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High pressure vapour liquid equilibrium of alkanolamine, water, carbon dioxide and methane systems

Øystein Jonassen[1], Inna Kim[2], Hallvard F. Svendsen[1]

[1]Norwegian University of Science and Technology

[2]SINTEF Materials and Chemistry

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Outline

- Introduction
  - *”A Green Sea” –project*
- Dimethylmonoethanolamine, DMMEA
- High pressure vapor-liquid equilibrium
- Conclusions

Background - ”A green sea” -project

- 43% of the remaining gas resources contain CO_2 and H_2S (world energy outlook, 2008)

	High H_2S only (tcm)	High CO_2 only (tcm)	High H_2S and CO_2 (tcm)	Total	
				(tcm)	% of total reserves
Mexico & Latin America	0,3	1,1	0,3	1,7	21
Europe	0,1	0,7	0,3	1,1	19
Former Soviet Union	0,8	10,1	7,3	18,2	34
Africa	0,0	0,5	0,5	1,0	8
Middle East	2,6	0,4	40,9	44,0	60
Asia-Pacific	0,3	4,4	2,3	7,1	46
World	**4,2**	**17,2**	**51,6**	**73,1**	**43**

World proven sour-gas reserves, 2006. Note: Excludes North America. High H_2S is more than 100 ppm, high CO_2 is more than 2%. Source: World Energy Outlook, 2008.

Background - ”A green sea”-project

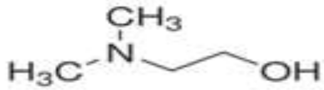
- Overall objective is to identify, mature and evaluate technologies and concepts for acid gas removal
  - *Absorption, Adsorption, Membranes, Cryogenic methods*
- Focus on offshore sweetening of natural gas
  - *High pressure*
  - *Small ”footprint”*
  - *Captured CO_2 can be used for increased oil recovery (IOR)*
  - *Pipe line specification (2.5% CO_2) and LNG specification (approx. 50ppm CO_2)*
- Identify new solvent systems for natural gas sweetening that are environmentally friendly.
- Project partners
  - *Statoil, Gassco, Petrobras and the Research Council of Norway*

Classification categories and criteria of chemicals used offshore as stated by the Norwegian Activities Regulation (PSA 2010)

Category	Criteria – ecotoxicity test	Actions
Black	• The priority list from Storting White Paper No. 21 • (2004-2005). • The OSPAR List of Chemicals for Priority Action Substances that: • Have biodegradability of BOD28 < 20% and bioaccumulation potential of Log Pow ≥ 5. • Have biodegradability of BOD28 < 20% and are toxic (LC50 or EC50 ≤ 10mg/l) • Are harmful in a mutagenic or reproductive manner.	Not discharged
Red	• Non-organic substances that have acute toxicity EC50 or LC50 ≤ 1 mg/l • Organic substances that have biodegradability BOD28 < 20% • Organic substances that meet two of the three following criteria: ○ Biodegradability BOD28 < 60% ○ Bioaccumulation potential Log Pow ≥ 3 and molecular weight < 700 or ○ Acute toxicity LC50 or EC50 ≤ 10 mg/l	Phased out or replaced
Yellow	• Substances that are not defined as red or black and, • Substance which are not on the PLONOR list	Accepted
Green	• Chemicals expected to have NO environmental effects • PLONOR list	Testing not required

Dimethylmonoethanolamine - DMMEA

- DMMEA is a tertiary amine



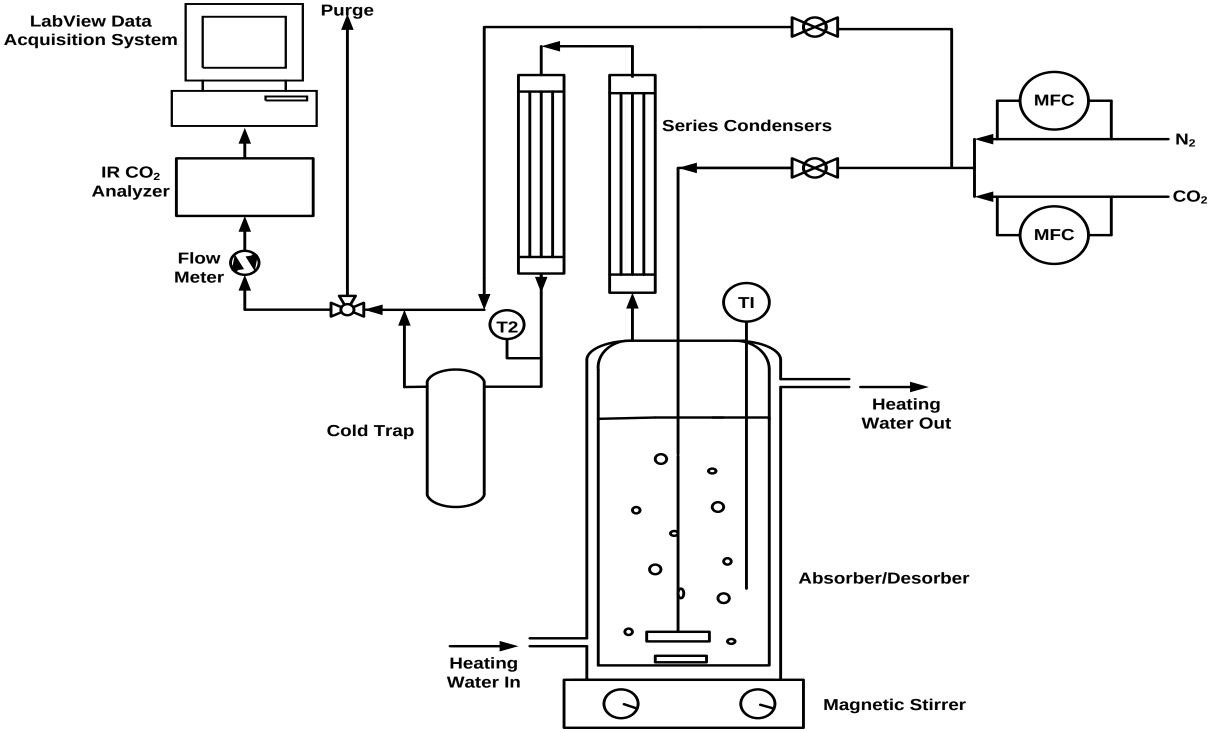
Chemical Structure of DMMEA

- DMMEA is a stronger base than MDEA (pKa of 9.2 vs 8.5 for MDEA)
- It is a smaller molecule than MDEA (DMMEA: 89.14 g/mol, MDEA: 119.16 g/mol)
- DMMEA is classified as a yellow chemical, (*Eide-Haugmo, PhD thesis 2011*)
  - *Readily biodegradeable*
  - *Low bioaccumulation potential*
  - *Not toxic*
- It showed lower thermal degradation after 5 weeks at 135°C with a loading of 0.5 mol CO_2/mol amine than MDEA (*Eide-Haugmo, PhD thesis 2011*)

Solvent screening - method

Rapid screening apparatus

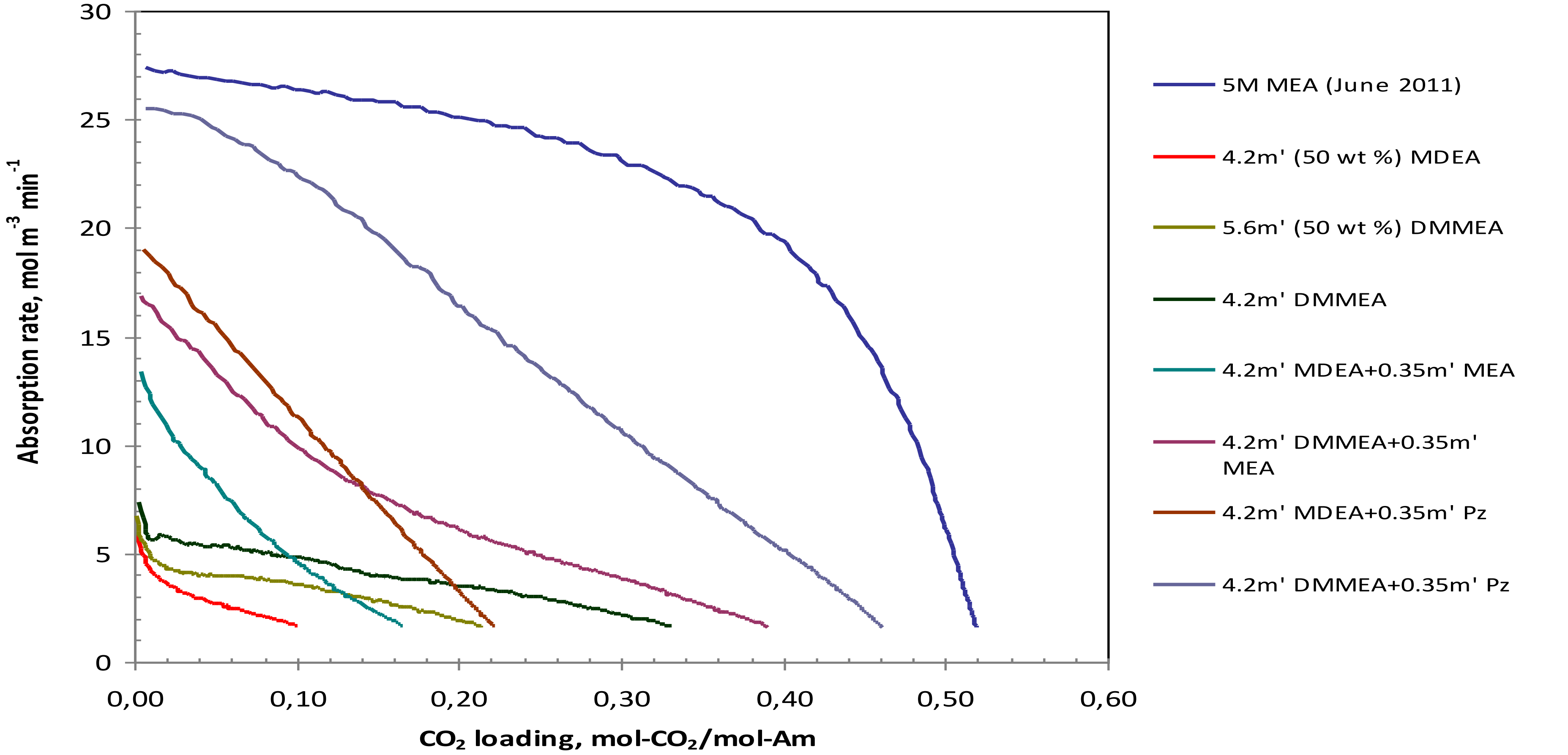
- *Absorption at 40°C*
- *Desorption at 80°C*
- *Atmospheric pressure*



