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Effect of Physical Properties on Measurement of Specific Heat Capacities of Amine Solutions by Differential Reaction Calorimetry

Takao Nakagaki^{1*}, Daiki Yoshidome^a, Akira Ozeki^a, Hiroshi Sato^b and Jun Arakawa^c

^aWaseda University, 3-4-1, Okubo, Shinjuku-ku, Tokyo 1698555, Japan

^bResearch Laboratory, IHI Corporation, Shin-nakahara-cho, Isogo-ku, Yokohama 2358501, Japan

^cEnergy & Plant Operations, IHI Corporation, 3-1-1, Toyosu, Koto-ku, Tokyo 1358710, Japan

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1. Introduction

Post combustion CO₂ Capture (PCC) has attracted attention as one of the most promising technologies for reducing greenhouse gas emissions from fossil fuel-fired power stations. Amine scrubbing for CO₂ capture from flue gas has been demonstrated in many projects because aqueous amine solutions have been established as a mature technology for PCC. A significant energy consumption in regenerating CO₂-rich solution is still a main problem to solve and many research organizations try to reduce regeneration heat required in the strippers.

Exploring novel amines or binary / tertiary blend amines is the main approach to reducing the regeneration energy required for CO₂ capture in strippers. Sensible heat of CO₂-rich solution is roughly determined by the product of mass flow, specific heat capacity of amines and temperature rise in strippers. It is quite necessary for screening a few candidates from many kinds of solutions and estimating the regeneration heat by employing the candidates to measure accurately specific heat capacities of amine solution. Many preceding researches reported that the specific heat capacities of aqueous amine solutions vary according to not only composition of solution including concentration but also temperature and CO₂ loading. Aspen Plus offers some example files of CO₂ capture process flow diagram (PFD) which cover well-known single and binary amine solutions referring related papers, and can calculate heat balance taking the change in specific heat capacity into account. In order to incorporate other amine solution system into the CO₂ capture process, Aspen Plus has a data regression tool to simulate physical properties including the specific heat capacity which should be experimentally obtained often by the user themselves.

Differential Reaction Calorimetry (DRC) is commercialized by several companies and widely used to quantify the specific heat capacity as well as heat of CO₂ absorption. It is a well-established technology including measurement theory and procedure. It is simple and convenient measurement method, but as Alozie et al.¹⁾ reported, measurement of specific heat capacity by using this type of calorimetric apparatus has a non-negligible experimental error affected by many factors, such as the stirring rate, the specific gravity and the viscosity. In this work, the isobaric specific heat capacities of various concentration monoethanolamine (MEA) aqueous solutions were measured by our in-house-made DRC apparatus and the effect of mainly transport properties on them was evaluated

* Corresponding author. Tel: +81-3-5286-2497; fax: +81-3-5286-2497.

E-mail address: takao.nakagaki@waseda.jp .

by using a basic dimensional analysis.

2. DRC apparatus

Schematic and photo of in-house-made DRC apparatus are shown in Fig. 1. The DRC apparatus consists of one pair of reactors surrounded with thermostatic brine jackets. One side is a working reactor and the other is a dummy reactor partially filled with 250.0 g of solution and both are agitated by each magnetic stirrer. An electric heater is inserted into each reactor, but only working reactor's heater is connected to a DC power controller to calibrate the thermal system by inputting a known electric energy into the solution losslessly and directly. A thermocouple is also inserted into each reactor and detects temperature difference with high-response temperature measurement system, which is logged with elapsed time.

For the sake of specific heat capacity measurement, 3W of electric power has been input into the solution of working reactor for 600 seconds and the logged temperature difference $\Delta T(t)$ increases with elapsed time t , which can be expressed as Eq. (1):

$$\Delta T(t) = \Delta T(0) + \frac{Q_c}{UA} \left\{ 1 - e^{-\frac{t}{\tau}} \right\} \quad (1)$$

where Q_c is the electric energy input by the heater for calibration, UA is the product of heat transfer coefficient and area obtained by $Q_c / \int_{t_0}^{t_{end}} \Delta T(t) dt$, τ is the time constant of calibration and determined by fitting the curve of the $\Delta T(t)$. Eventually, the specific heat capacity C_p is obtained by Eq. (2):

$$\tau = \frac{mC_p + C_i}{UA} \quad (2)$$

where m is mass of solution, C_i is intrinsic heat capacity of the reactor and measured by using water in advance.

