TRONDHEIM CCS CONFERENCE

CO_2 CAPTURE, TRANSPORT AND STORAGE

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Heat of absorption of CO_2 in aqueous ammonia, piperazine solutions and their mixtures

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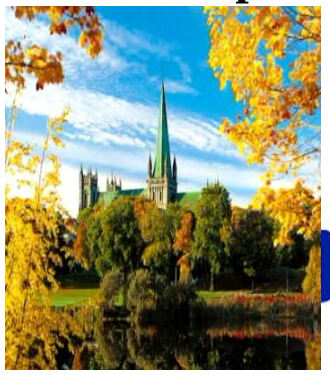


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Outline

- Introduction
- Experimental apparatus and methods
- Results and discussion
- Conclusions

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Introduction

- Back ground
  - ✓ CO_2 Capture → Chemical absorption
- Research area
  - ✓ Heat of absorption ΔH_{abs}
- Absorbent
  - ✓ Aqueous ammonia (Qin F., 2010)
  - ✓ Piperazine solution (Hilliard M., 2008; Kim I., 2009)
  - ✓ NH_3/PZ blended solution

Chemical reactions of CO_2 with NH_3 (aq)

The reaction of CO_2 with NH_3 (aq) is deeply discussed by Kohl et al (1997) and Yeh et al (2005). The total reaction can be described as the equation (1):

$$CO_2 + NH_3 + H_2O \rightleftarrows NH_4HCO_3 \qquad \Delta H_{rx}=64.26 \text{ kJ/mol} \quad (1)$$

The actual process of the reaction can be described as step-by-step reactions. First of all, reaction (2) occurs as:

$$CO_2 + 2NH_3 \rightleftarrows NH_2COONH_4 \qquad \Delta H_{rx}=72.32 \text{ kJ/mol} \quad (2)$$

Then, NH_2COONH_4 has an irreversible reaction (3) in solution:

$$NH_2COONH_4 + H_2O \rightleftarrows NH_4HCO_3 + NH_3 \qquad \Delta H_{rx}=8.06 \text{ kJ/mol} \quad (3)$$

At the same time, the following two reactions are possible to occur:

$$CO_2 + 2NH_3 + H_2O \rightleftarrows (NH_4)_2CO_3 \qquad \Delta H_{rx}=101.22 \text{ kJ/mol} \quad (4)$$

$$CO_2 + H_2O + (NH_4)_2CO_3 \rightleftarrows 2NH_4HCO_3 \qquad \Delta H_{rx}=26.88 \text{ kJ/mol} \quad (5)$$

Chemical reactions of CO_2 with PZ solution

Heat of reaction of CO_2 with PZ solution was determined mainly by the following two reversible reactions (Bishnoi and Rochelle, 2000; Ermatchkov et al., 2002; Derks and Versteeg, 2006).

First of all, at the beginning of the absorption process, reaction (6) mainly determined the ΔH_{abs}:

$$PZ + H_2O + CO_2 \rightleftarrows PZCOO^- + H_3O^+ \qquad (6)$$

As the absorption process going on, the CO_2 loading of solution increased, free PZ decreased, and the generation of $PZCOO^-$made reaction (7) gradually began to occur.

$$PZCOO^- + H_2O + CO_2 \rightleftarrows PZ(COO^-)_2 + H_3O^+ \qquad (7)$$

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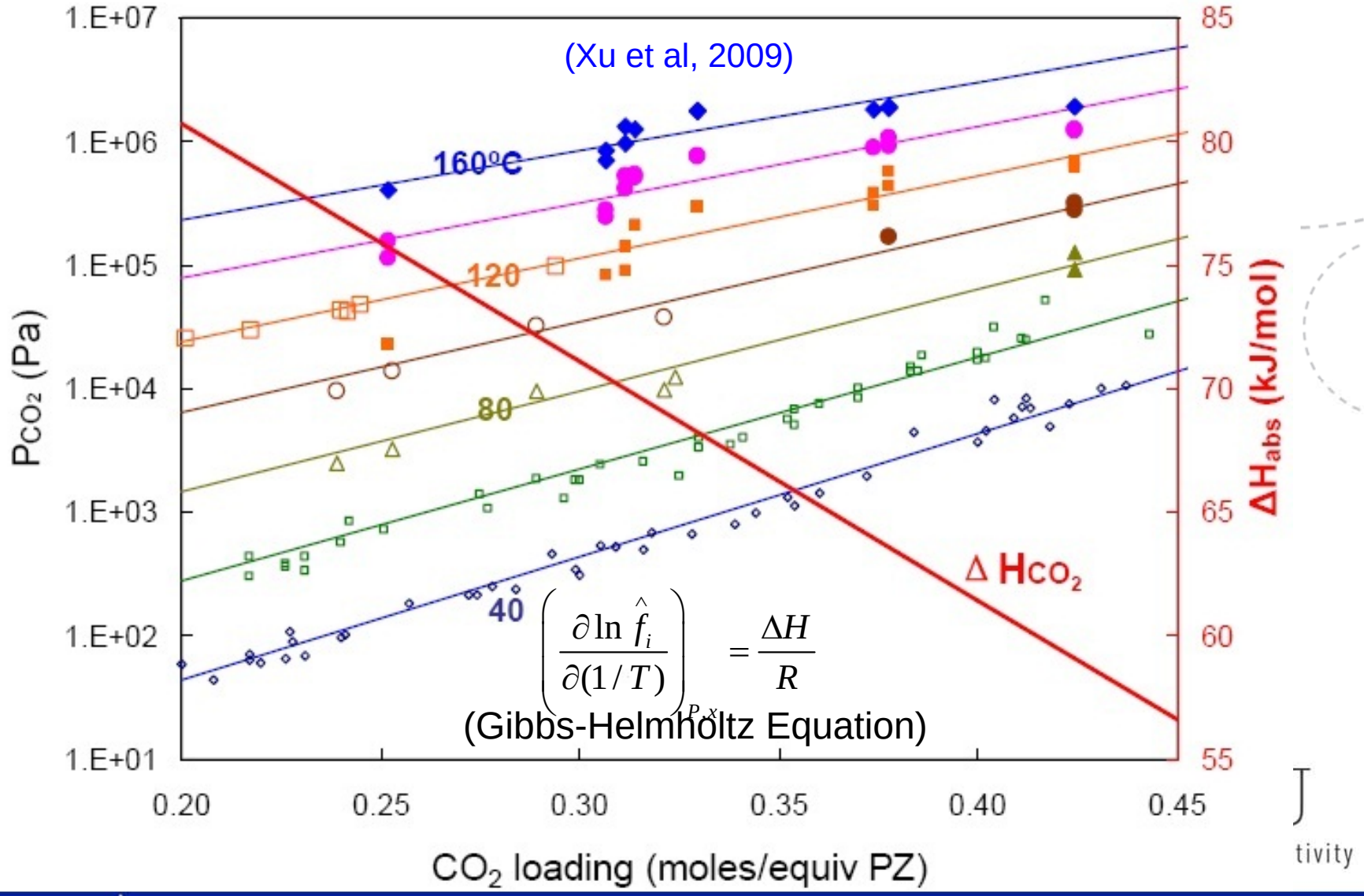
ΔH_{abs} estimated by VLE data



$$\left(\frac{\partial \ln \hat{f}_i}{\partial (1/T)}\right)_{P,x} = \frac{\Delta H}{R}$$

