



## Freezing Point Depression of Aqueous Solutions of DEEA, MAPA and DEEA-MAPA with and without CO<sub>2</sub> Loading

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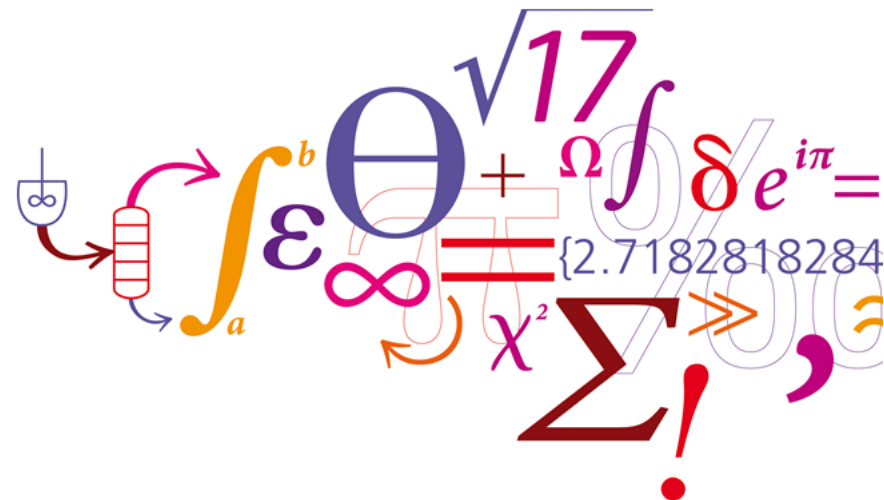
# Freezing Point Depression of Aqueous Solutions of DEEA, MAPA and DEEA-MAPA with and without CO<sub>2</sub> Loading

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Supervisor: Assoc. Prof. Kaj Thomsen

2nd ICEPE, 20-22 June, 2011



# PRESENTATION OUTLINE

- **Introduction**
- **Materials**
- **Reaction Mechanism**
- **Experimental Method**
- **Results**
- **Conclusions**
- **Future Work**

# INTRODUCTION

## Freezing Point Depression:

The phenomenon in which the freezing point of a Liquid (Solvent) is depressed when another compound is added in it. This means that the solution has lower freezing than the pure solvent.

## Why we need Freezing Point Depression Data???

- We want to model H<sub>2</sub>O-DEEA-MAPA-CO<sub>2</sub> system
- Water activity is a key parameter for the amount of water evaporated in the desorber
- Low water activity means less evaporation of water in the desorber and low energy consumption during solvent regeneration
- Water activity can be determined very accurately from Freezing point data