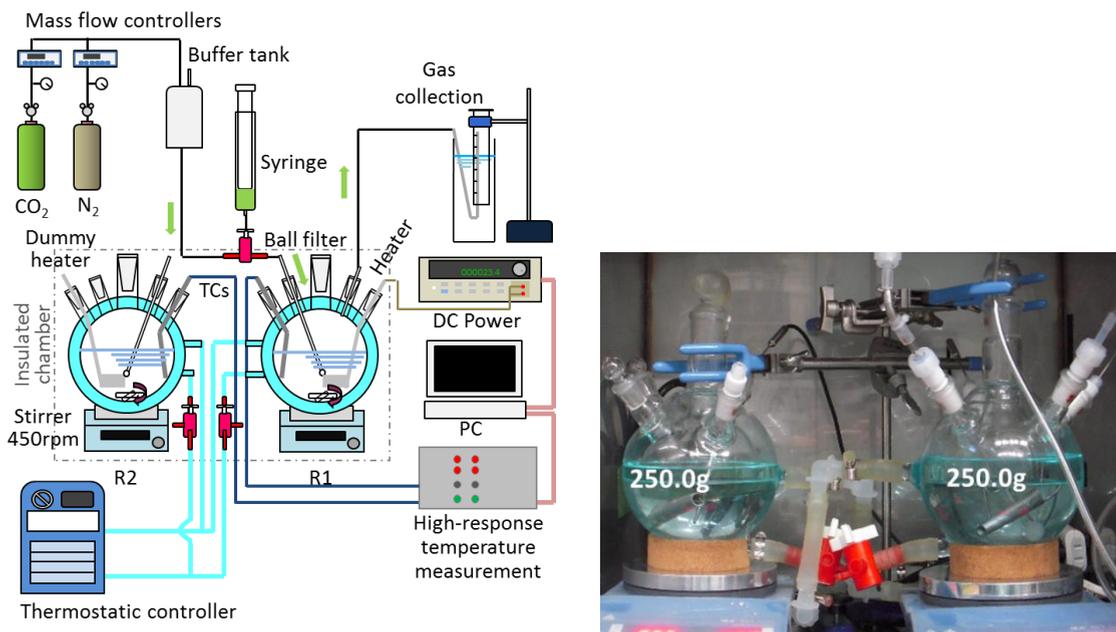


Fig. 1 Schematic and photo of in-house-made Differential Reaction Calorimetry (DRC) apparatus

According to the above procedure, the C_p of various concentration of MEA solution was measured at 40 °C. Figure 2 plots the measurement result and literatureⁱⁱ⁾ value. The C_p decrease with increase in concentration, and the discrepancy between this work and literature also increase. The C_i should be investigated because it is only value that is not measured simultaneously with the target solution.

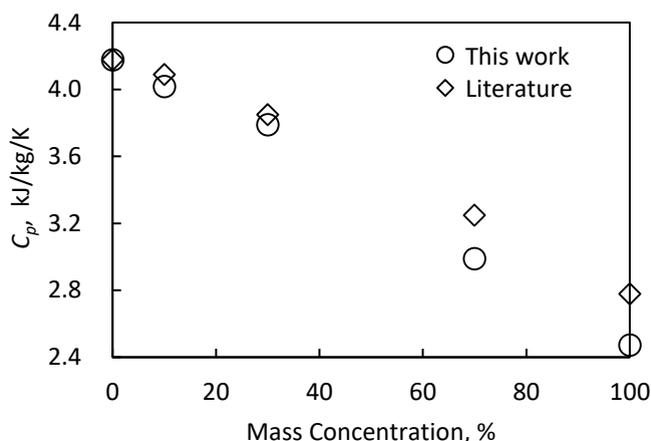


Fig. 2 C_p of various concentration of MEA solution measured at 40 °C

3. Effect of Physical Properties on Measurement of C_p

The intrinsic heat capacity of the reactor C_i includes that of the inserted objects such as the electric heater, the thermocouple, the magnetic rotator and the dosing tube, but these values does not depend on reagent solutions and even on temperature within a narrow range. Figure 3 plots the C_i versus temperature using pure water and pure ethylene glycol of which properties largely differ from that of water, as shown in Table 1. The C_i of ethylene glycol is different from that of water, and this 80 J/K difference implies that physical properties may affect the C_p measurement resulting from the change in C_i .

