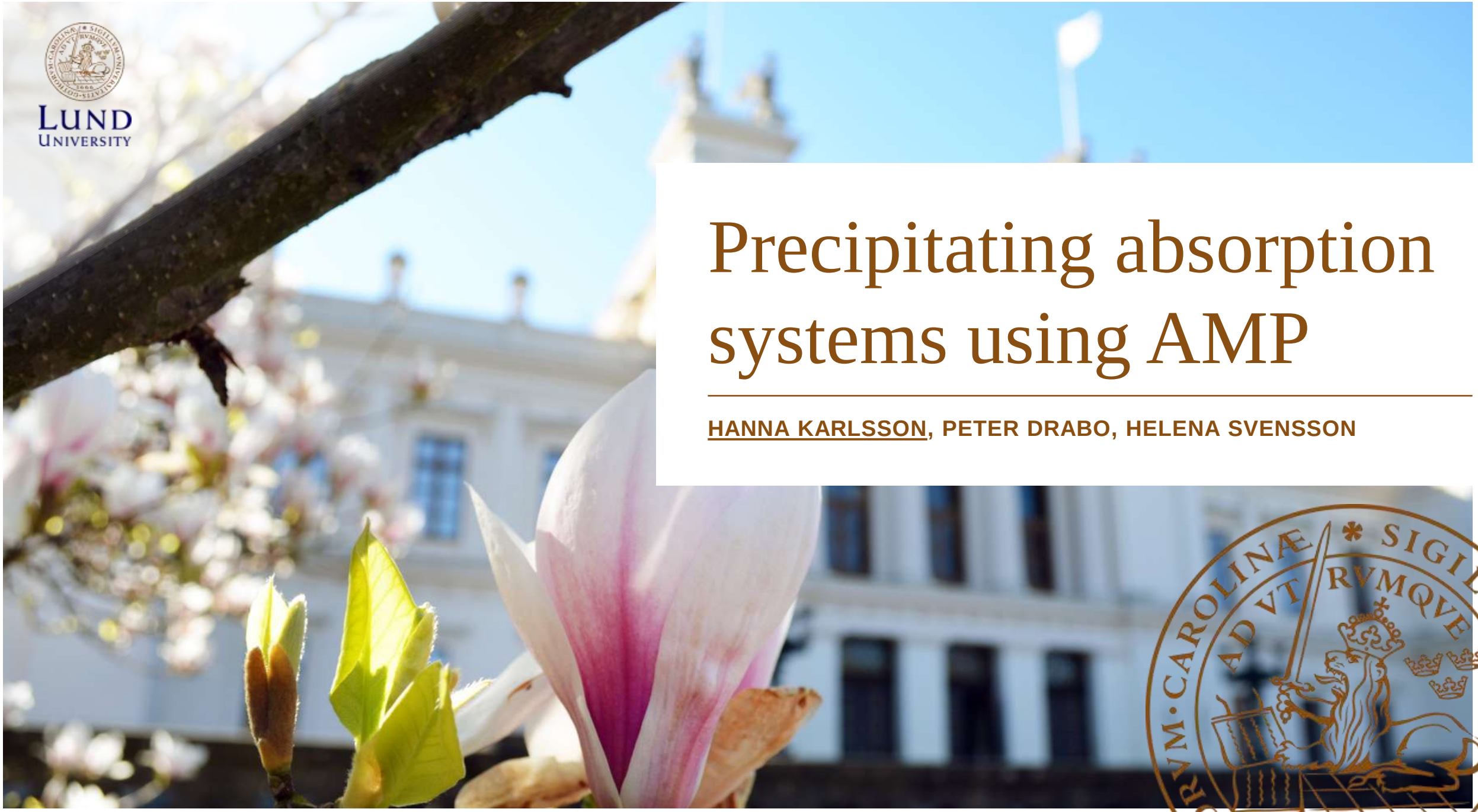


Precipitating absorption systems using AMP

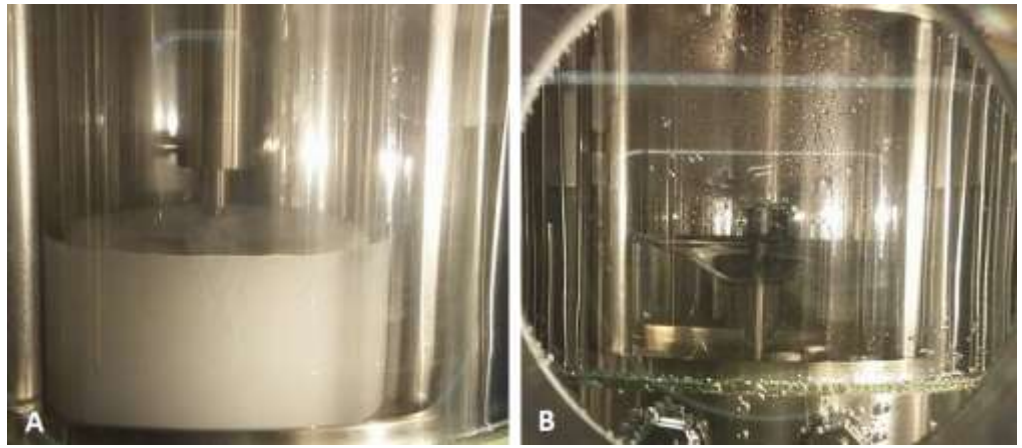
HANNA KARLSSON, PETER DRABO, HELENA SVENSSON

Introduction

- Non-aqueous systems
  - Organic solvents with higher CO_2 solubility compared to water

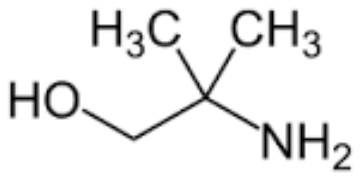
- Bi-phasic system
  - Liquid which precipitates when reacted with CO_2
  - Only part of the stream heated for regeneration

- Low regeneration temperature
  - 70-90 °C compared to 120 °C for aqueous systems
  - Excess heat for regeneration



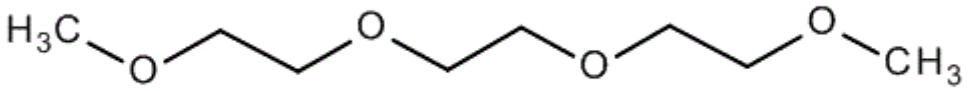
Introduction – current system

Amine:

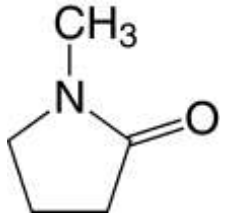


AMP
(2-amino-2-methyl-1-propanol)

Solvents:



TEGDME
(Triethylene glycol dimethyl ether)



NMP
(*N*-methyl-2-pyrrolidone)

Introduction – reaction mechanism

$CO_2(g) \leftrightarrow CO_2(sol)$ (1) Dissolution

$CO_2(sol) + RNH_2(sol) \leftrightarrow RNH_2^+COO^-(sol)$ (2) Zwitter ion formation

$RNH_2^+COO^-(sol) + RNH_2(sol) \leftrightarrow RNH_3^+(sol) + RNHCOO^-(sol)$ (3) Carbamate formation

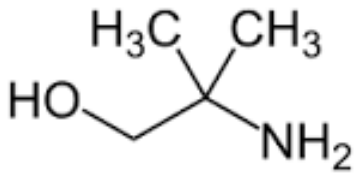
$RNH_3^+(sol) + RNHCOO^-(sol) \leftrightarrow RNH_3^+RNHCOO^-(s)$ (4) Carbamate precipitation

Maximum loading due to chemical reaction : 0.5 mol CO_2/mol AMP

H. Svensson, C. Hulteberg, H.T. Karlsson Energy Procedia 2014, 63, 750–757.
H. Svensson, V. Zejnullahu Velasco, C. Hulteberg, H.T. Karlsson Int. J. Greenh. Gas Control 2014, 30, 1–8.