(Gibbs-Helmholtz Equation)

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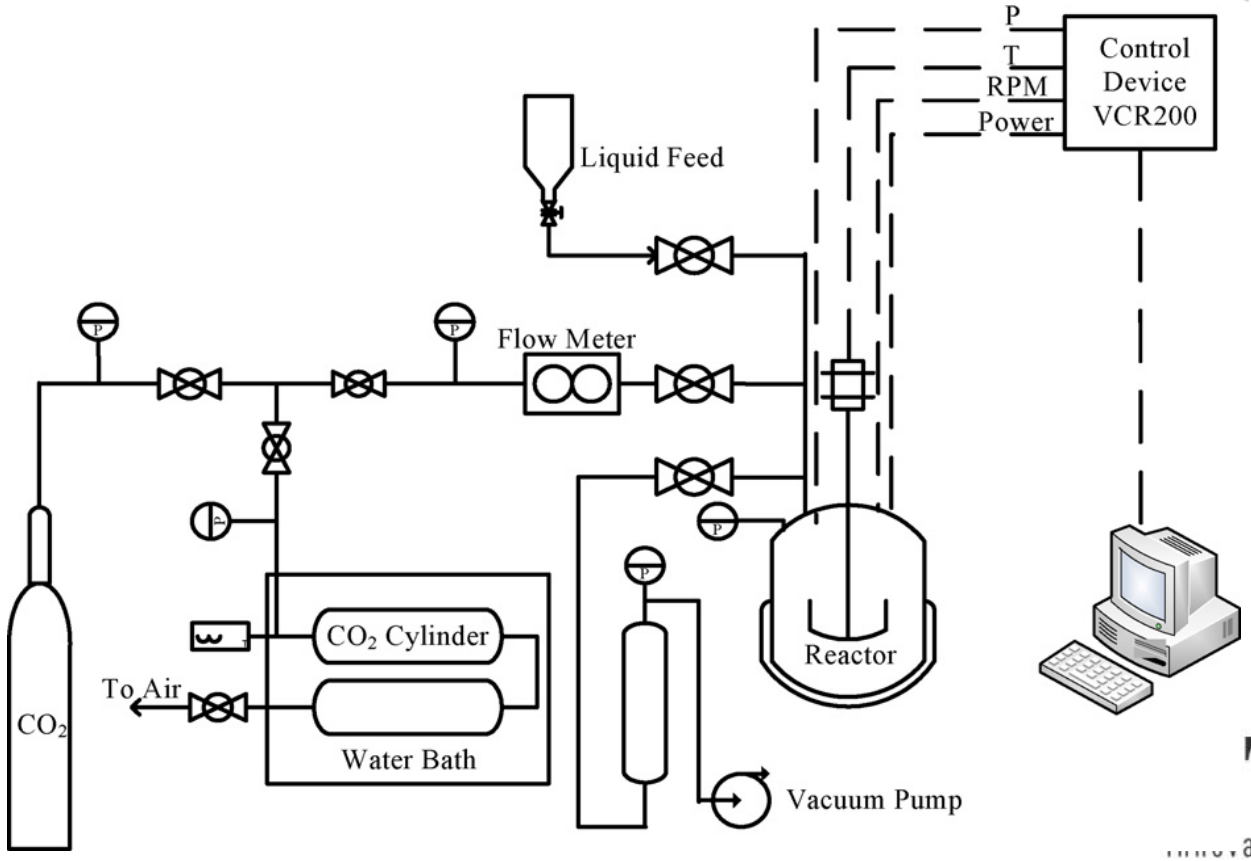
Experimental apparatus in this work

- The experimental setup of the 2L reaction calorimeter CPA-122 (ChemiSens AB, Lund, Sweden)



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Experimental methods

n_{CO2} (mol) added from the cylinder in to

the reactor c

Robinson equ

$$p = \frac{RT}{v-b} - \frac{}{v^2+}$$

$$a = 0.457235\frac{R^2}{p}$$

$$b = 0.07780\frac{R\,T_c}{p_c}$$

The uncertai

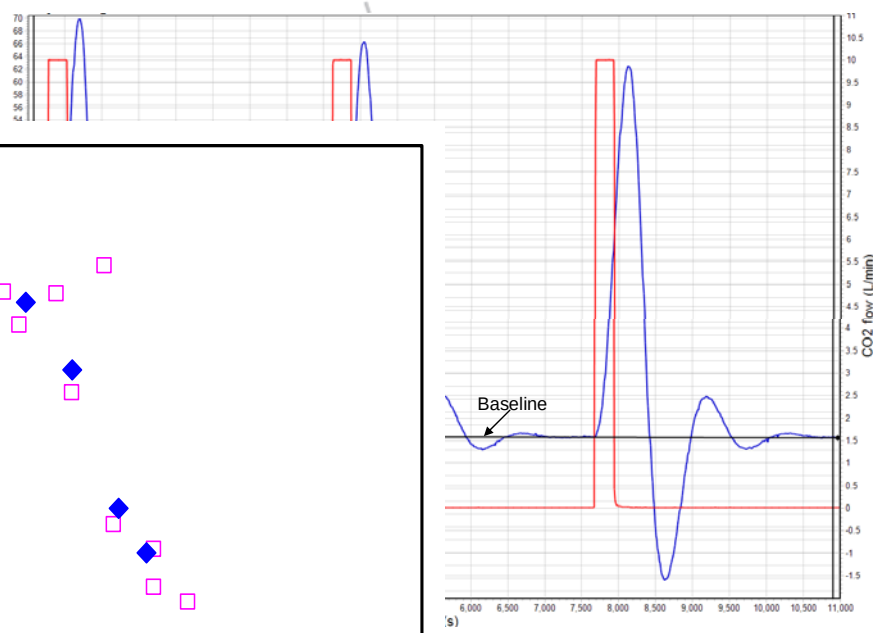
been estimated

contain NH_3 sys

NH_3 changed in

The total un

$$\frac{\delta \Delta H_{abs}}{\Delta H_{abs}} = \sqrt{\left(\frac{\delta Q}{Q_{total}}\right.}$$



CO_2 flow

alculation of total heat

ted to be 0.5% at 40℃,

0℃.

