to be useful as a screening method for mixing hazards.

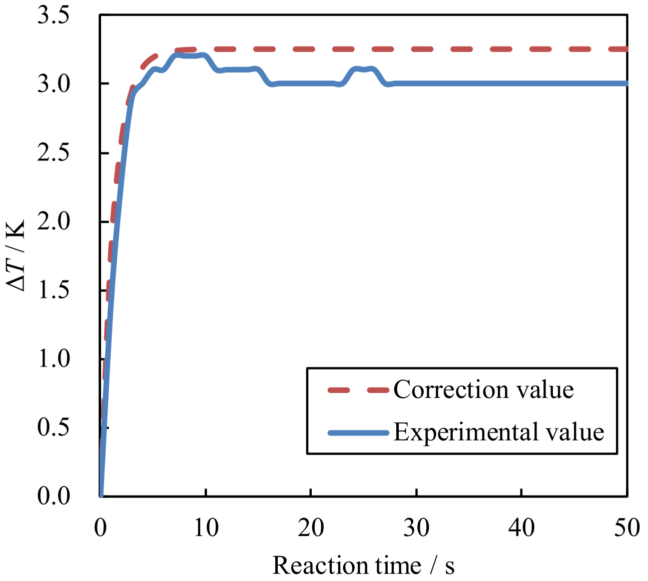

Fig. 8 Relationship between ΔT and reaction time for neutralization

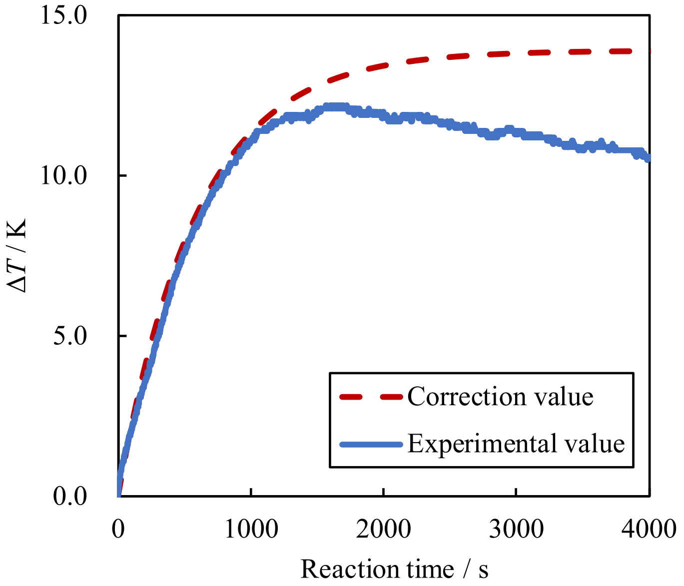

Fig. 9 Relationship between ΔT and reaction time for hydration

Table 3 ΔT_{max}, $\Delta T_{corr.}$, and heat of reaction using hydration reaction

	ΔT_{max}, $\Delta T_{corr.}$ / K	Heat of reaction / kJ mol^{-1}
Experimental value	12.2	51.7
Correction value	13.9	58.9

Validation of utility of SDVT

The test-tube test and SDVT were compared by measurement of the hydration reaction.

Fig. 10 shows the relationship between ΔT and reaction time for the hydration reaction using the test-tube test and SDVT, ΔT, versus reaction time.

In the test-tube test and SDVT, ΔT_{max} was 5.10 K and 12.2 K, and $\Delta T_{corr.}$ was 12.8 K and 13.9 K, respectively for a difference of ΔT_{max} of approximately 7.0 K. It is assumed that this difference was due to the low adiabaticity of the test-tube. The difference of $\Delta T_{corr.}$ was only around 1.0 K. Therefore, it is expected that the test-tube test can obtain measurements results equivalent to SDVT by correcting for the heat dissipation in the case of a first-order reaction. On the other hand, when it is impossible to specify the type of reaction, correction for heat dissipation cannot be performed. In that case, it is preferable to use SDVT, because there is a possibly of underestimation using the test-tube test.

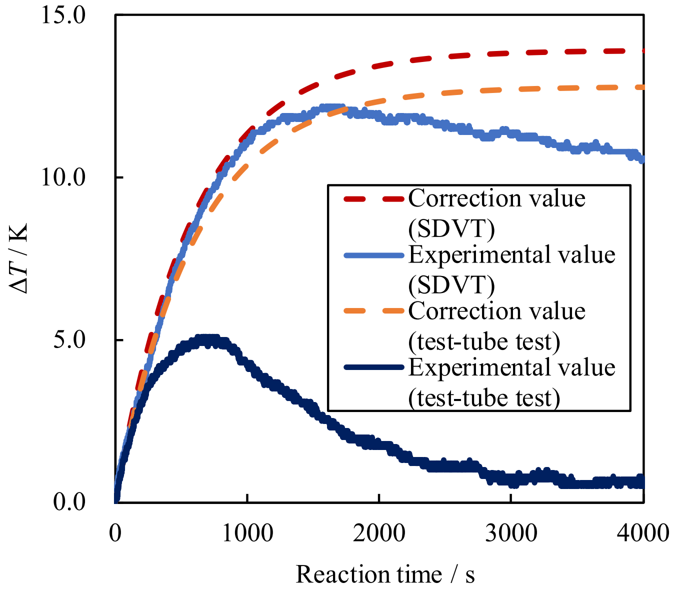

Fig. 10 Relationship between Δ*T* and reaction time for the hydration reaction using test-tube test and SDVT

Conclusions

To safely and appropriately evaluate mixing hazard in chemical processes, we developed the small-scale Dewar vessel test (SDVT). The SDVT needs much less sample-size than the UN Dewar vessel, and it also has an advantage in the heat-insulation comparing the test-tube test and the beaker test. The SDVT has great potential to alternate the UN Dewar vessel test, the test-tube test, and the beaker test. For wide use of the SDVT, the optimal experimental conditions and accuracy of SDVT must be demonstrated.

We assessed the optimal experimental conditions for SDVT. The position of sample injection was at the liquid surface of the sample; The position of sample injection was at the liquid surface of the sample; the amount of sample was 10 mL; the stirring speed was 750 rpm; and the surrounding temperature was [room temperature] > [start temperature]. Experimental results based on proposed conditions exhibited high accuracy and reproducibility. Correcting for the heat dissipation in the first-order reaction, SDVT estimated the reasonable heat of reaction compared to the theoretical value.

We examined whether mixing hazard could be evaluated more simply and appropriately than test-tube and beaker by using high adiabatic Dewar vessel. The test-tube test could not evaluate heat of reaction and the mixing hazard adequately due to its poor adiabaticity. The present SDVT provides better estimation for thermal risks than typical test-tube or beaker tests.

The SDVT proposed herein is helpful for the investigation of mixing hazard because the test can be conducted easily using small sample size. In future work, the heat dissipation correction for the *n*th-order reaction must be considered to generalize the estimation method using the SDVT.

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