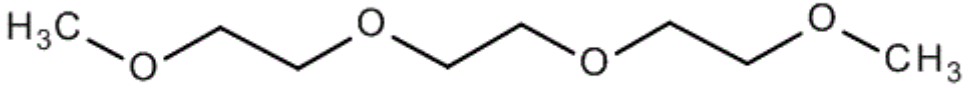
Introduction – current system

Amine:

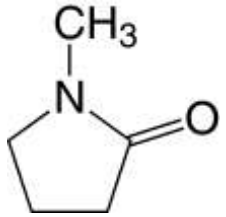


AMP
(2-amino-2-methyl-1-propanol)

Solvents:



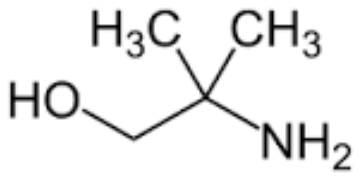
TEGDME
(Triethylene glycol dimethyl ether)



NMP
(*N*-methyl-2-pyrrolidone)

Introduction – current system

Amine:



AMP
(2-amino-2-methyl-1-propanol)

Solvents:

Toxic to reproduction (EU)

Aim

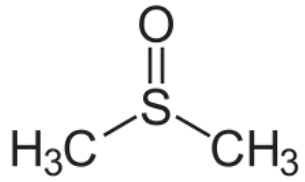
Investigate alternative organic solvents that can be used in combination with AMP as a precipitating CO_2 absorbing system.

Aim

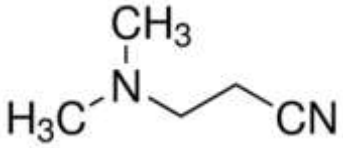
Investigate alternative organic solvents that can be used in combination with AMP as a precipitating CO_2 absorbing system.

- Enable precipitation of the AMP-carbamate
- High solubility of CO_2
- Boiling point above 100 °C
- Non-toxic
- Preferably low viscosity

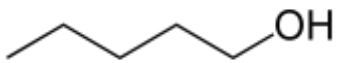
Solvents investigated



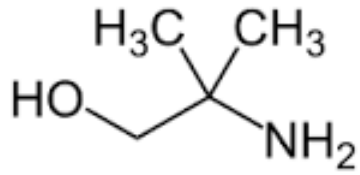
DMSO
(Dimethyl Sulfoxide)



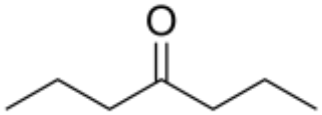
3DMAPN
(3-Dimethylaminopropoinitrile)



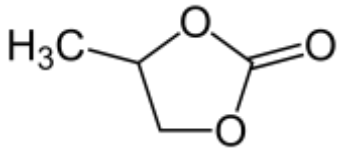
1P
(1-Pentanol)



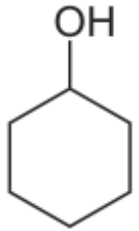
AMP
(2-amino-2-methyl-1-propanol)



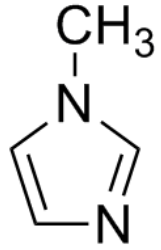
4H
(4-Heptanone)



PC
(Propylene carbonate)