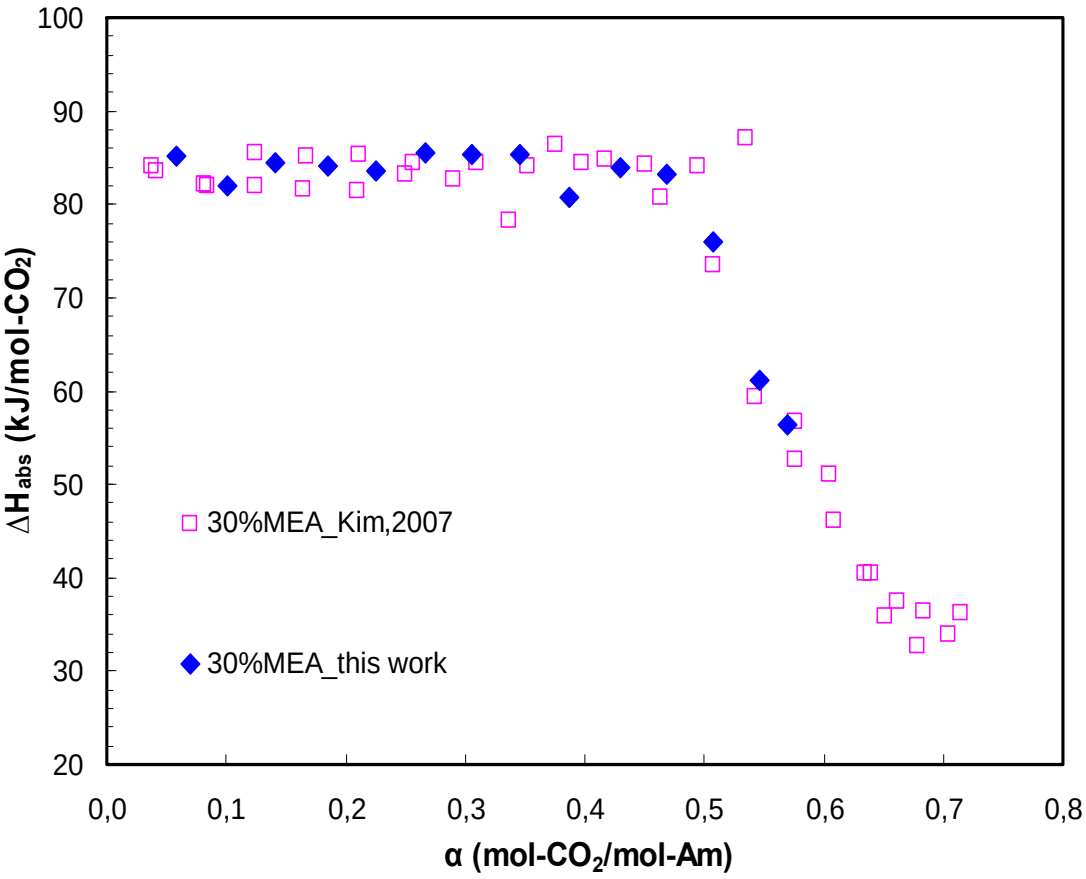


Fig.3. Heat of absorption of CO_2 with 30wt% MEA compared with Kim's experimental data at 40℃

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Experimental section

- NH_3 (aq)

✓ Concentration: 3.1 m (5 wt%)

✓ Temperature: 40℃, 60℃, 80℃

- PZ solution

✓ Concentration: 0.86 m (6.9 wt%)

✓ Temperature: 40℃, 60℃, 80℃

- NH_3/PZ blended solution

✓ Concentration:

3.1m NH_3+0.86m PZ; 3.1m NH_3+0.43m PZ; 1.5m NH_3+0.86m PZ

✓ Temperature: 40℃, 60℃, 80℃

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Chemicals

- CO_2 (AGA, ⩾99.99% pure)
- Distilled water (NTNU Lab)
- Piperazine (SIGMA-ALDRICH, > 99 % pure)
- Ammonia (SIGMA-ALDRICH, ⩾ 25wt%)
- All the concentrations of tested solutions were determined by Metrohm 809 Titrando auto titrator.

Heat of absorption of CO_2 in NH_3 (aq)