Solvent screening – systems tested

System	Component 1		Component 2	
	Name	**C, mol/kg-solution**	**Name**	**C, mol/kg-solution**
1	MDEA	**4.2**	-	**-**
2	DMMEA	**5.6**	-	**-**
3	DMMEA	**4.2**	-	**-**
4	MDEA	**4.2**	MEA	**0.35**
5	DMMEA	**4.2**	MEA	**0.35**
6	MDEA	**4.2**	Piperazine	**0.35**
7	DMMEA	**4.2**	Piperazine	**0.35**

Solvent screening - results



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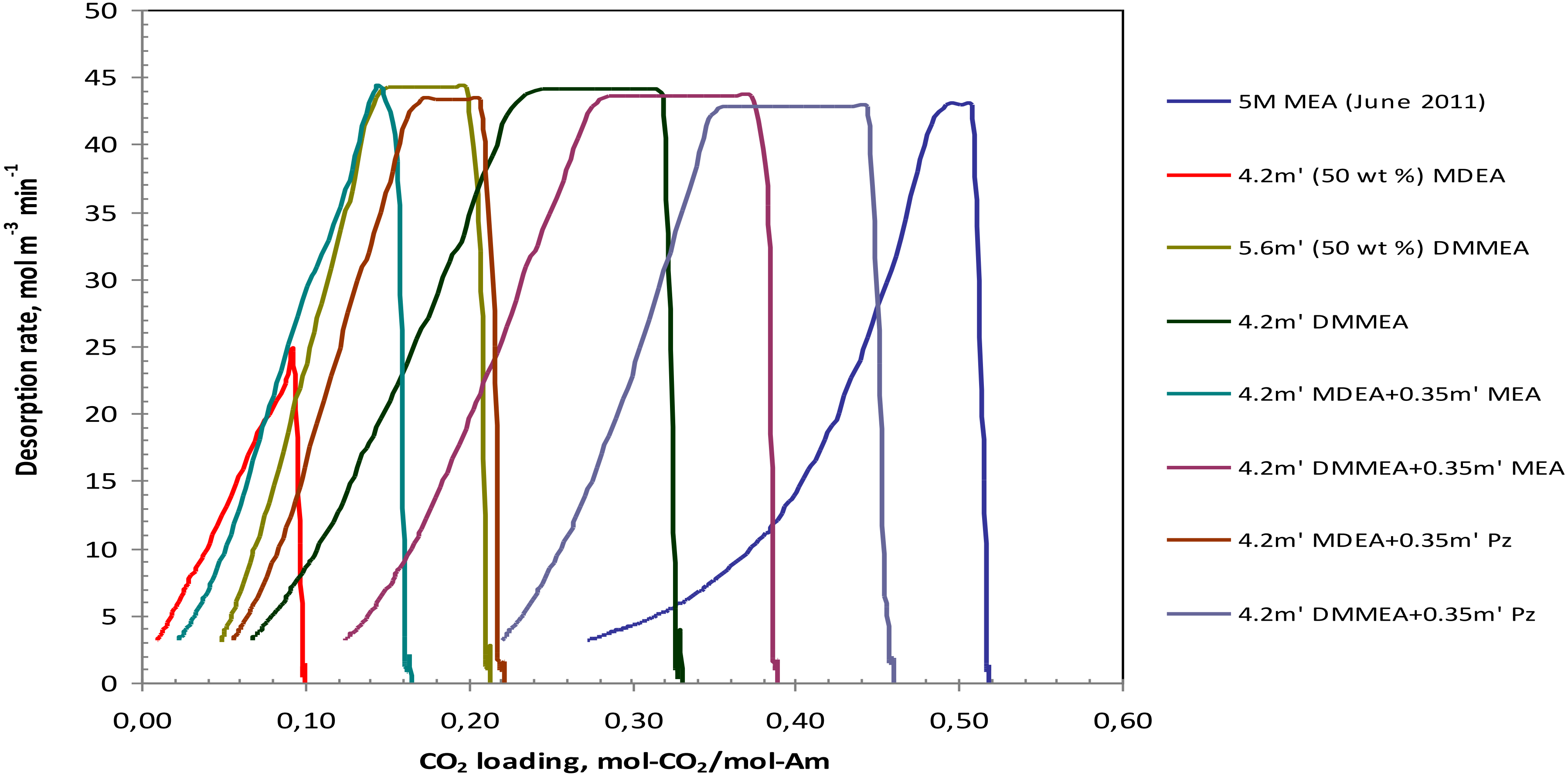
Solvent screening - results



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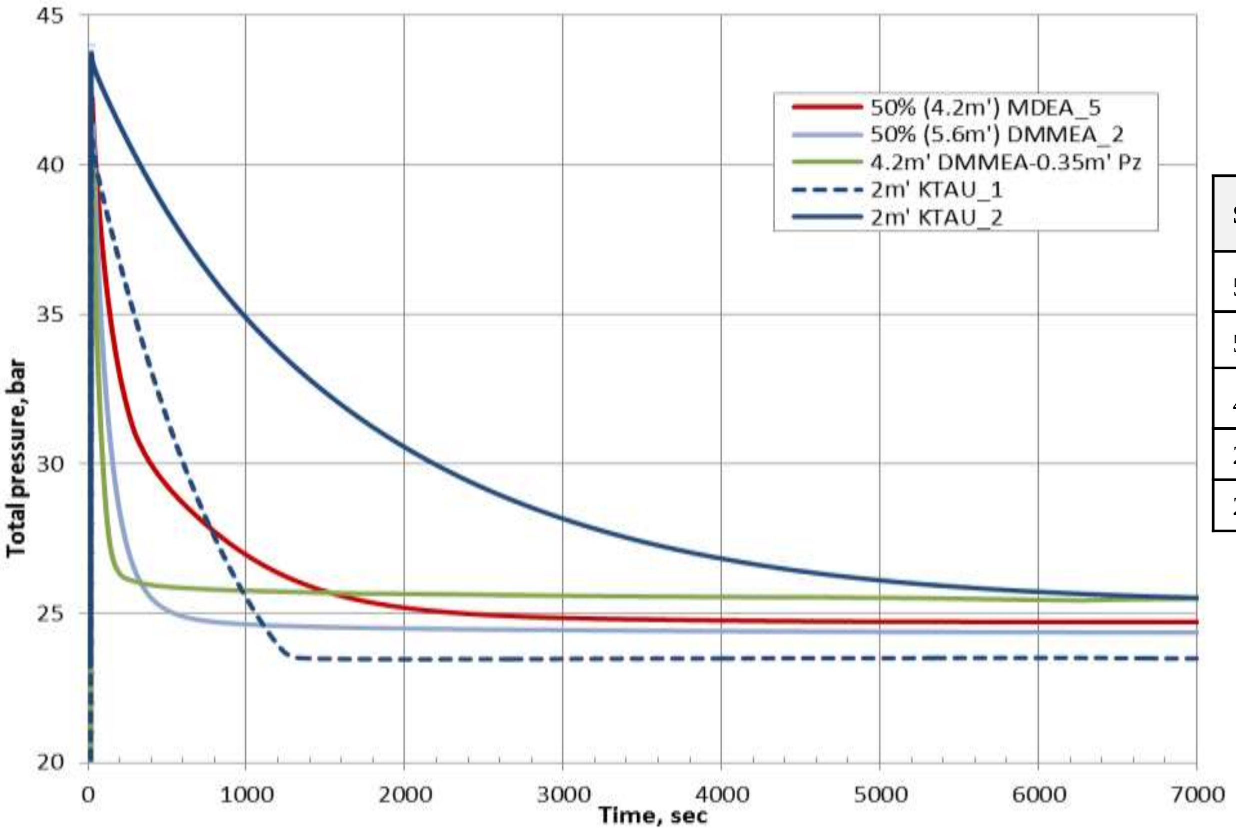
High pressure solvent screening - results



System	Loading	P_{CO2}, kPa
50% MDEA	0.257	29.086
50% DMMEA	0.203	5.065
4.2m' DMMEA+0.35m' Pz	0.229	12.923
2m' Ktau_1	0.116	8.707
2m' Ktau_2	0.280	241.16