# MATERIALS

- **2-(Diethylamino)-ethanol OR DEEA (99%)**

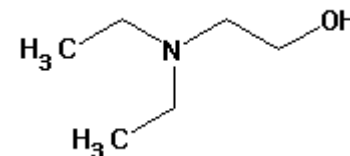
Clear liquid with light yellow colour

Freezing point = -70 °C

Boiling point = 163 °C

pH = 11.5 at 100 g/l at 20 °C

Completely soluble in water



- **3-(Methylamino)propylamine OR MAPA (97-98%)**

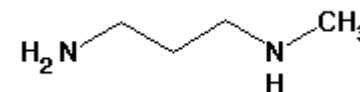
Clear and colourless liquid

Freezing point = -72 °C

Boiling point = 140 °C

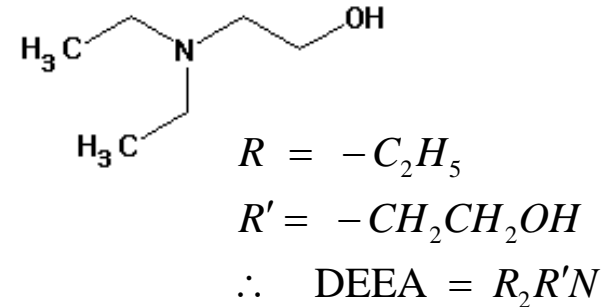
pH = 13.5 at 100 g/l at 20 °C

Completely soluble in water

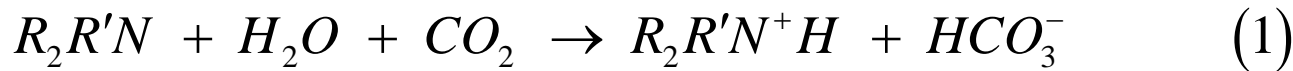


# REACTION MECHANISM

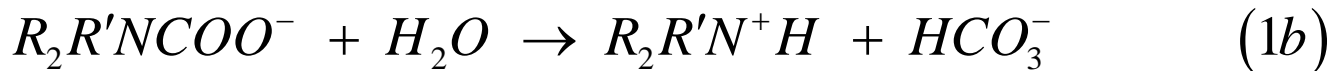
## 2-(Diethylamino)-ethanol OR DEEA



### Base catalytic effect on hydration of $CO_2$



### Zwitterion mechanism



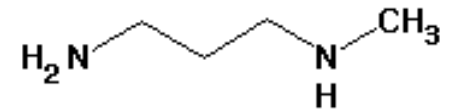
Following reactions may also take place simultaneously



[Ref] Vaidya, P. D.; Kenig, E. Y. A Study on  $CO_2$  Absorption Kinetics by Aqueous Solutions of *N,N*-Diethylethanolamine and *N*-Ethylethanolamine. *Chem. Eng. Technol.* **2009**, 32, No. 4, 556-563