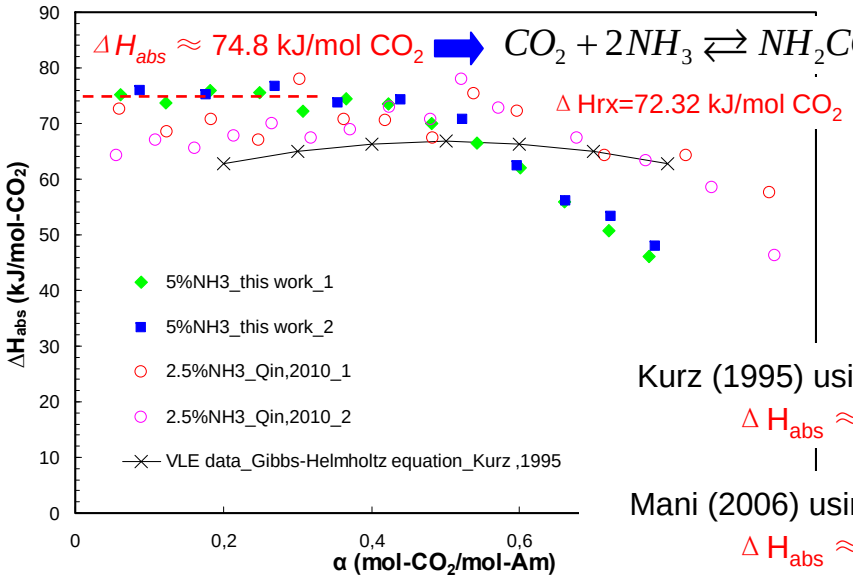

Fig.4. Heat of absorption of CO_2 with NH_3 (aq) at 40℃

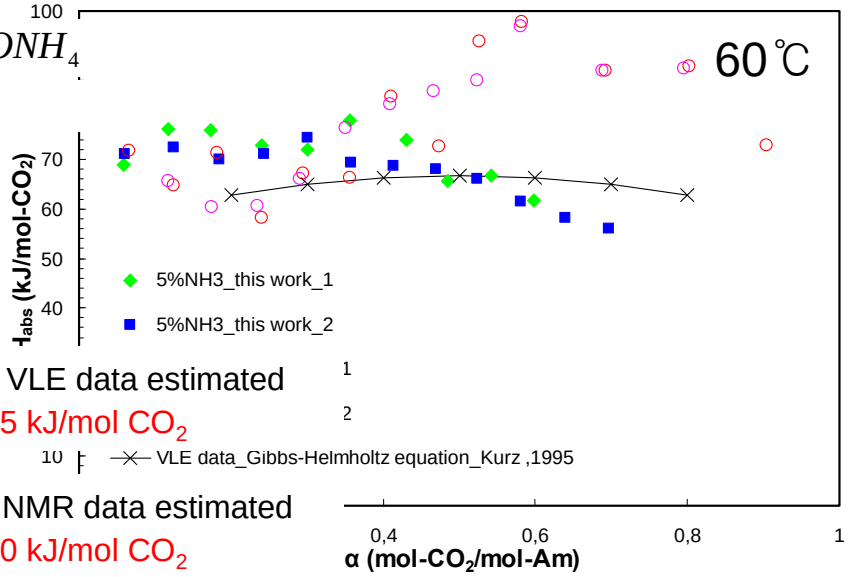

Fig.5. Heat of absorption of CO_2 with NH_3 (aq) at 60℃

Kurz (1995) using VLE data estimated

$\Delta H_{abs} \approx 65$ kJ/mol CO_2

Mani (2006) using NMR data estimated

$\Delta H_{abs} \approx 80$ kJ/mol CO_2

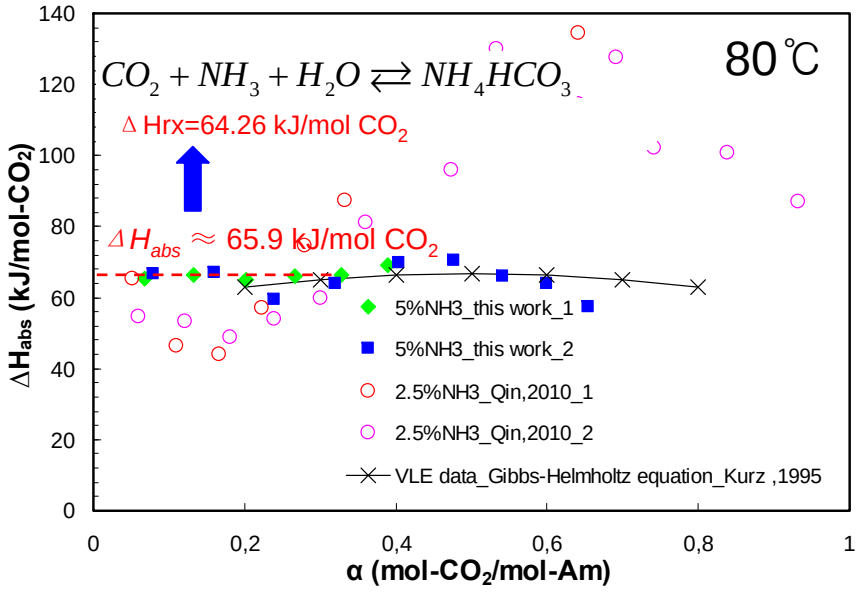

Fig.6. Heat of absorption of CO_2 with NH_3 (aq) at 80℃

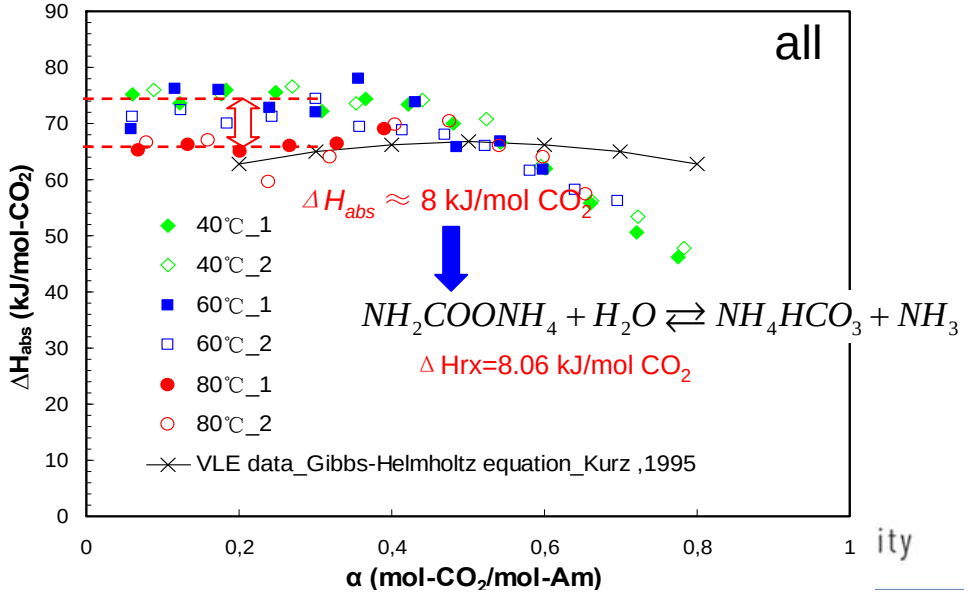

Fig.7. Heat of absorption of CO_2 with 5wt% NH_3 (aq) at 40, 60 and 80℃

Heat of absorption of CO_2 in PZ solutions

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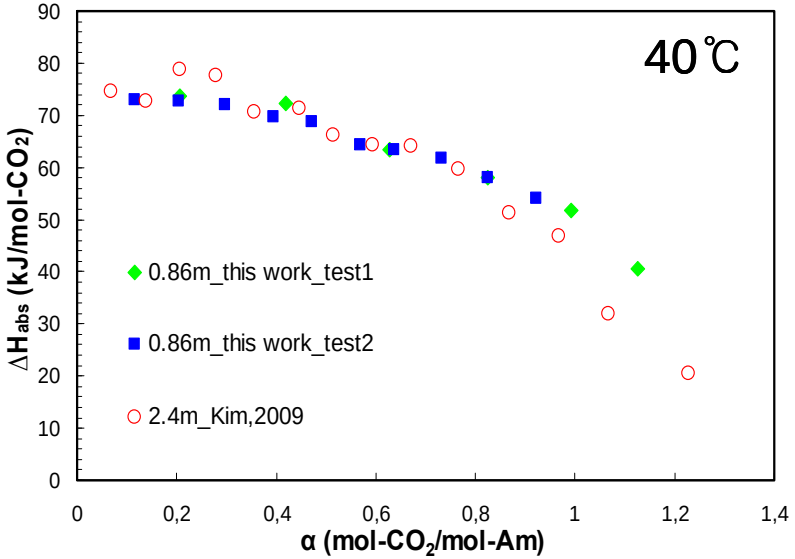