Absorption curves from the high pressure screening experiments. Absorption temperature 40oC, 50 % CO2 – 50 % CH4 gas mixture

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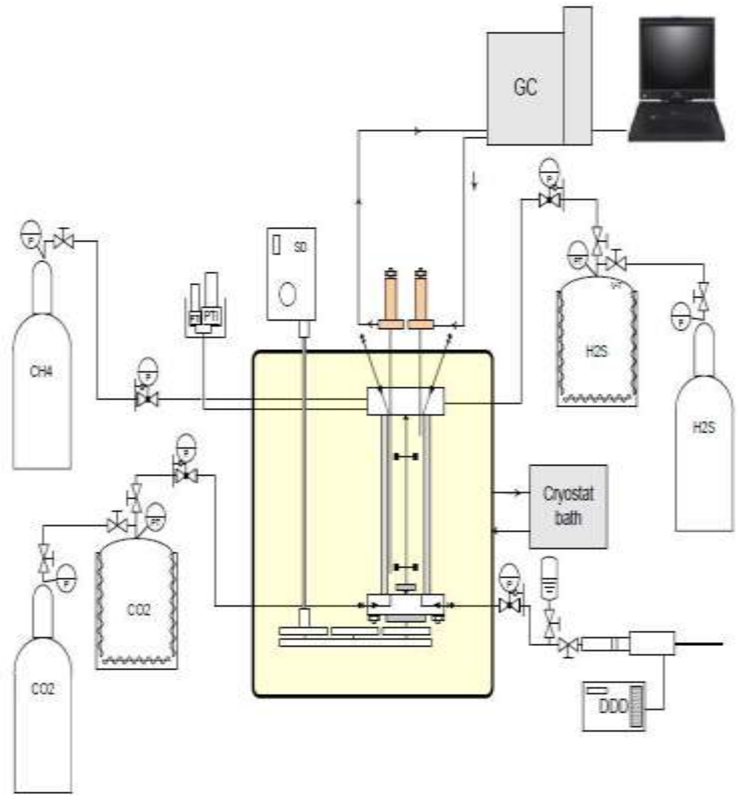
High pressure VLE – method

- Pressure region
  - *0 – 20 MPa*
- Temperature region
  - *(-20) - 180°C*

- Equilibrium cell
  - *Sapphire tube equilibrium cell (approx. 32cm3)*
  - *Possibility for adding other impurities (mercaptans)*
- Sample analysis
  - *Online gas chromotograph (GC)*
    - *Vapor phase and gas phase*



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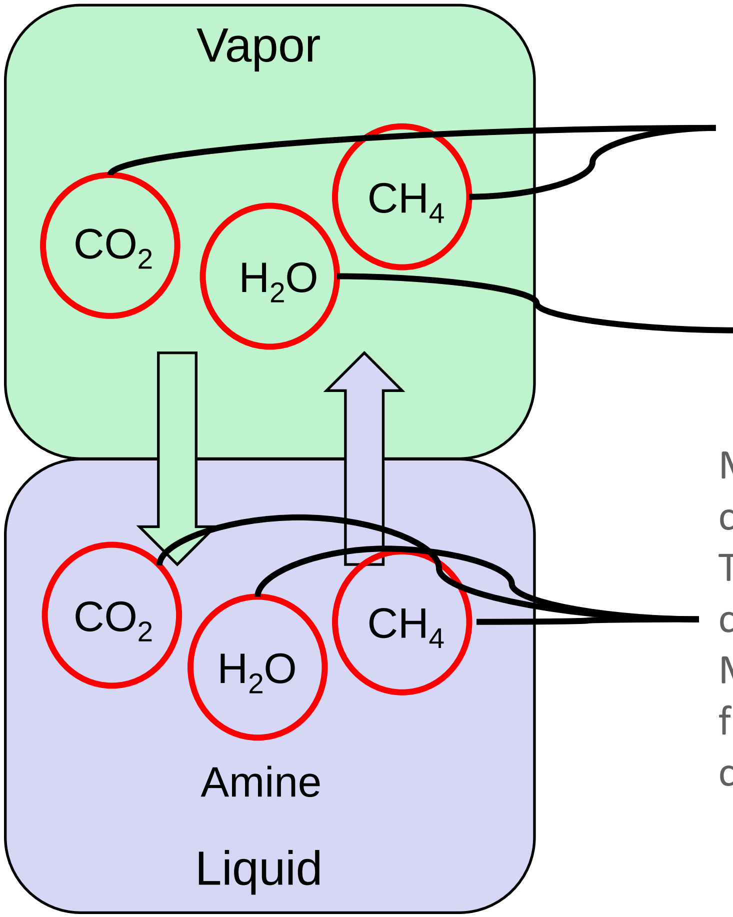
High pressure VLE



Mole fractions determined using gas chromatography. Partial pressures calculated from Daltons law.

Difficult to measure the water content in the vapor phase using GC. It is therefore neglected.

Mole fractions determined using gas chromatography.
The water/amine ratio is assumed to be constant.
Moles of amine in the sample is calculated from the GC measurement of the water content in the sample.