# REACTION MECHANISM

## 3-(Methylamino)propylamine OR MAPA



$$R = -C_3H_6 \quad \text{and} \quad R' = -CH_3$$

$$\therefore \text{MAPA} = H_2NRR'NH$$

### Protonation:



8 Possible  
species of  
MAPA

### Carbamate:

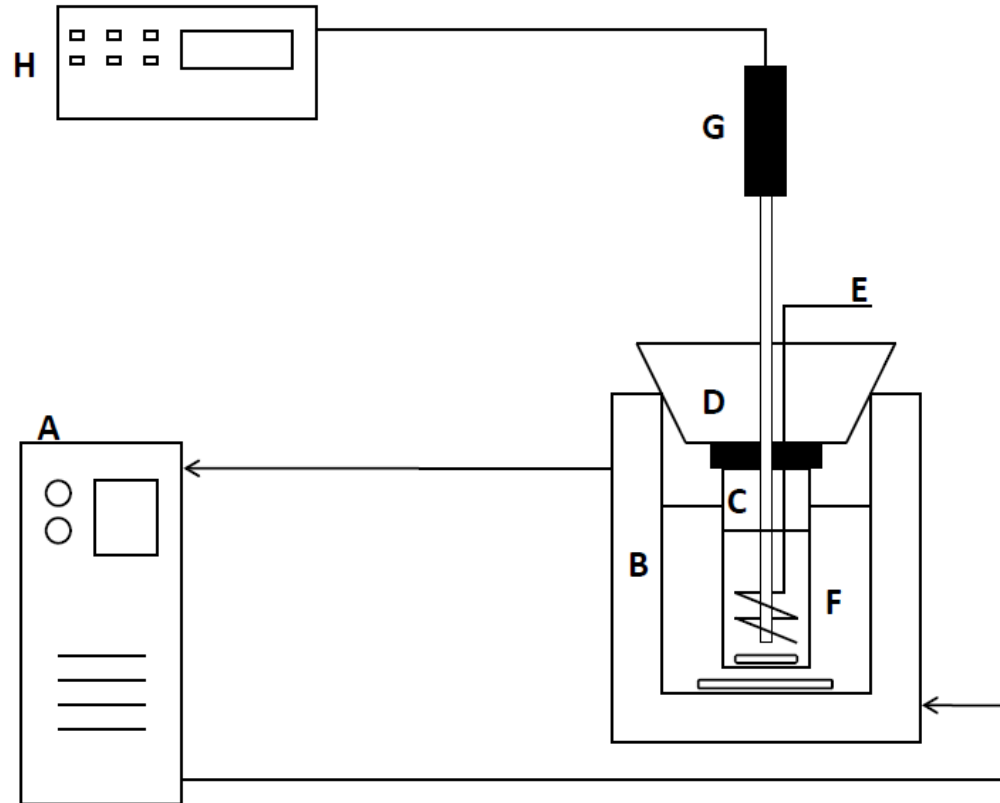


### Protonated Carbamate:



# EXPERIMENTAL METHOD

- A, Thermostatic bath with ethanol