Fig.8. Heat of absorption of CO_2 with PZ solution at 40℃

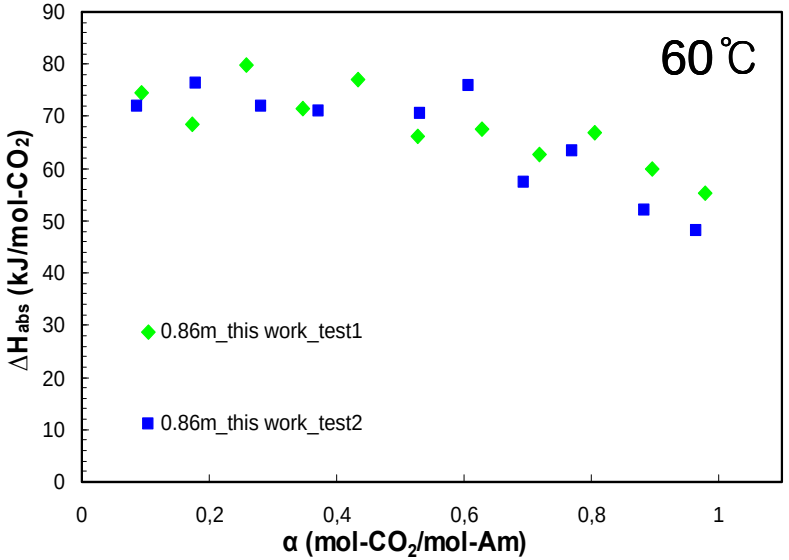

Fig.9. Heat of absorption of CO_2 with PZ solution at 60℃

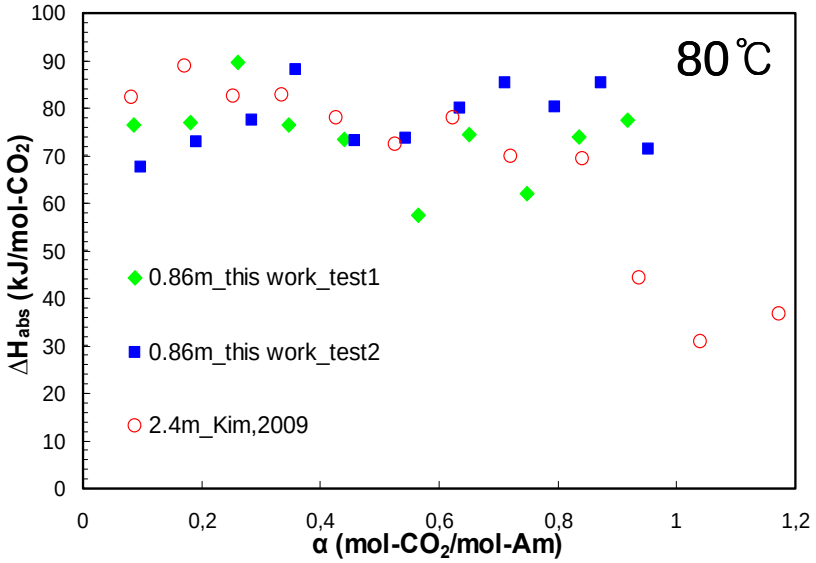

Fig.10. Heat of absorption of CO_2 with PZ solution at 80℃

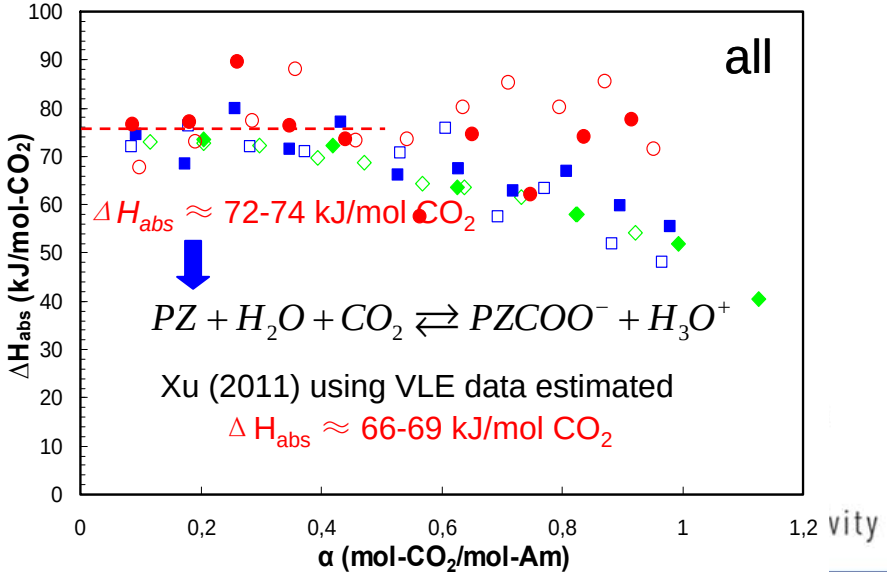

Fig.11. Heat of absorption of CO_2 with 0.86m PZ solution at 40, 60 and 80℃

Heat of absorption of CO_2 in 3.1m NH_3/0.86m PZ blended solutons

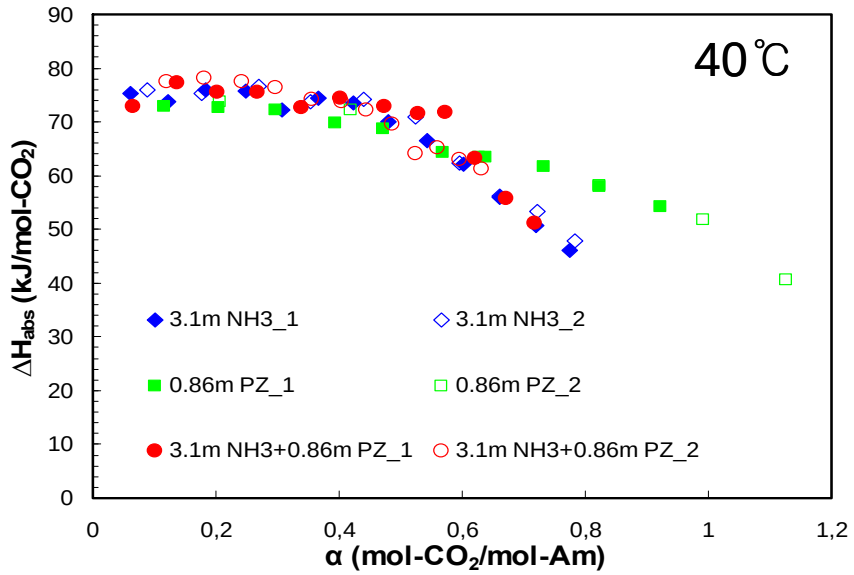

Fig.14. Heat of absorption of CO_2 with NH_3/PZ blended solutions at 40℃