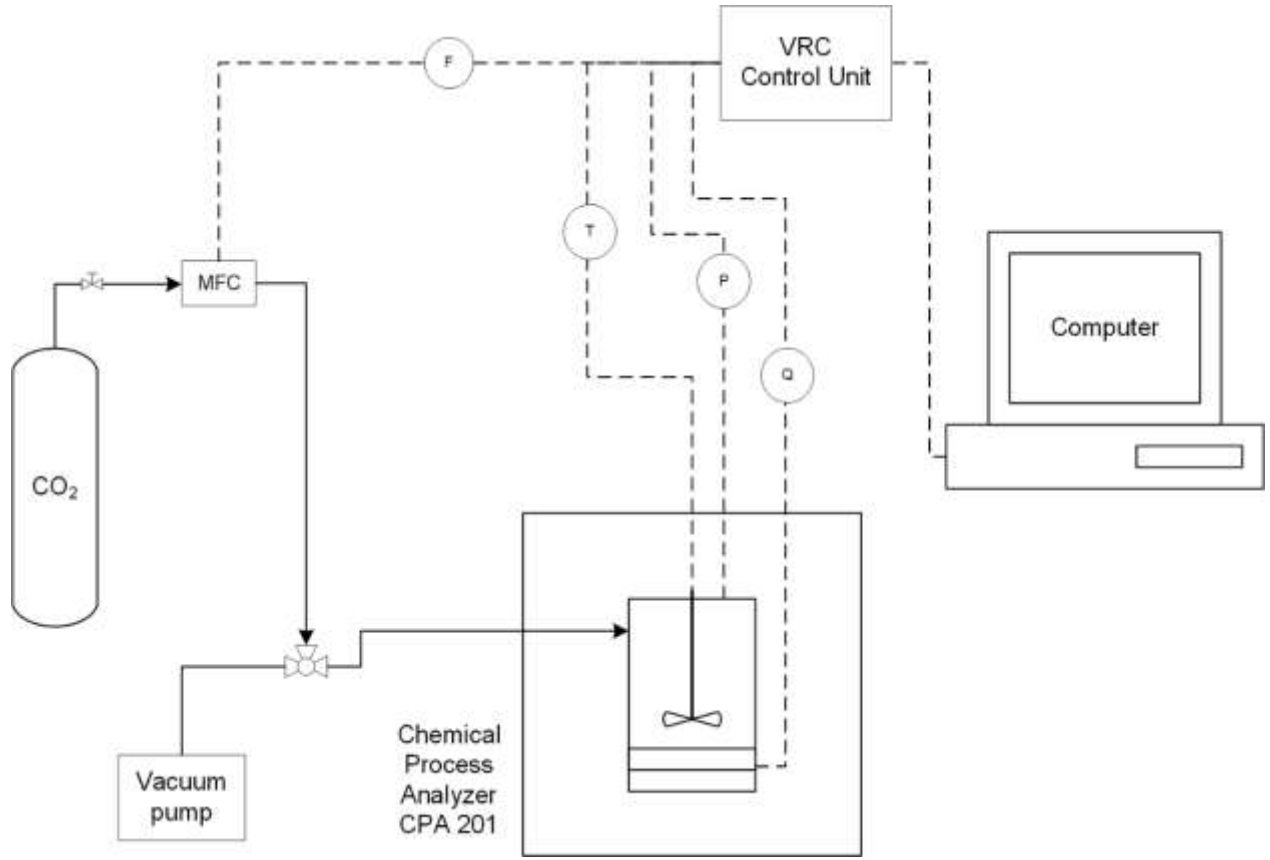


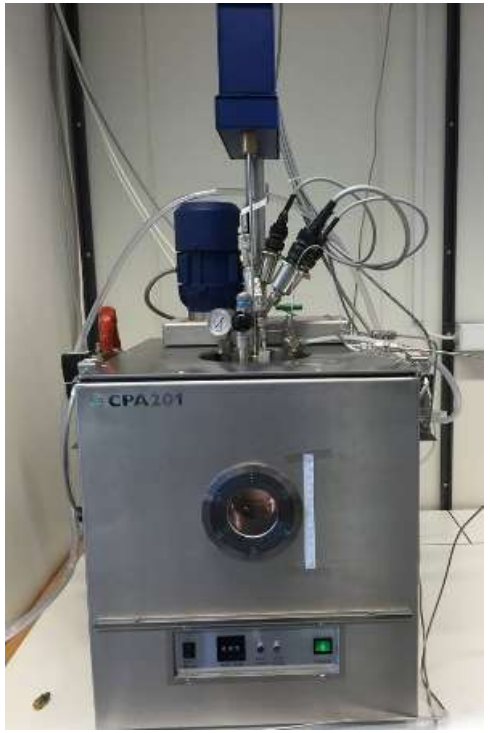
CH
(Cyclohexanol)