- B, Cooling jacket
- C, Sample glass with magnetic stirrer
- D, Rubber stopper with sample glass lid
- E, Device for manual stirring
- F, Controlled temperature ethanol bath with magnetic stirrer
- G, Pt100 Thermometer
- H, Data acquisition unit

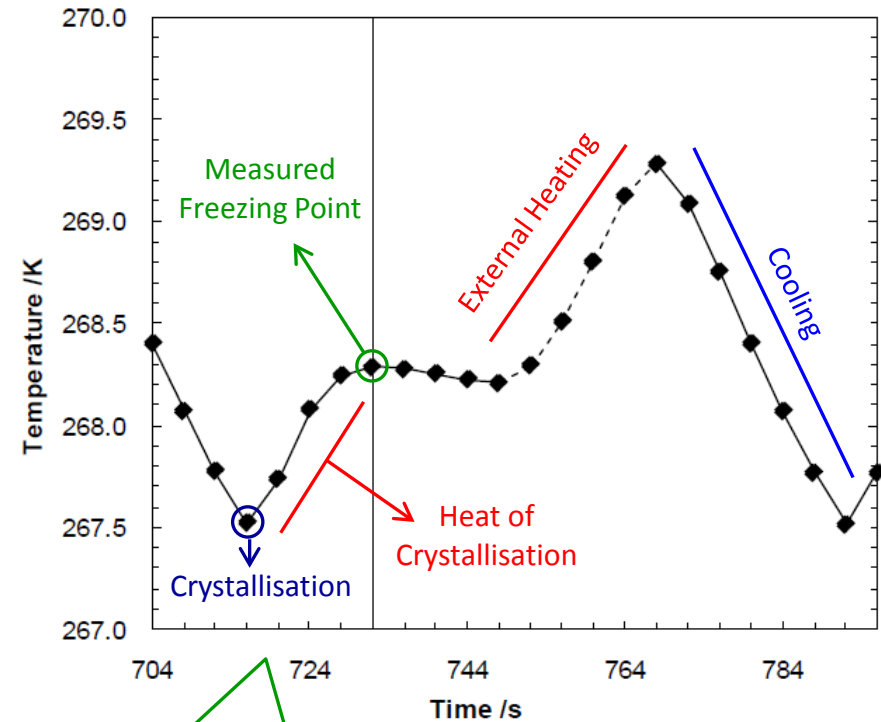
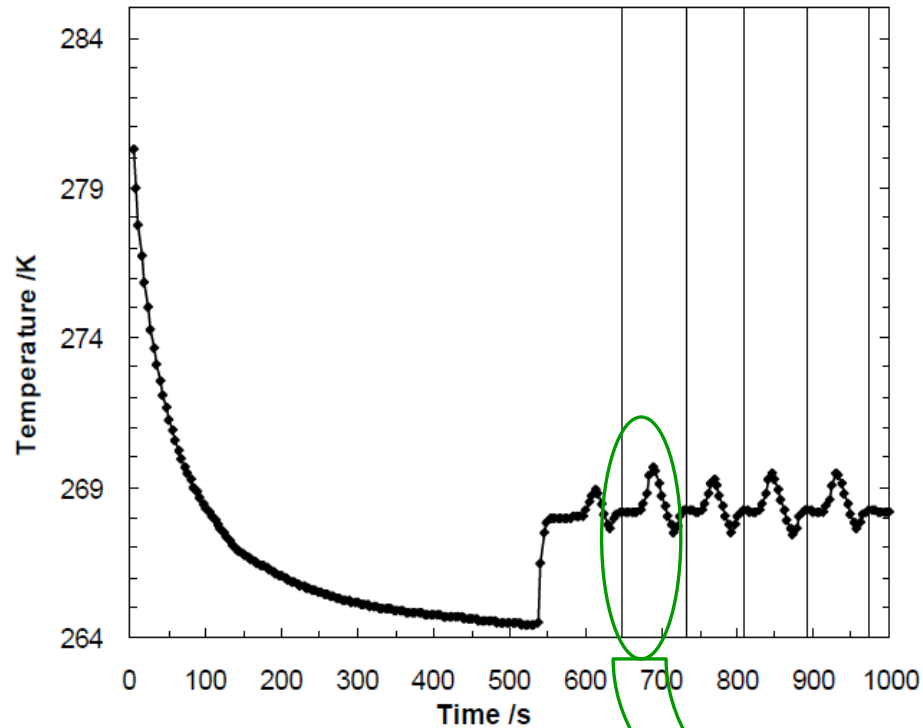