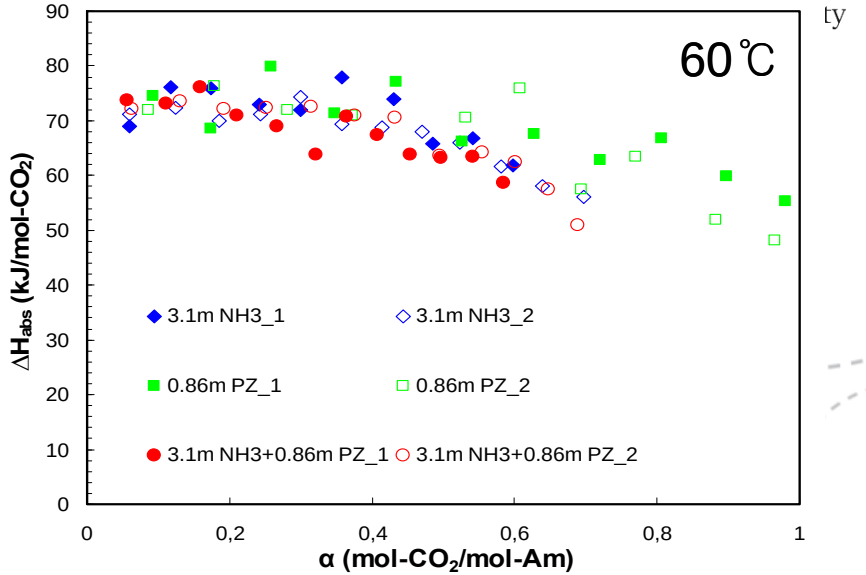

Fig.15. Heat of absorption of CO_2 with NH_3/PZ blended solutions at 60℃

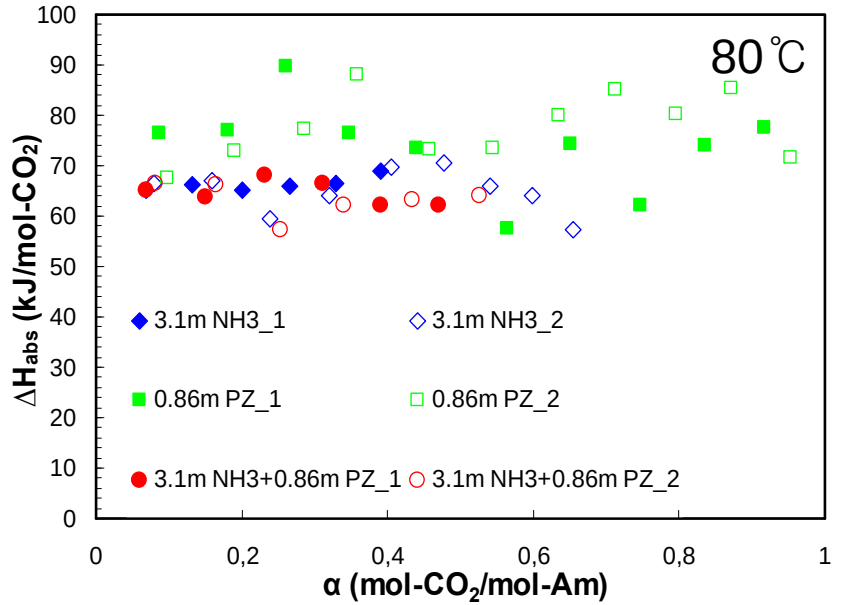

Fig.16. Heat of absorption of CO_2 with NH_3/PZ blended solutions at 80℃

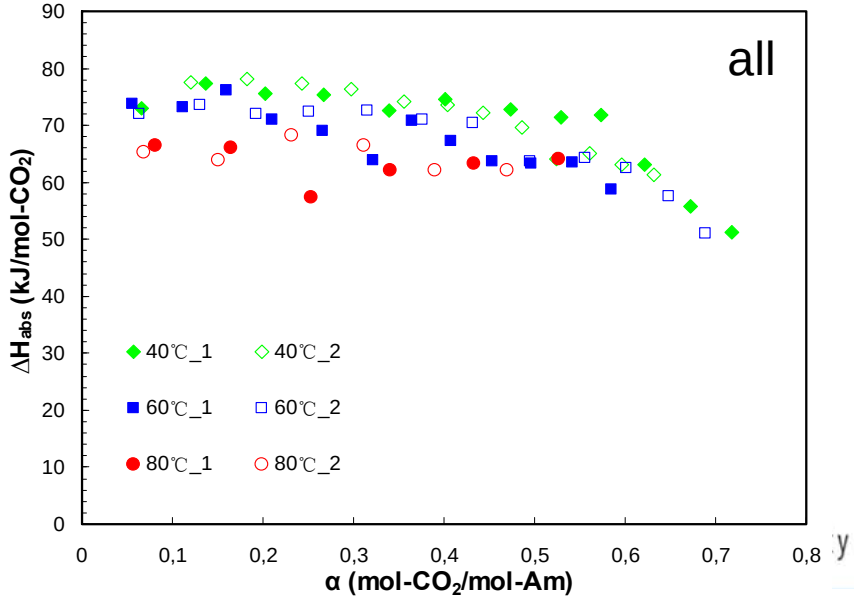

Fig.19. Heat of absorption of CO_2 with NH_3/PZ blended solutions at 40-80℃

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Effect of PZ concentration to the heat of absorption

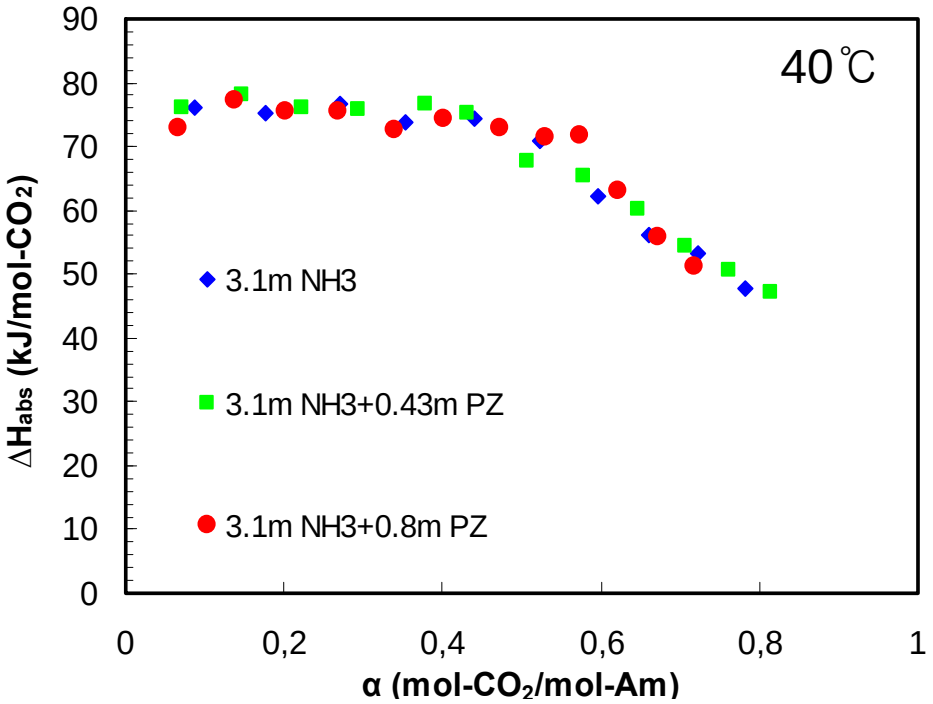

Fig.17. Heat of absorption of CO_2 with NH_3 (aq) and NH_3 blended PZ in different concentrations at 40℃