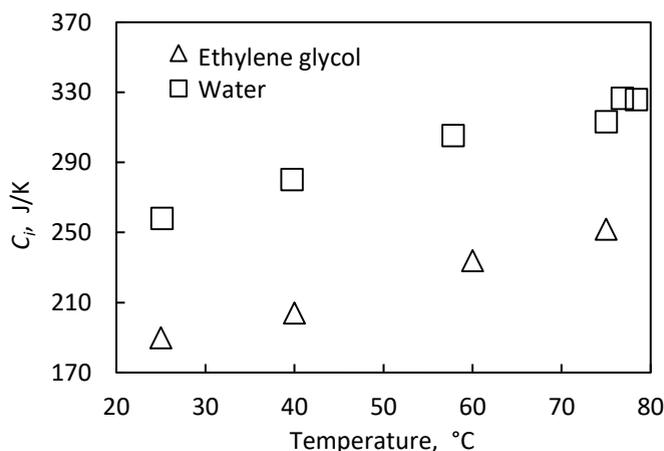


Fig. 3 Intrinsic heat capacity of the reactor C_i versus temperature quantified by using ethylene glycol or water

Table 1 Physical properties of ethylene glycol and water at 40 °C

| Reagent | Density, ρ (kg/m ³) | Specific heat capacity, C_p (kJ/kg/K) | Viscosity, μ (mPa·s) | Thermal conductivity, λ (W/m/K) |
|-----------------|--------------------------------------|---|--------------------------|---|
| Ethylene glycol | 1100 | 2.47 | 9.13 | 0.256 |
| Water | 992 | 4.18 | 0.653 | 0.628 |

Three influencing factors on the difference of $\Delta C_i=80$ J/K between ethylene glycol and water are assumed. Firstly,

temperature distribution in the solution may affect the ΔC_i . The difference between maximum and minimum temperatures, which are expected at nearby the electric heater and nearby the wall, respectively, were measured by using pure water and pure MEA. However, both of the $\int_{t_0}^{t_{end}} \Delta T(t) dt$ were below 2.0 K·s at the most, which was equivalent to only 0.5% of Q_c . Therefore, the effect of temperature distribution is negligible. Secondary, the logged $\Delta T(t)$ fluctuated figurally, but effect of the fluctuation on the ΔC_i was only below 3% and negligible. Finally, effect of change in the UA , which depends on physical properties of solutions, was evaluated by a basic dimensional analysis.

Equation (2) can be expressed as Eq. (3) by roughly modelling the reactor as a sphere.

$$\left(\frac{4\pi}{\frac{1}{\alpha_1 r_1} + \frac{1}{\lambda_g \left(\frac{1}{r_1} - \frac{1}{r_2} \right)} + \frac{1}{\alpha_2 r_2}} + U' \right) \cdot \tau = m C_p + C_i \quad (3)$$

where r_1 is the radius of the inner glass wall contacting the solution, α_1 is the heat transfer coefficient between the inner glass wall and the solution, λ_g is the thermal conductivity of the glass wall, r_2 is radius of outer glass wall contacting the brine, α_2 is the heat transfer coefficient between the outer glass wall and the brine, U' is the other thermal resistance. In the combined thermal conductance expressed as the denominator in the parenthesis, the second and third terms are relatively small against the first term and can be ignored as a first approximation. Therefore, Eq. (3) is simplified into Eq. (4).