1MIMI
(1-Methylimidazole)

Experimental Set-up





Experimental

Solvent	Henry's Constant 25°C	Henry's Constant 40°C	Solubility 25Wt% AMP 25°C	Solubility 25Wt% AMP 40°C
DMSO	X	X	X	X
3DMAPN	X	X	X	X
1P	X	X	X	X
PC	X		X	
4H	X		X	
CH		X		X
1MIMI			X	

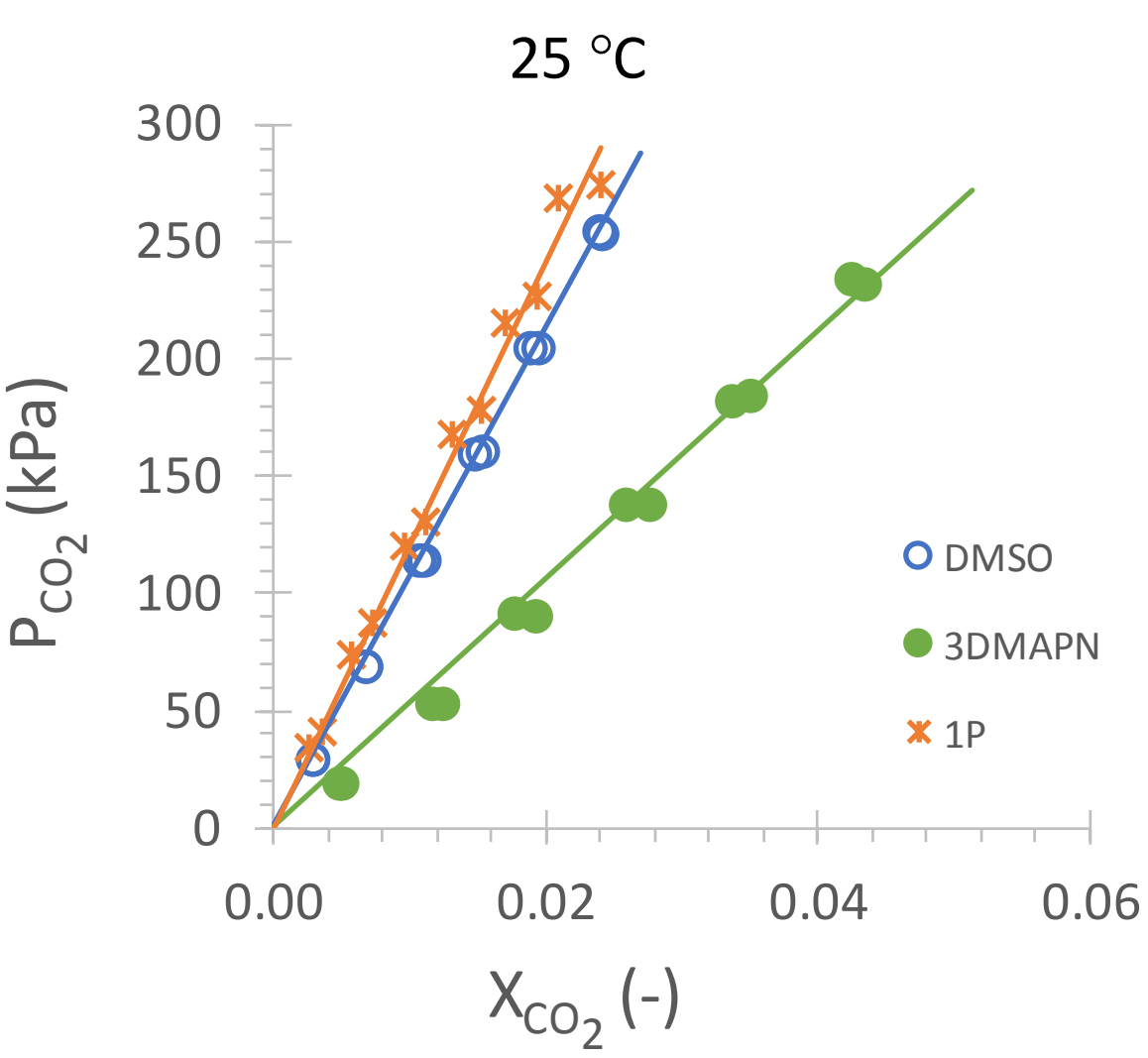
Experimental

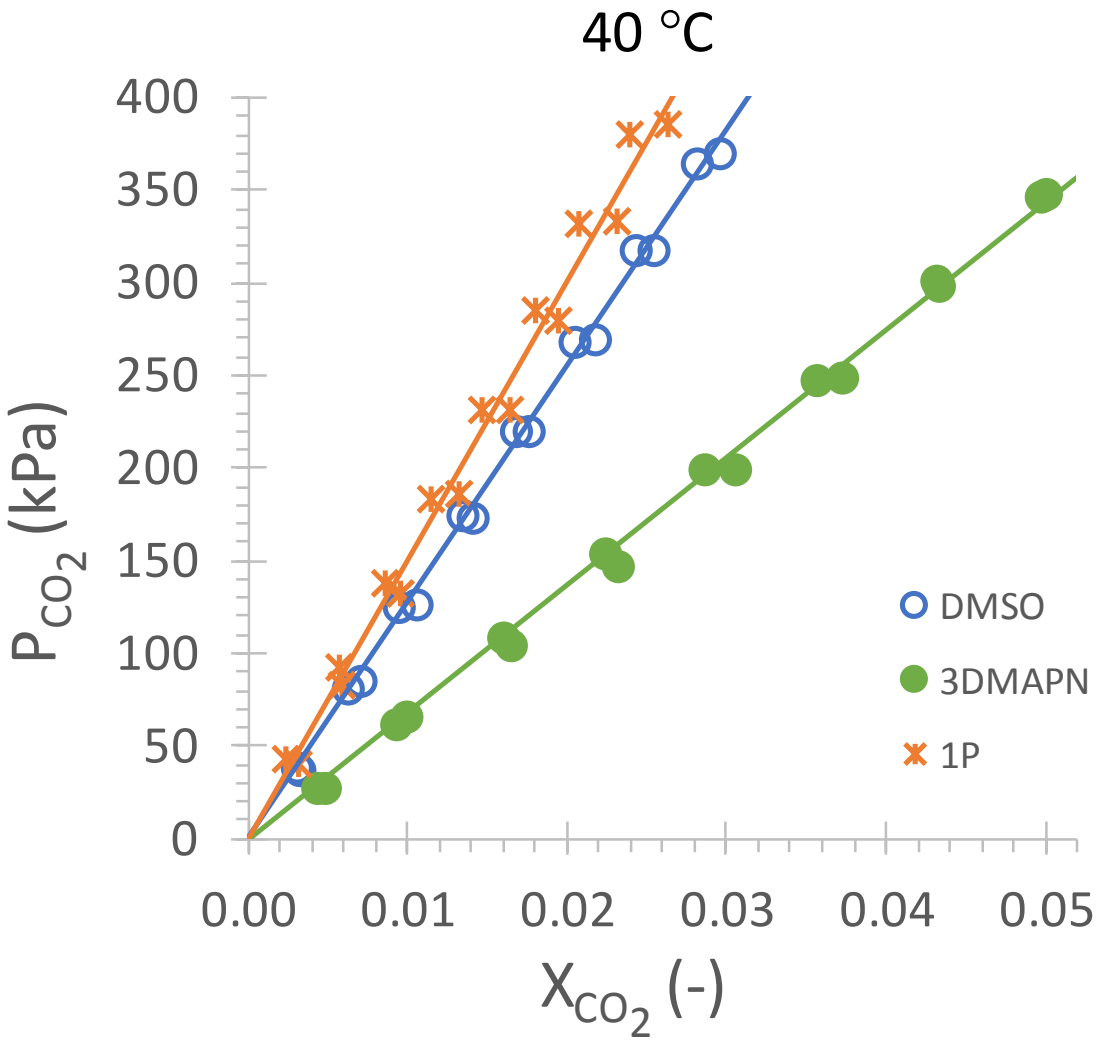
Solvent	Henry's Constant 25°C	Henry's Constant 40°C	Solubility 25Wt% AMP 25°C	Solubility 25Wt% AMP 40°C
DMSO	X	X	X	X
3DMAPN	X	X	X	X
1P	X	X	X	X
PC	X		X	
4H	X		X	
CH		X		X
1MIMI			X	