Experimental Setup

[Ref] Fosbøl, P. L.; Pedersen, M. G.; Thomsen, K. Freezing Point Depressions of Aqueous MEA, MDEA, and MEA-MDEA Measured with a New Apparatus. *J. Chem. & Eng. Data* **2010**, Special Issue: John M. Prausnitz Festschrift



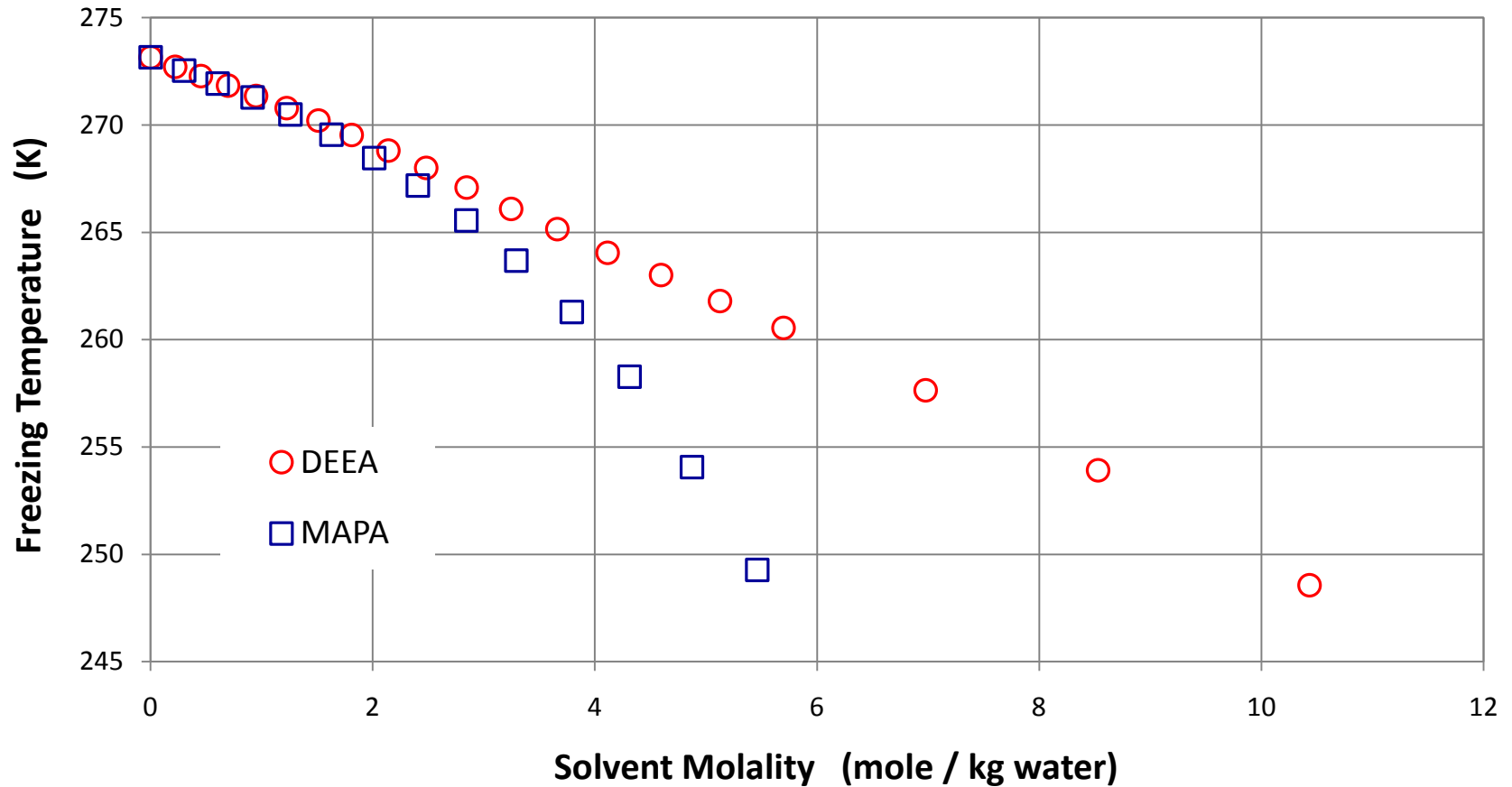
# EXPERIMENTAL METHOD



[Ref] Fosbøl, P. L.; Pedersen, M. G.; Thomsen, K. Freezing Point Depressions of Aqueous MEA, MDEA, and MEA-MDEA Measured with a New Apparatus. *J. Chem. & Eng. Data* **2010**, Special Issue: John M. Prausnitz Festschrift