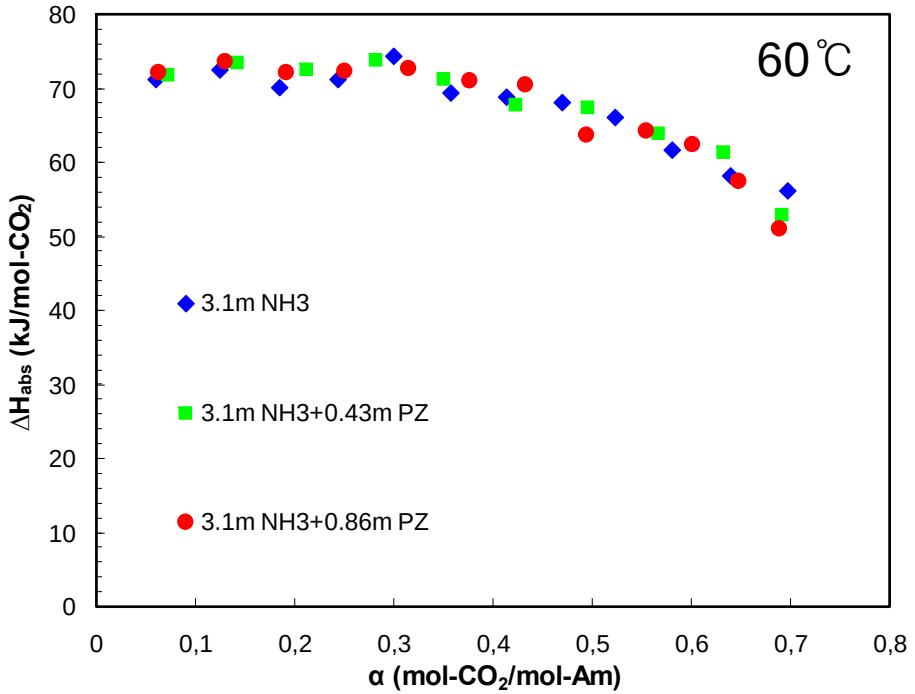

Fig.18. Heat of absorption of CO_2 with NH_3 (aq) and NH_3 blended PZ in different concentrations at 60℃

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Comparison of NH_3/PZ blends with MEA/PZ blends at 40°C

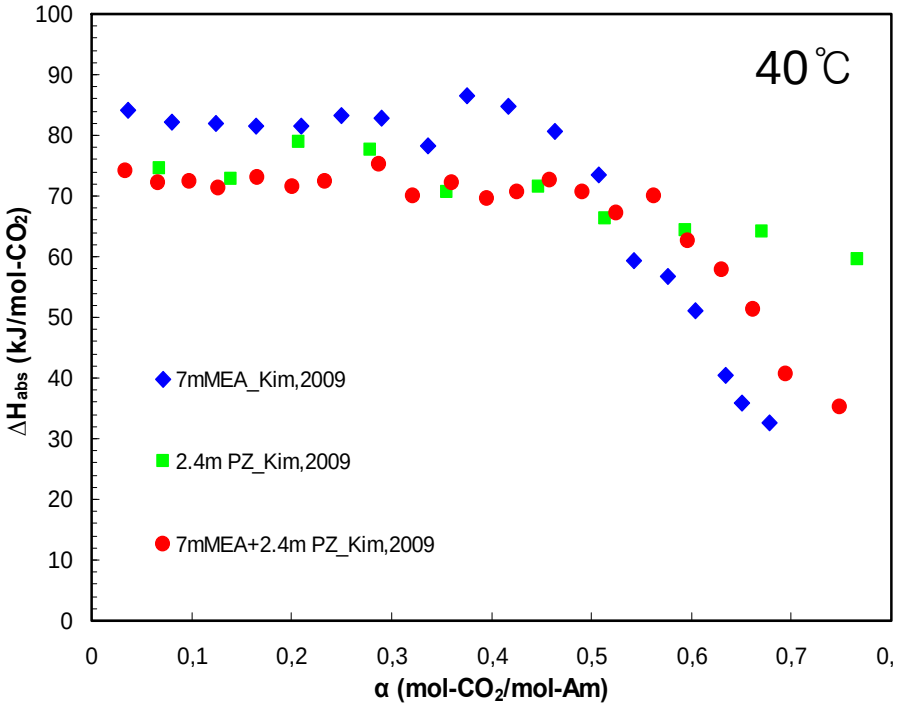

Fig.20. Heat of absorption of CO_2 with MEA/PZ blended solutions compared with individual MEA and PZ solutions at 40℃

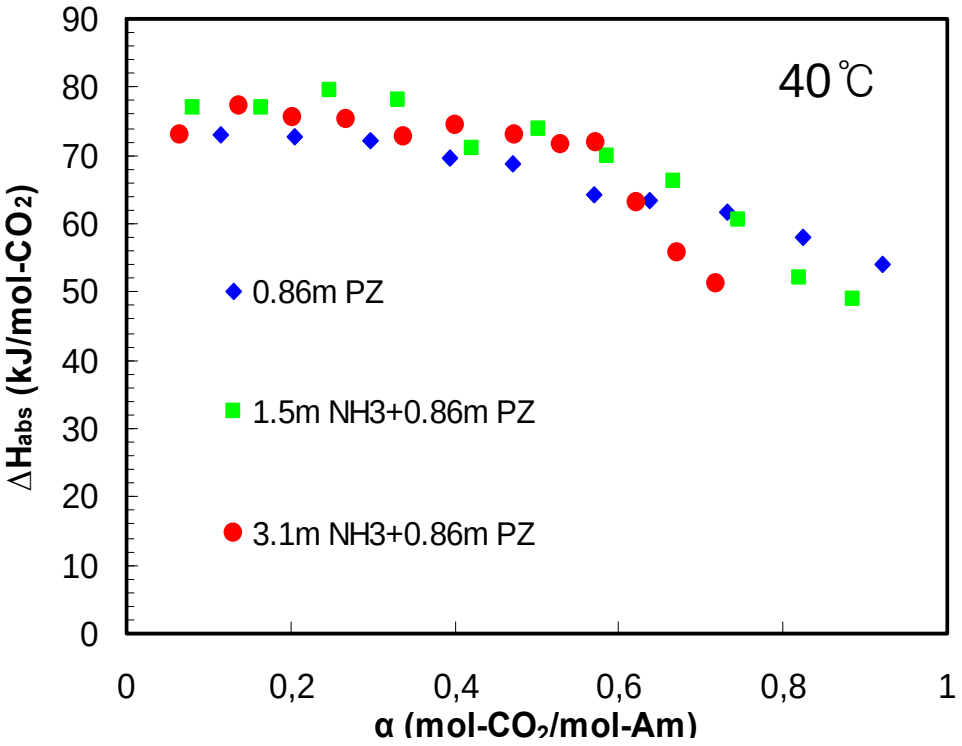

Fig.21. Heat of absorption of CO_2 with PZ and PZ blended NH_3 (aq) in different concentrations at 40 ℃