$$(\alpha_1 \cdot 4\pi r_1 + U') \cdot \tau = m C_p + C_i \quad (4)$$

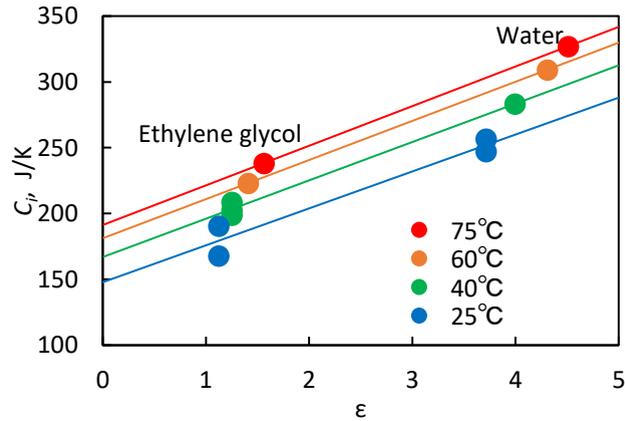
The Reynolds number of the stirred solution is approximately $Re \approx 50$. According to the theory of thermal boundary layer in laminar flows, the Nusselt number can be expressed as $Nu = a \cdot Re^{0.5} \cdot Pr^{1/3}$. The order dependence on each physical property of α_1 is determined as Eq. (5).

$$\alpha_1 = \frac{\lambda_f}{L} \cdot Nu = k \cdot \lambda^{2/3} \cdot \rho^{1/2} \cdot C_p^{1/3} \cdot \mu^{-1/6} = k \cdot \varepsilon \quad (5)$$

Eventually, the can be expressed as the first order equation in the lumped property ε .

$$C_i = k' \cdot \tau \cdot \varepsilon + U' \cdot \tau - m C_p \quad (6)$$

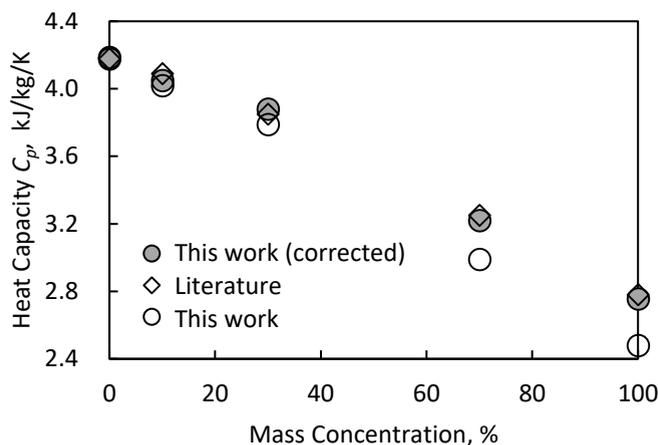
The right side of Eq. (6) includes the targeted variable C_p . Therefore, an iterative calculation with assumed C_p should be conducted until the C_p and C_i converge. Figure 4 depicts the C_i versus ε computed from the iteration applying the experimental result and physical properties of water and ethylene glycol at each temperature. Slopes of all lines are almost coincident with each other, while dependency of each properties on temperature differs between water and ethylene glycol. It can be argued that the difference of C_i shown in Fig. 3 is explainable in terms of the



spherical reactor model.

Fig. 4 Intrinsic heat capacity of the reactor C_i versus lumped property ε at each temperature

Finally, the corrected C_p of MEA with revised C_i are shown Fig. (5). The discrepancy between this work and literature decreased to below 1.0%.

Fig. 4 Corrected C_p of various concentration of MEA solution measured at 40 °C

4. Conclusions

We clarified the main cause of non-negligible experimental error in the measurement of specific heat capacity obtained by using calorimetric apparatus such as DRCs. Physical properties of reagent solution, especially thermal conductivity and density may affect the intrinsic heat capacity of the reactor and consequently affect the specific heat capacity of reagent solution. The simple linear approximation by the influencing factor derived from the basic dimensional analysis and the iterative calculation can correct the measured specific heat capacity and approach to finding the true value.

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⁽ⁱ⁾ Alozie, D. M., et al., *Org. Process Res. Dev.*, **15** (2011) pp. 1412-1419

⁽ⁱⁱ⁾ Weiland, R.H., GPA Research Report No. 152, August (1996)