Experimental procedure

Filling the cell with solvent and increasing temperature

Adding CO_2 to the cell

At equilibrium, both phases are sampled

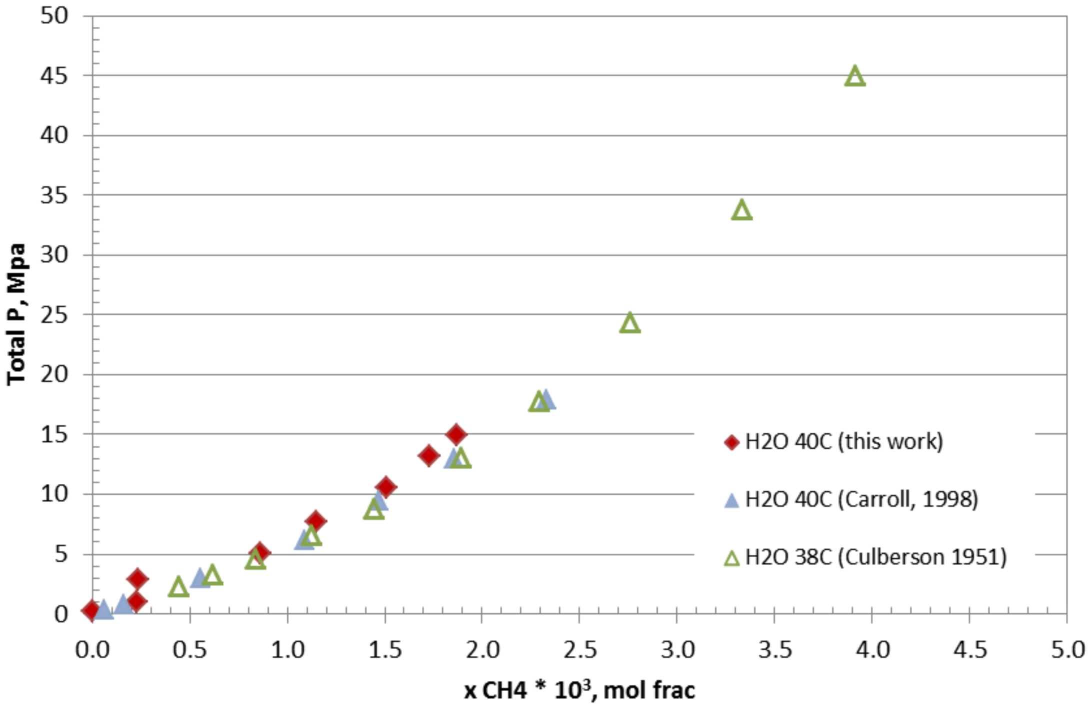
Pressure = 45 bar

Pressure is further increased with methane

At equilibrium, both phases are sampled

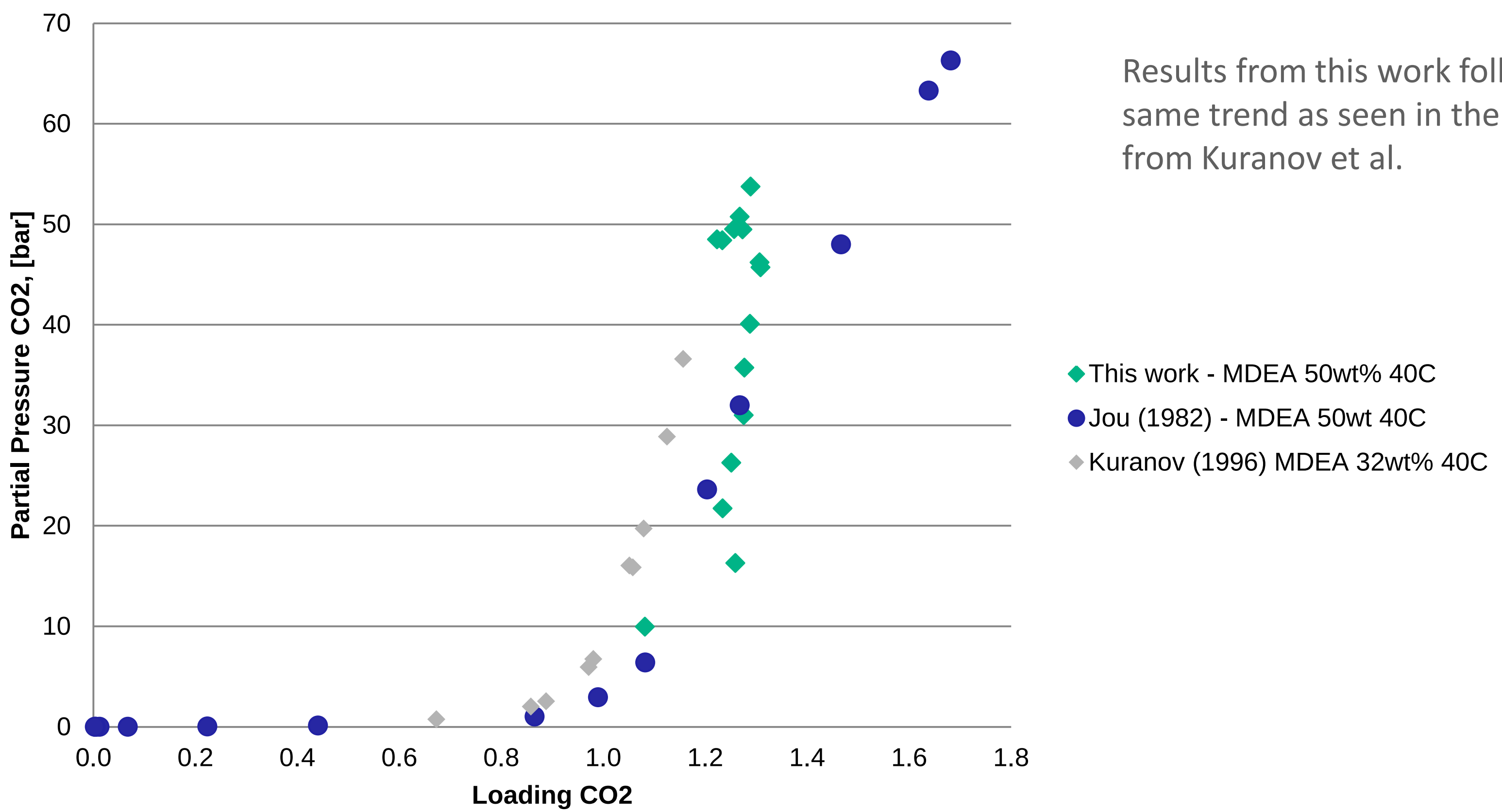
Pressure = 150bar

Methane solubility in water – verifying the experimental method



- Validity of the experimental set-up
- Slightly lower solubility of methane from this work
- Methane solubility results sensitive towards the GC calibration curve of water

Equilibrium CO_2 partial pressures



Results from this work follow the same trend as seen in the data from Kuranov et al.

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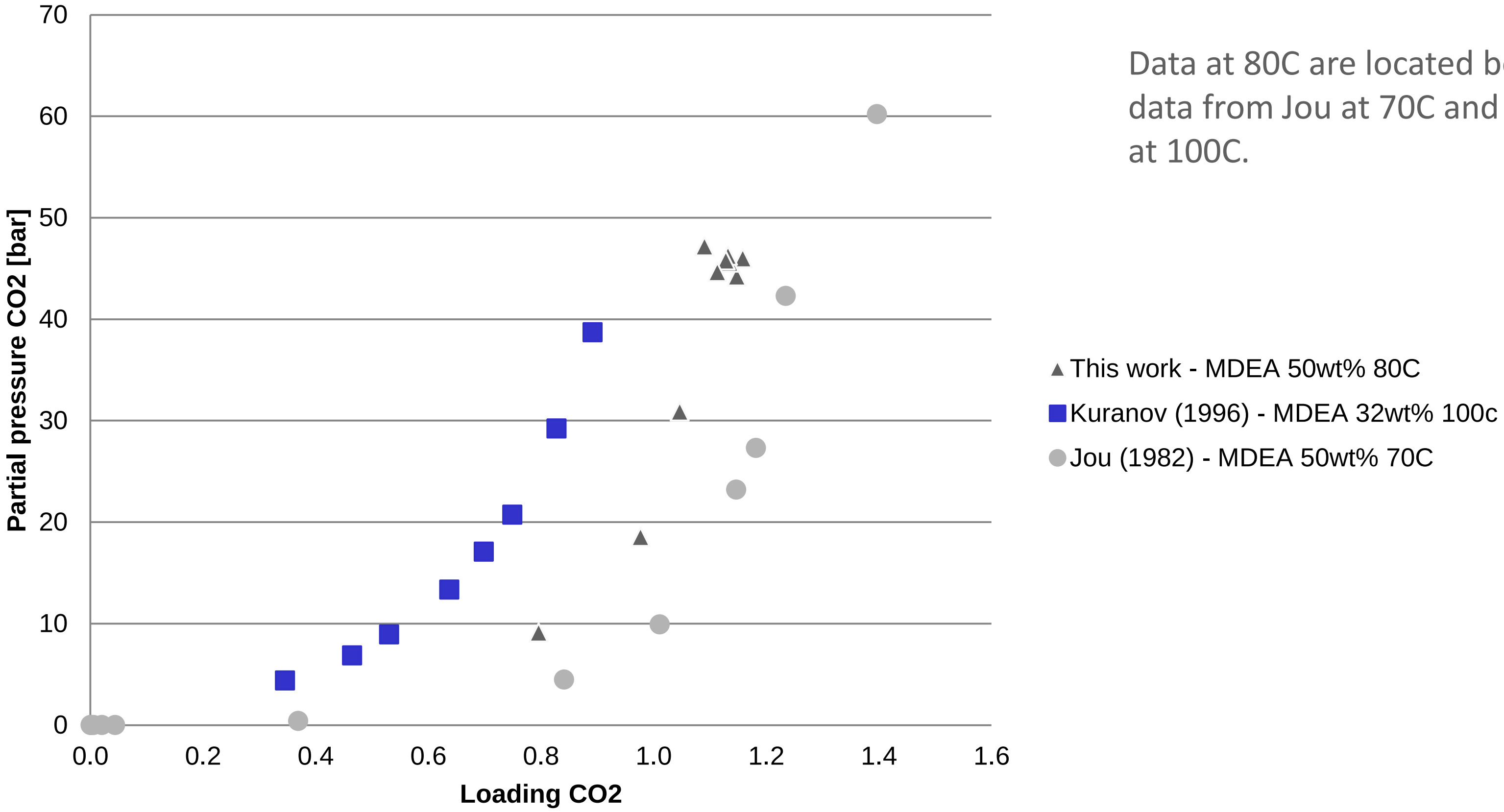
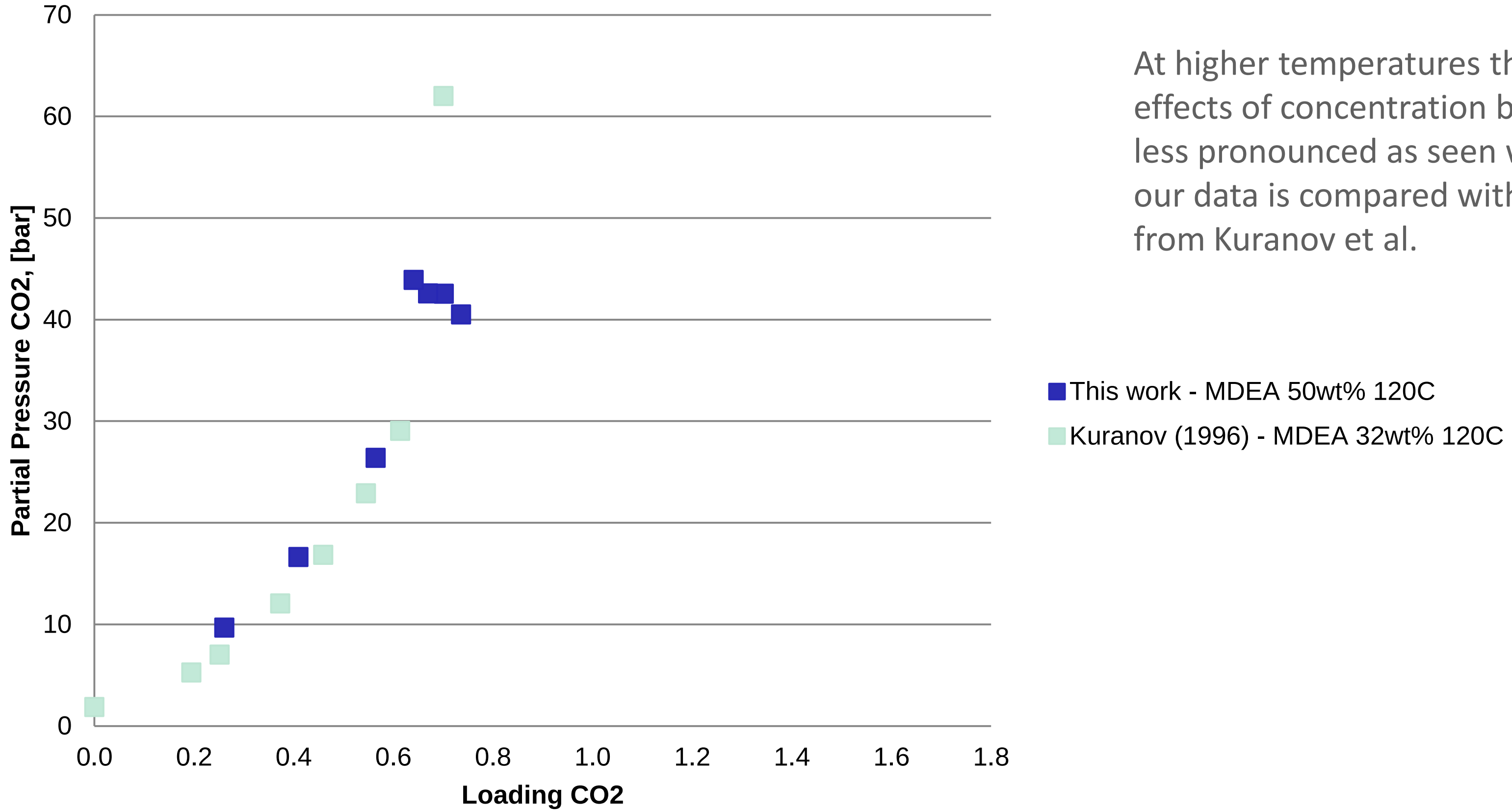
Equilibrium CO_2 partial pressures