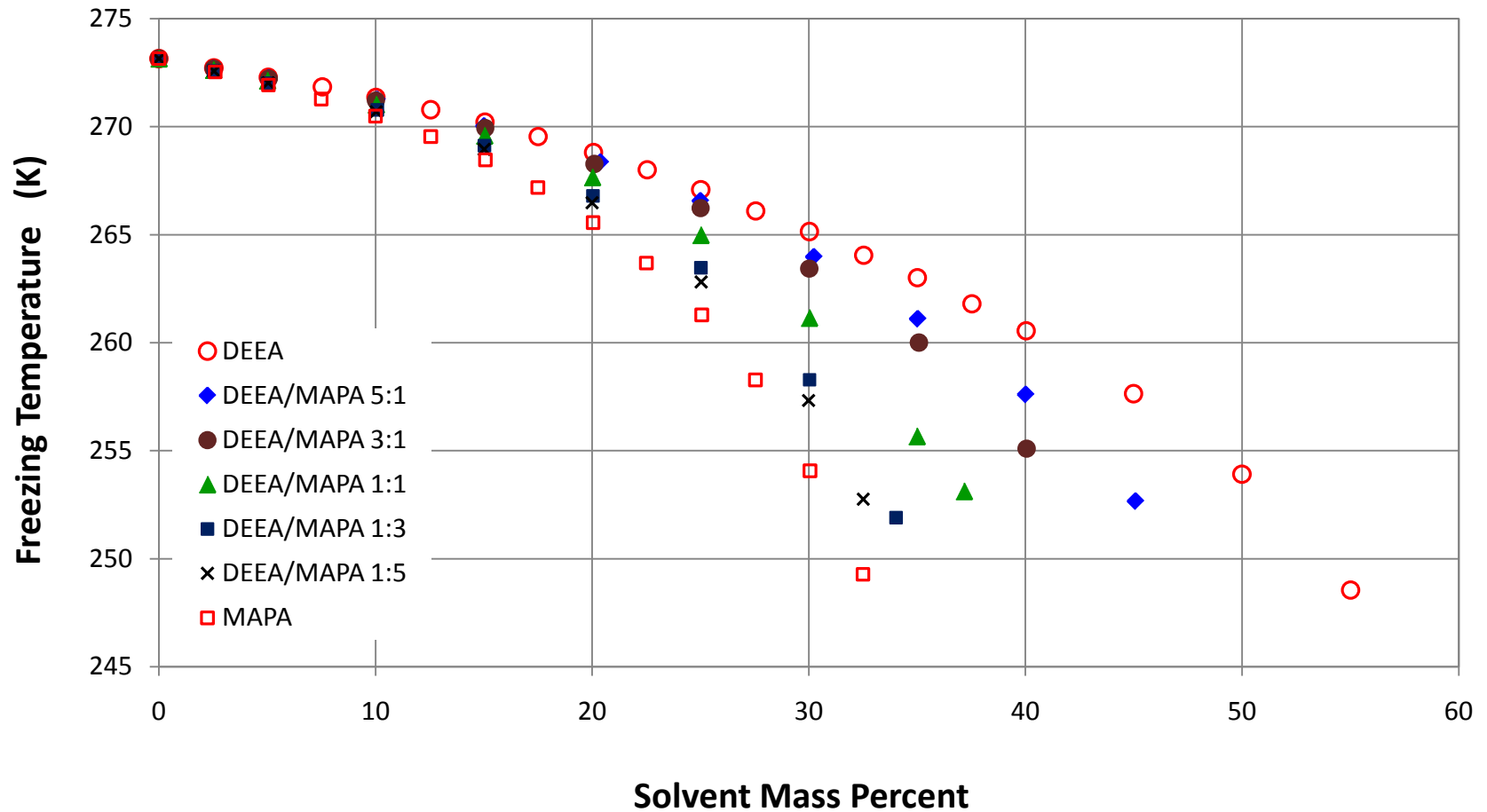
# RESULTS

## Aqueous solutions of DEEA and MAPA



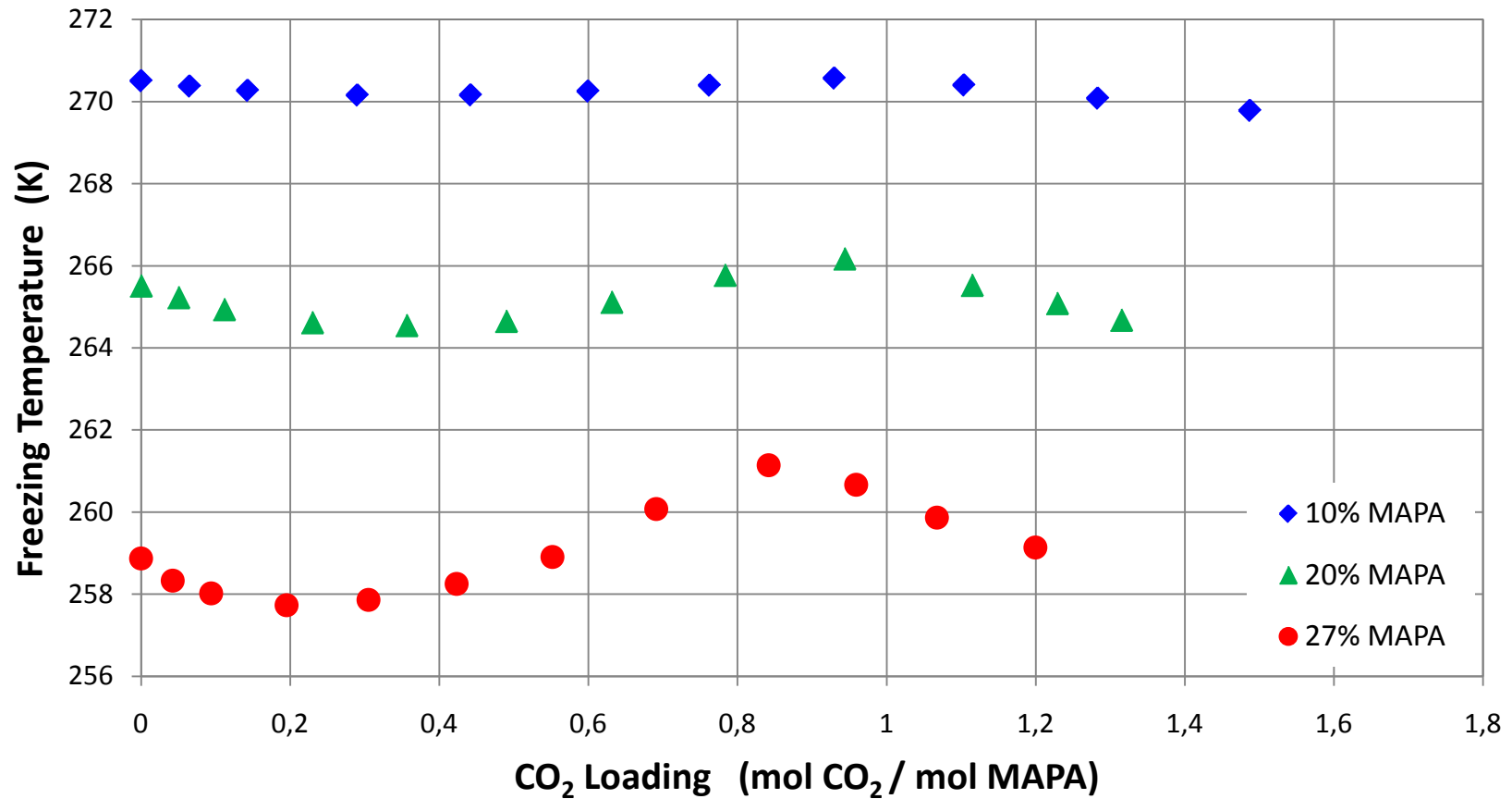
# RESULTS

## Aqueous solutions of DEEA-MAPA with different molar ratios



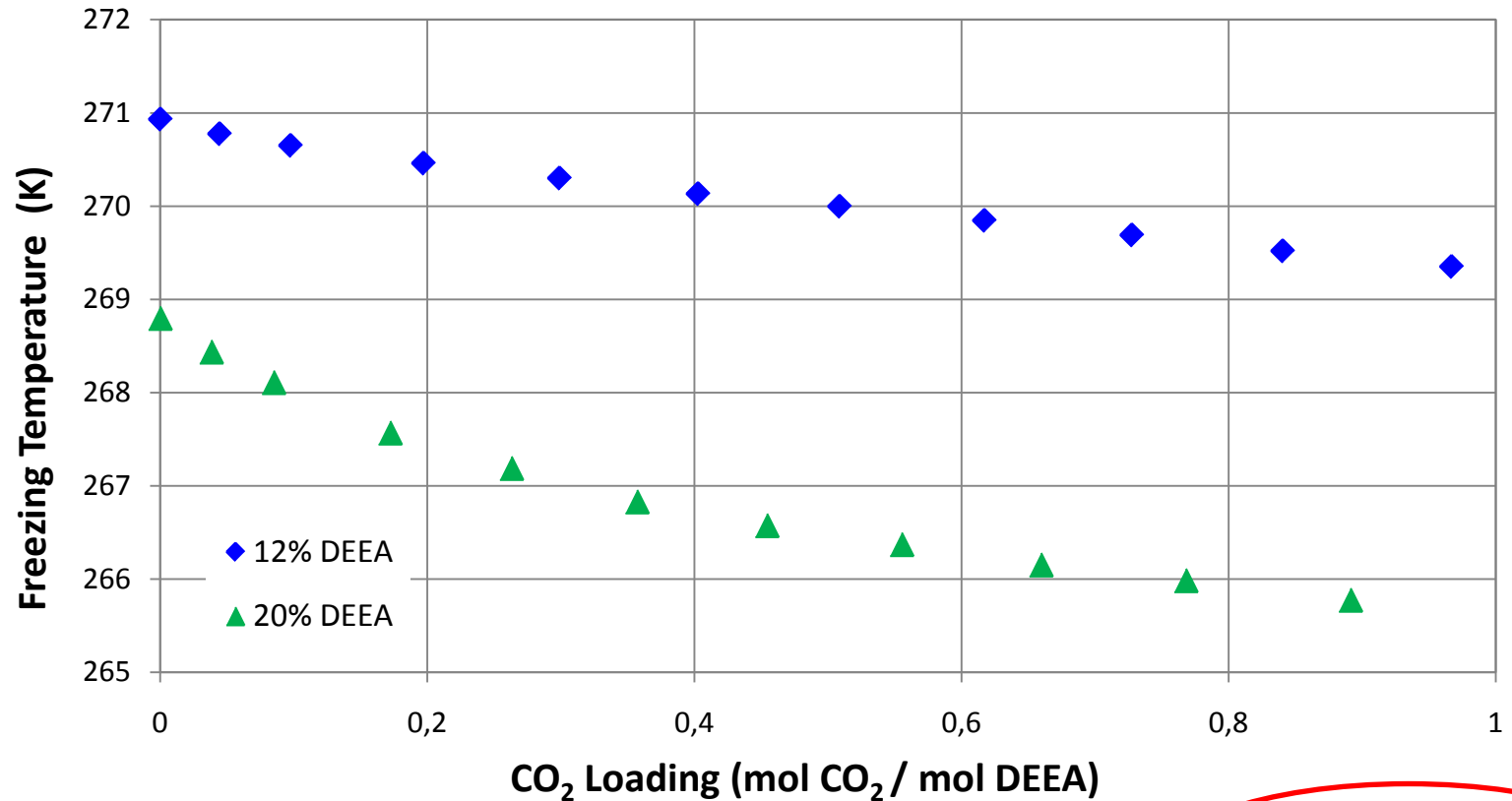
# RESULTS

## Aqueous solutions of MAPA loaded with CO<sub>2</sub>



# RESULTS

## Aqueous solutions of DEEA loaded with CO<sub>2</sub>



Work in Progress for 30%  
and 35% DEEA solutions