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NH_3/PZ blended solutions compared with other mixtures

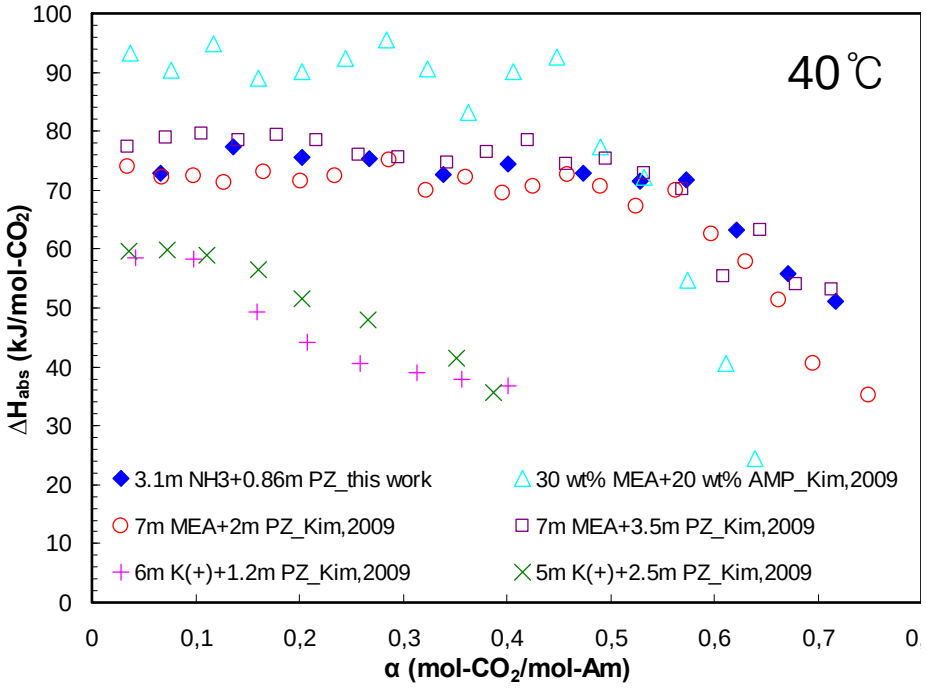

Fig.22. Heat of absorption of CO_2 with NH_3/PZ blended solutions measured by this work compared with other mixtures at 40℃

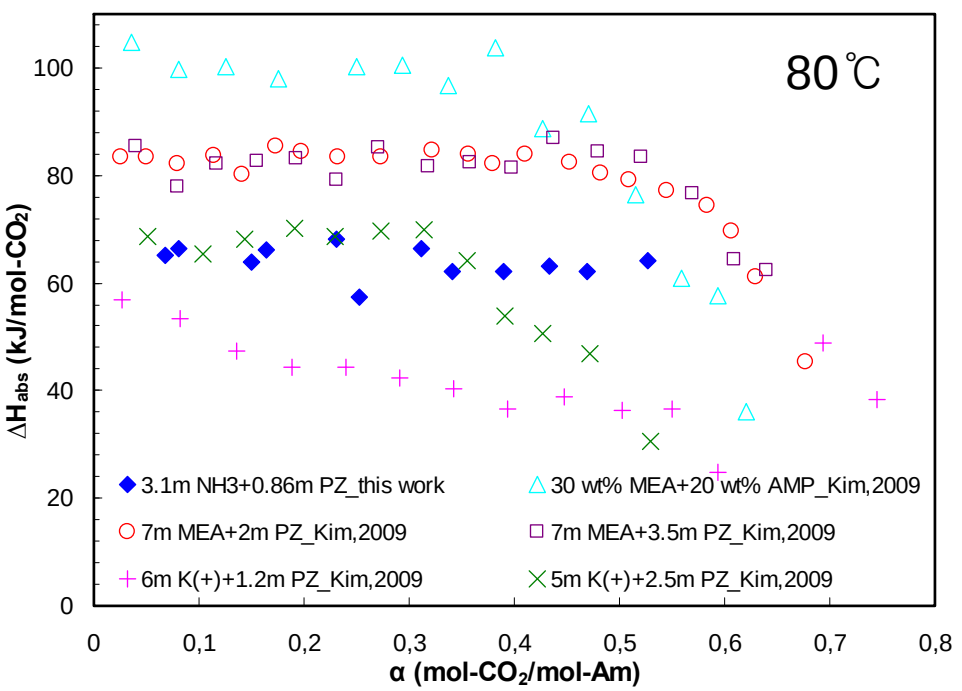

Fig.23. Heat of absorption of CO_2 with NH_3/PZ blended solutions measured by this work compared with other mixtures at 80℃

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Conclusions

- A reaction calorimeter CPA-122 was used to determine the heats of absorption (ΔH_{abs}) of CO_2 in NH_3 (aq), PZ solutions and their mixtures at 40, 60 and 80℃. The trends of ΔH_{abs} changing with CO_2 loading α were obtained at each temperature.
- ΔH_{abs} of CO_2 in 5 wt% NH_3 (aq) at low CO_2 loading interval (0-0.5) was estimated to be 74.8 kJ/mol CO_2 at 40℃ and 65.9 kJ/mol CO_2 at 80℃.
- ΔH_{abs} of CO_2 in 0.86m PZ solution were estimated to be 72-74 kJ/mol CO_2 at low CO_2 loading interval (0-0.5) at 40-80℃.
- ΔH_{abs} of CO_2 in NH_3/PZ blended solutions were measured and found to demonstrate a high degree of consistency with only NH_3 (aq)'s results during entire CO_2 loading interval at each temperature.
- The mechanism of the heat of absorption controlled by the reactions of CO_2 with NH_3 and PZ in the mixtures was also discussed.

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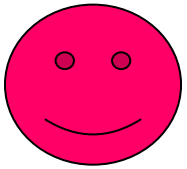
Thank you for your attention!



Questions?

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