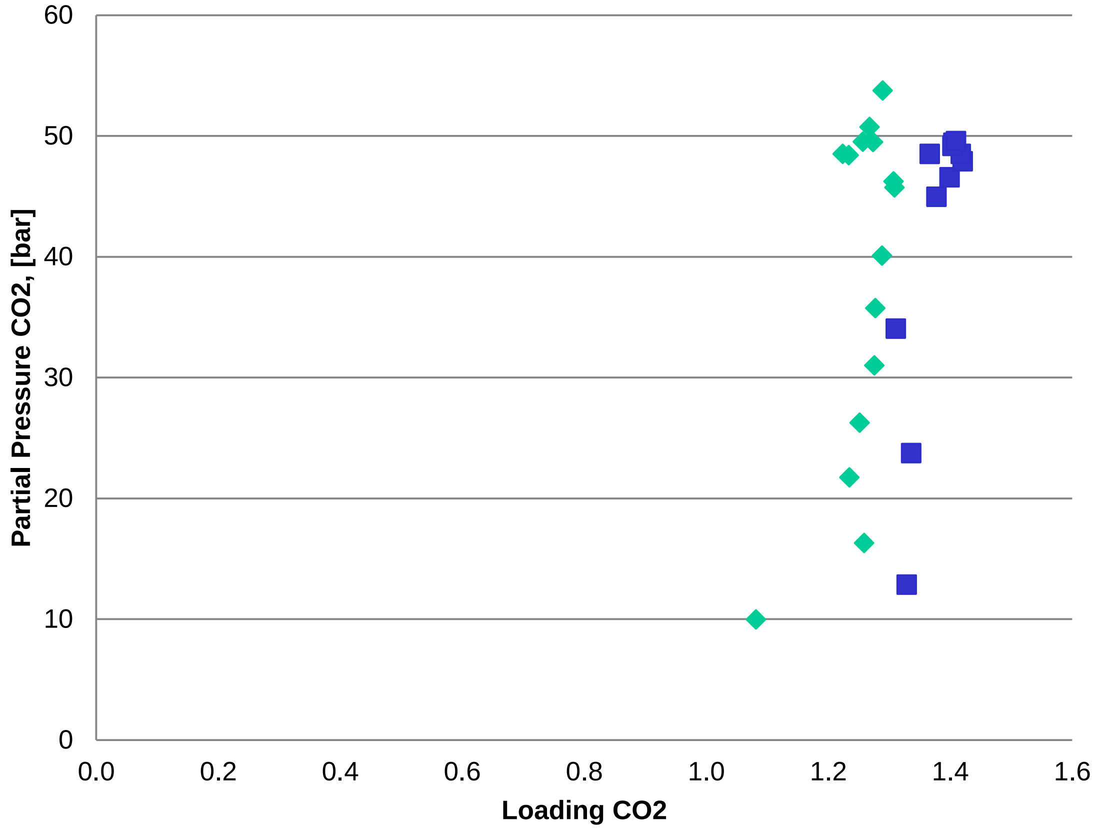
Data at 80C are located between data from Jou at 70C and Kuranov at 100C.

Equilibrium CO_2 partial pressures



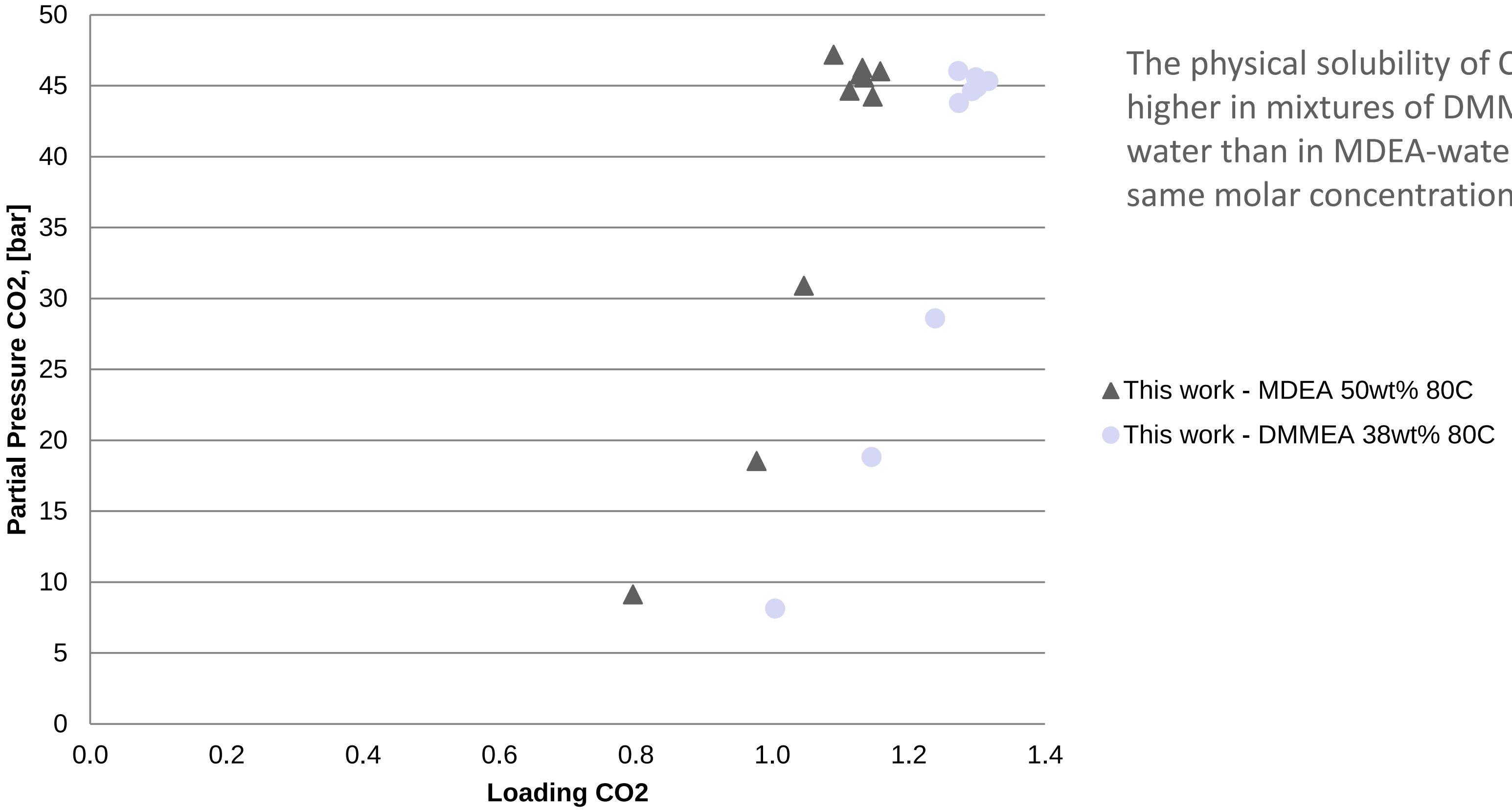
At higher temperatures the effects of concentration becomes less pronounced as seen when our data is compared with data from Kuranov et al.