# CONCLUSIONS

- Freezing point depression (FPD) are measured for H<sub>2</sub>O-DEEA and H<sub>2</sub>O-MAPA and also for H<sub>2</sub>O-DEEA-MAPA for different molar ratios of DEEA/MAPA [Data point = 76]
- FPD are measured for H<sub>2</sub>O-DEEA-CO<sub>2</sub> and H<sub>2</sub>O-MAPA-CO<sub>2</sub> systems at different CO<sub>2</sub> loading [Data points = 57]
- Measured freezing point data illustrates that the MAPA-water interaction is stronger than DEEA-water interaction
- The measured data can be used for modeling CO<sub>2</sub> absorption/desorption system when aqueous blend of DEEA/MAPA is used

# FUTURE WORK

- Measurement of FPD for 30% and 35% DEEA solutions with different CO<sub>2</sub> loadings
- Measurement of freezing points For aqueous solutions of DEEA-MAPA with different molar ratios loaded with CO<sub>2</sub>
- Development of correlations for the freezing points as a function of the solution composition
- Thermodynamic modeling of H<sub>2</sub>O-DEEA-MAPA-CO<sub>2</sub> system using Extended UNIQUAC model

**THANK YOU  
FOR  
YOUR ATTENTION**

**QUESTIONS ??????**