Equilibrium CO_2 partial pressures – MDEA vs DMMEA



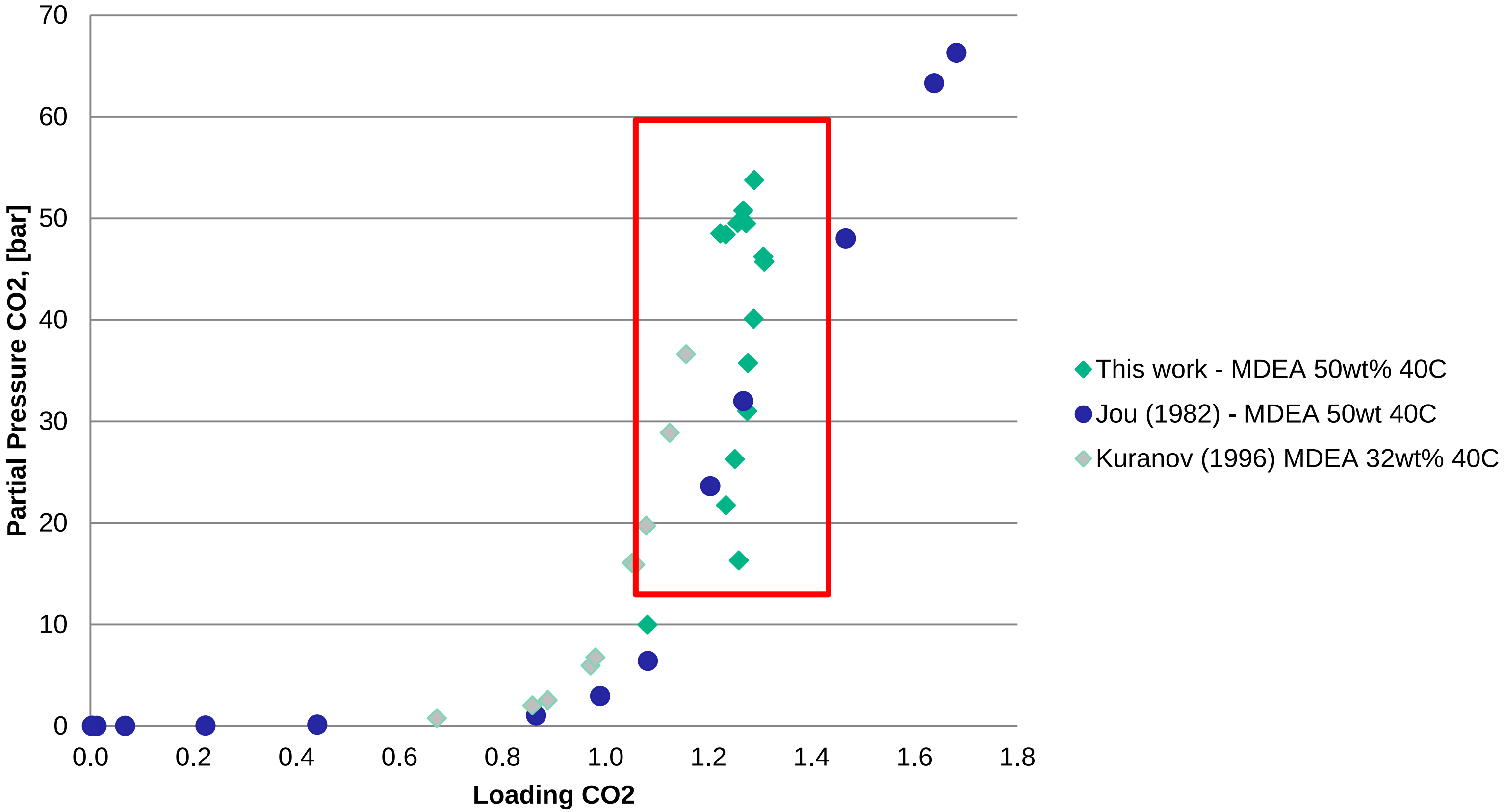
The physical solubility of CO_2 is higher in mixtures of DMMEA-water than in MDEA-water at the same molar concentration.

Equilibrium CO_2 partial pressures – MDEA vs DMMEA



The physical solubility of CO_2 is higher in mixtures of DMMEA-water than in MDEA-water at the same molar concentration.

How does the addition of methane affect the CO_2 liquid loading?



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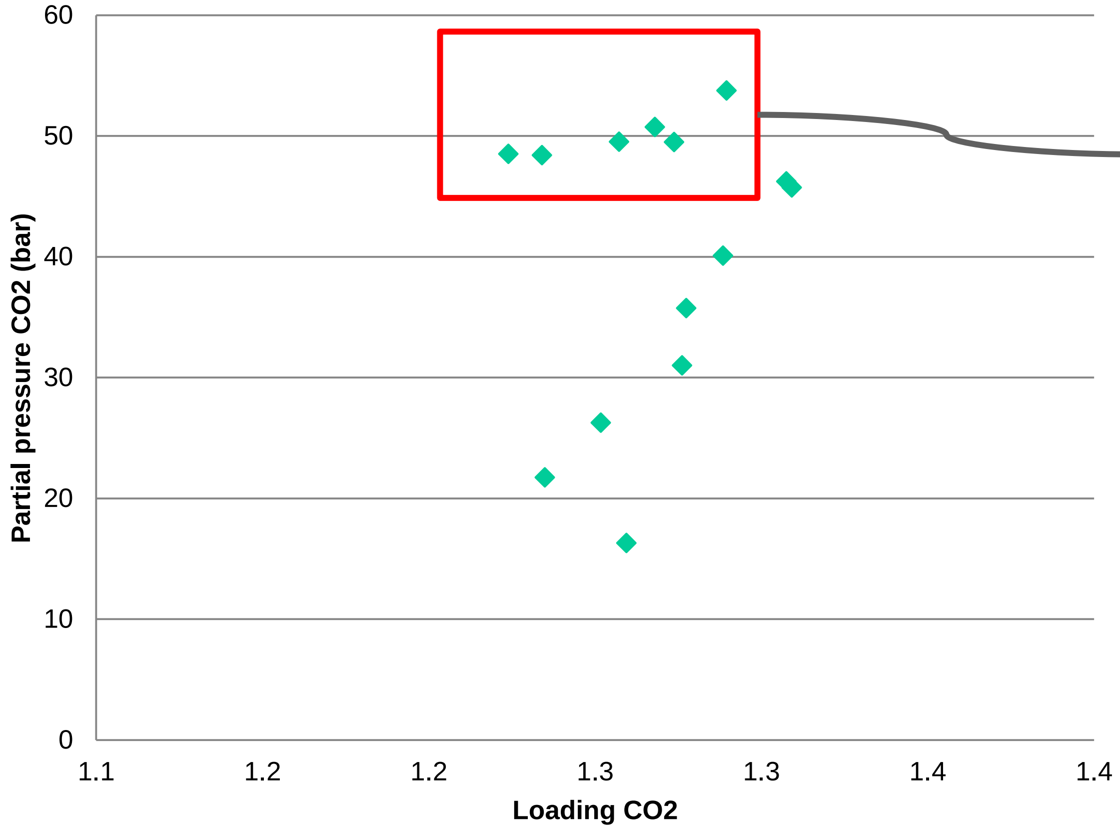
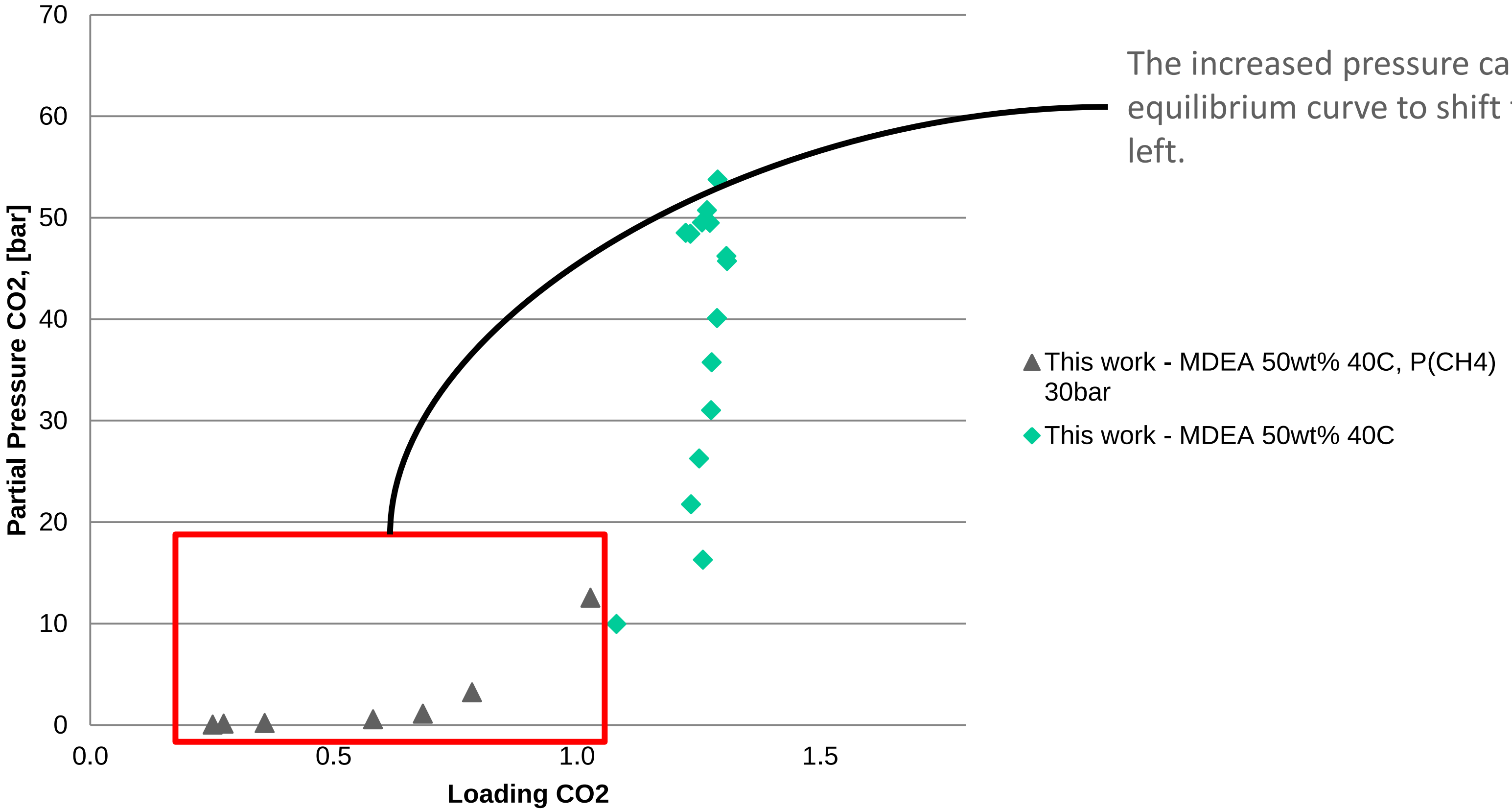
How does the addition of methane affect the CO_2 liquid loading?



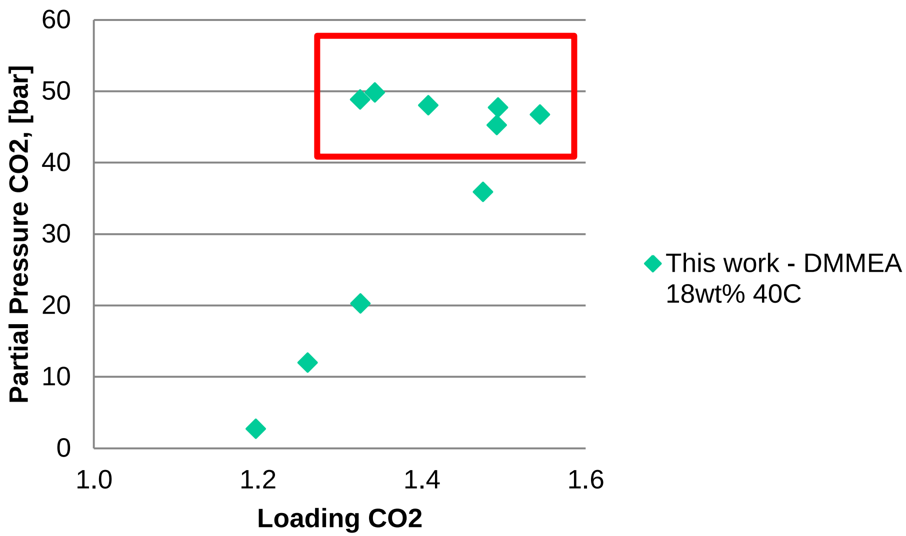
Methane is added to the cell. Increasing the total pressure and causing methane to dissolve in the liquid phase as the partial pressure of methane increases

How does the addition of methane affect the CO_2 liquid loading?

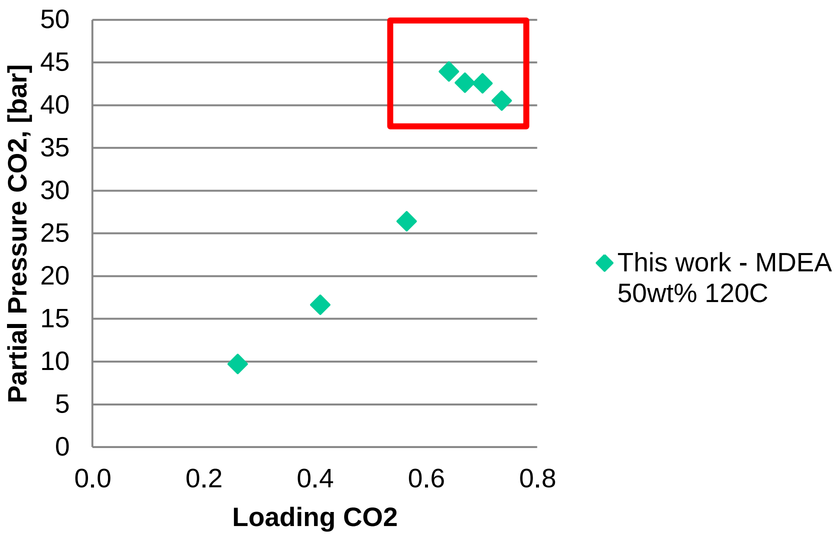


The increased pressure causes the equilibrium curve to shift to the left.

Is this behaviour visible in other experiments?



It is visible in all tests in various degrees.



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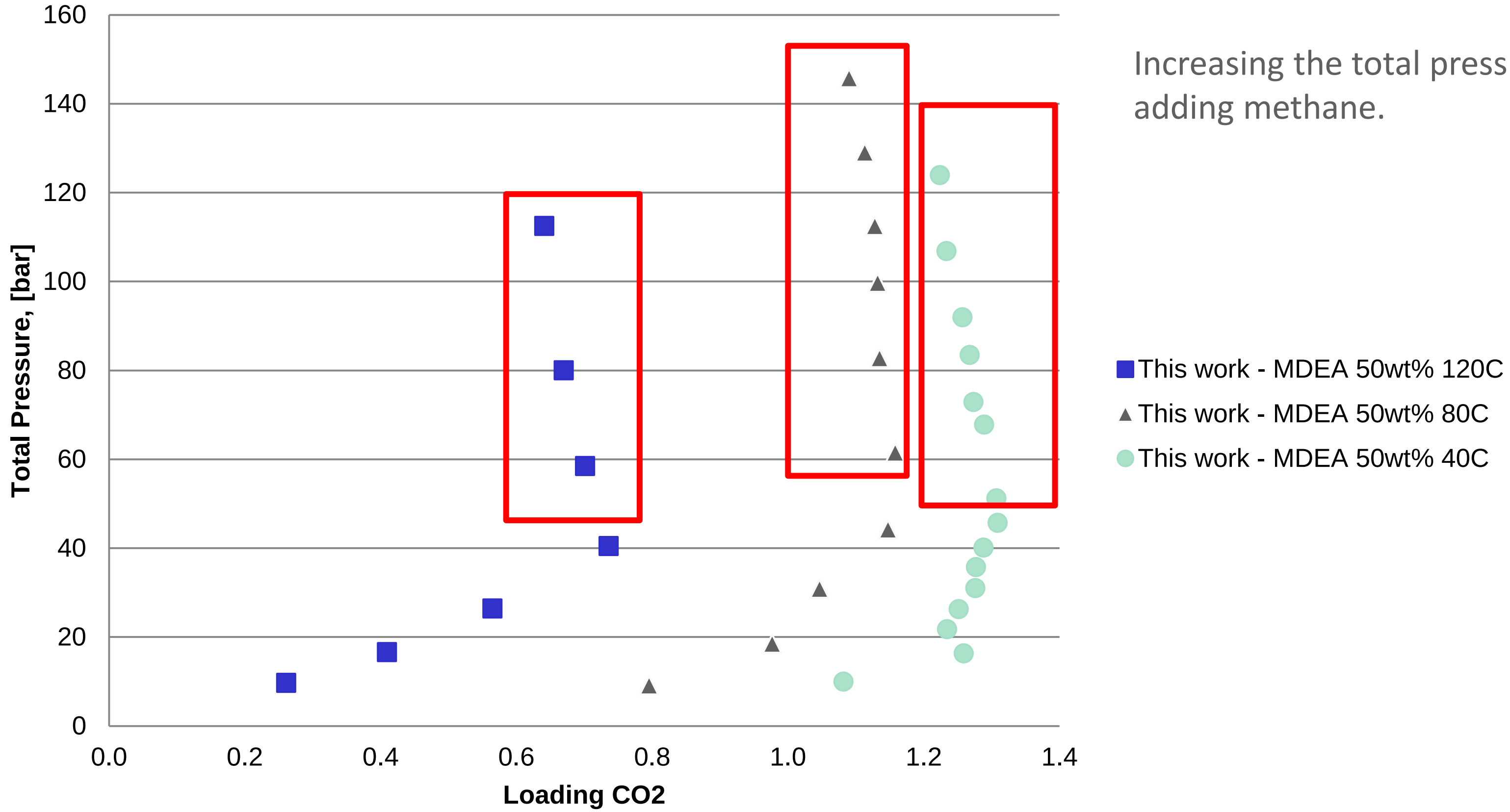
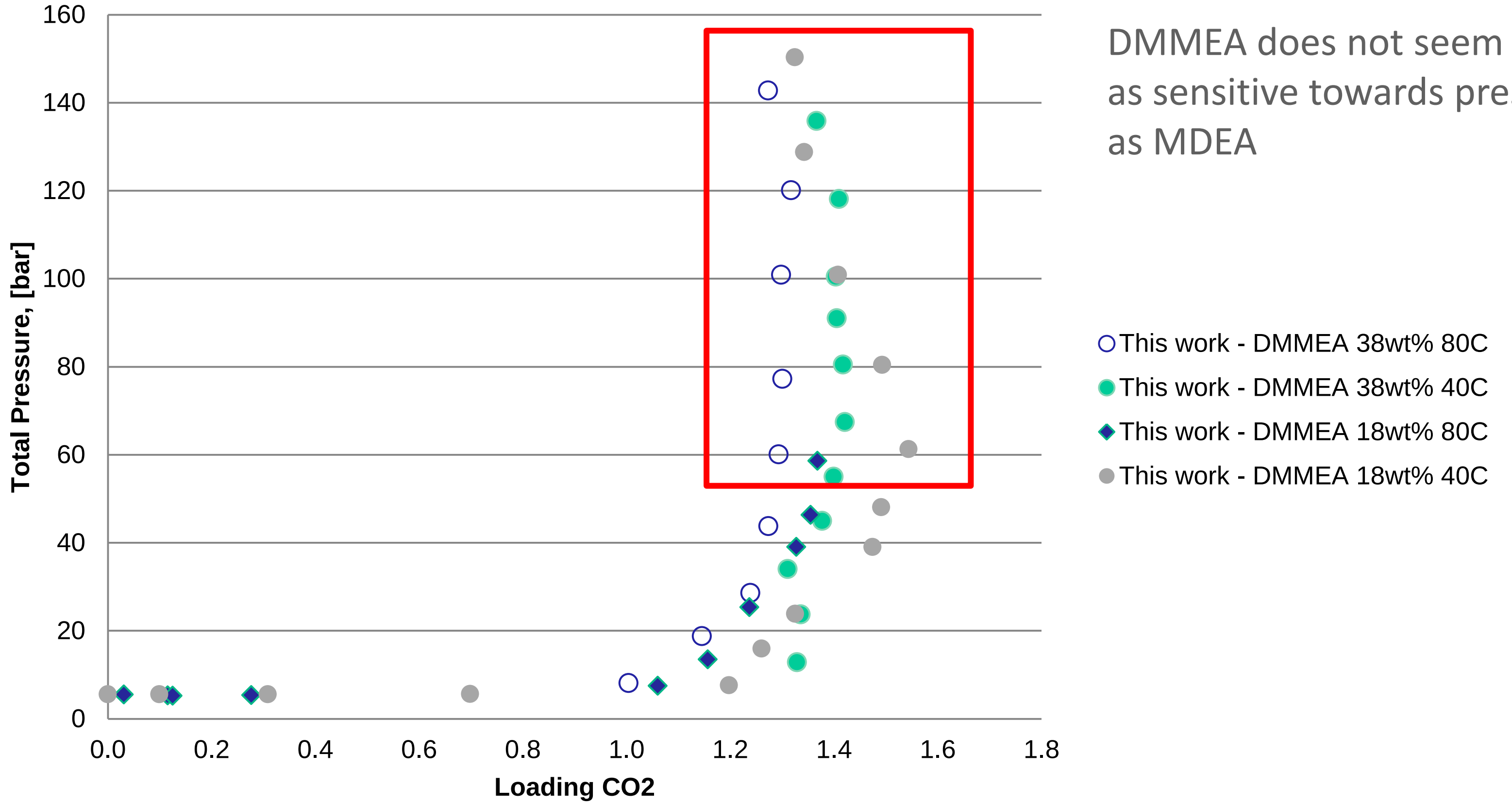


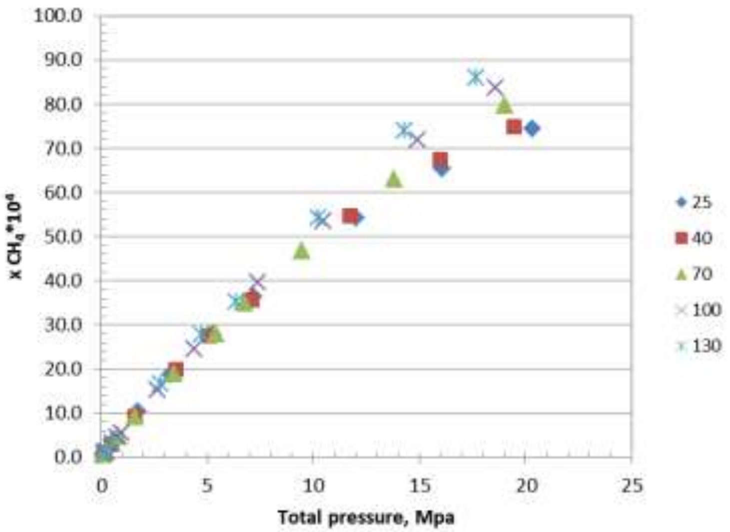
Increasing the total pressure by adding methane.

Is this behaviour visible in other experiments?



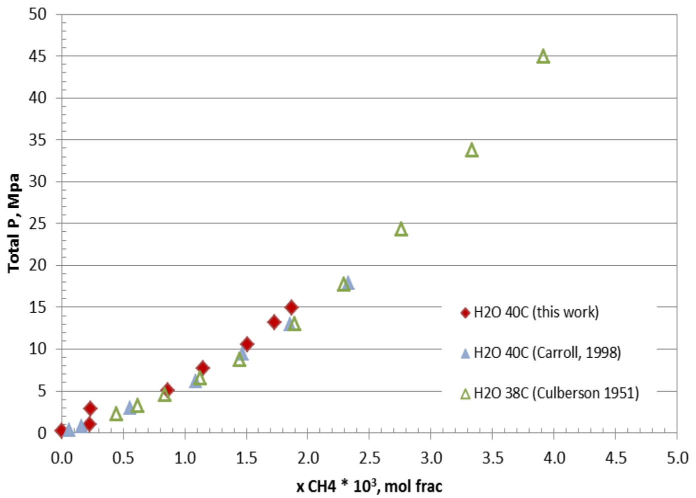
DMMEA does not seem to be as sensitive towards pressure as MDEA

What is causing the effect?
Presence of Methane in the liquid phase?



Solubility of methane in pure MDEA (Jou, 2006)

The solubility of methane in water and pure MDEA is low



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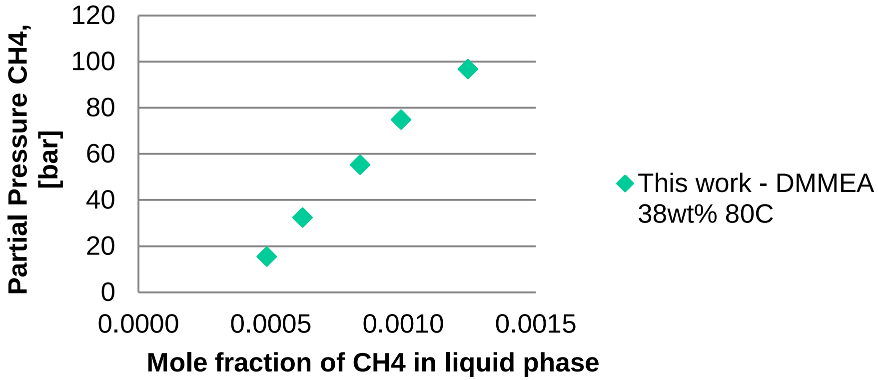
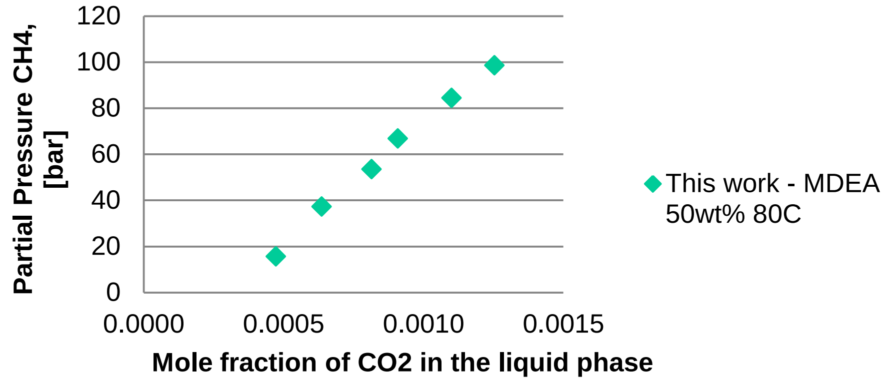
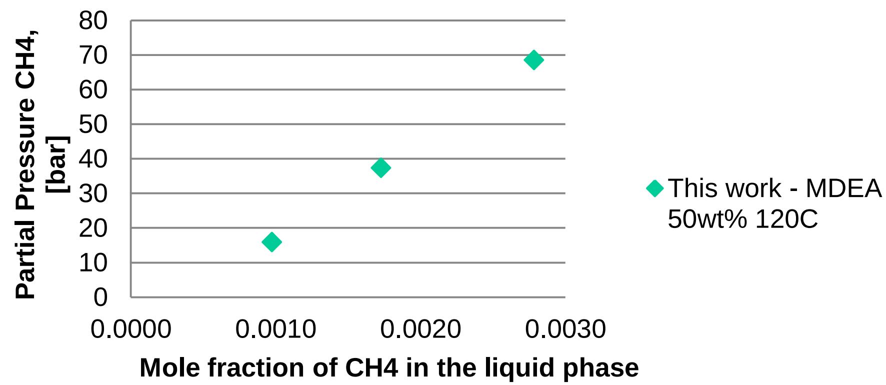
What is causing the effect? Presence of Methane in the liquid?





Dissolved hydrocarbons in the liquid phase will influence the dielectric constant (measure of polarity) of the amine.

The mole fraction of methane in the liquid phase is low.



What is causing the effect? The increased pressure?

The Poynting correction

The vapor-liquid equilibrium of CO_2 can be calculated by equalizing the fugacity values of both phases

$$f^{V}_{CO_2} = f^{L}_{CO_2}$$

Rewritten

$$\phi_{CO_2} y_{CO_2} P = x_{CO_2} \gamma_{CO_2} H_{CO_2} \exp\left[\frac{\bar{v}^{\infty}_{CO_2}(P - P^{s}_{CO_2})}{RT}\right]$$

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What is causing the effect?
The increased pressure?

The Poynting correction

$$\underbrace{\varphi_{CO_2} y_{CO_2}}_{\text{Constant}} P = \gamma_{CO_2} m_{CO_2} H_{CO_2} \underbrace{\exp\left[\frac{\bar{v}^{\infty}_{CO_2}\left(P - P^{s}_{CO_2}\right)}{RT}\right]}_{\text{Poynting correction}}$$

Constant

Poynting correction
(molar volume of CO_2 in the liquid)

Increases with pressure

Reduction in liquid CO_2 concentration

φ_{CO_2} = fugacity coefficient
y_{CO_2} = vapor mole fraction
P = total pressure
γ_{CO_2} = activity coefficient
H_{CO_2} = Henry constant
m_{CO_2} = molality

Conclusion

- DMMEA seems to be a faster solvent than MDEA
- The solubility of methane in the amine solvents is low.
- There is a reduction in the liquid phase CO_2 at higher pressures for MDEA and to some degree DMMEA.
- The systems will be modeled with the electrolyte-NRTL equation.

Acknowledgements

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