Results

Solvent	Henry's Constant 25°C	Henry's Constant 40°C	Solubility 25Wt% AMP 25°C	Solubility 25Wt% AMP 40°C
DMSO	X	X	X	X
3DMAPN	X	X	X	X
1P	X	X	X	X
PC	X		X	
4H	X		X	
CH		X		X
1MIMI			X	

Physical Solubility – pure solvents





Henry's Constant

25 °C

Solvent	H_{CO2} (MPa)
3DMAPN	5.29
NMP	6.97*
DMSO	10.7
1P	12.1
H_2O	163#

40 °C

Solvent	H_{CO2} (MPa)
3DMAPN	6.87
NMP	8.85**
DMSO	12.8
1P	15.1
H_2O	235#

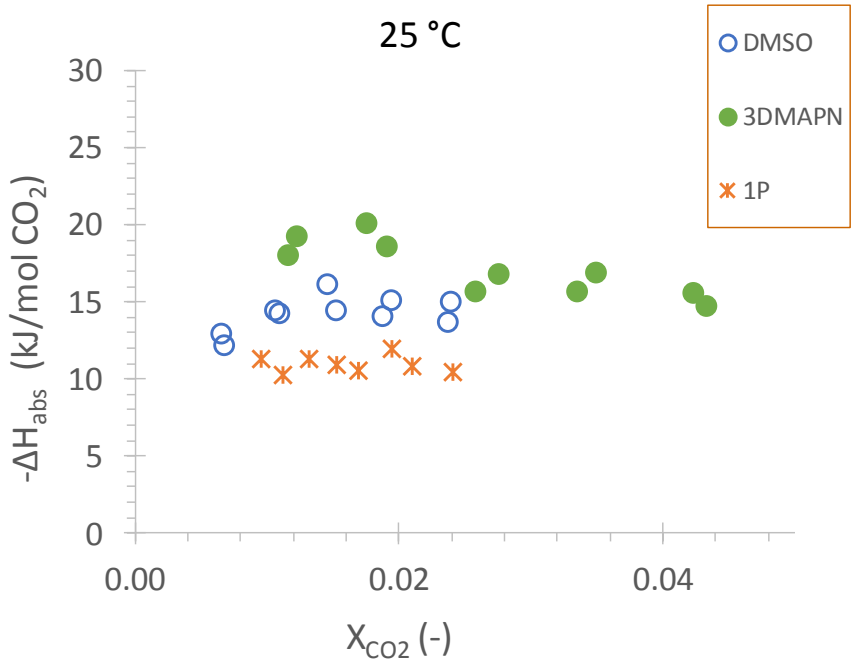
CO_2 solubility:

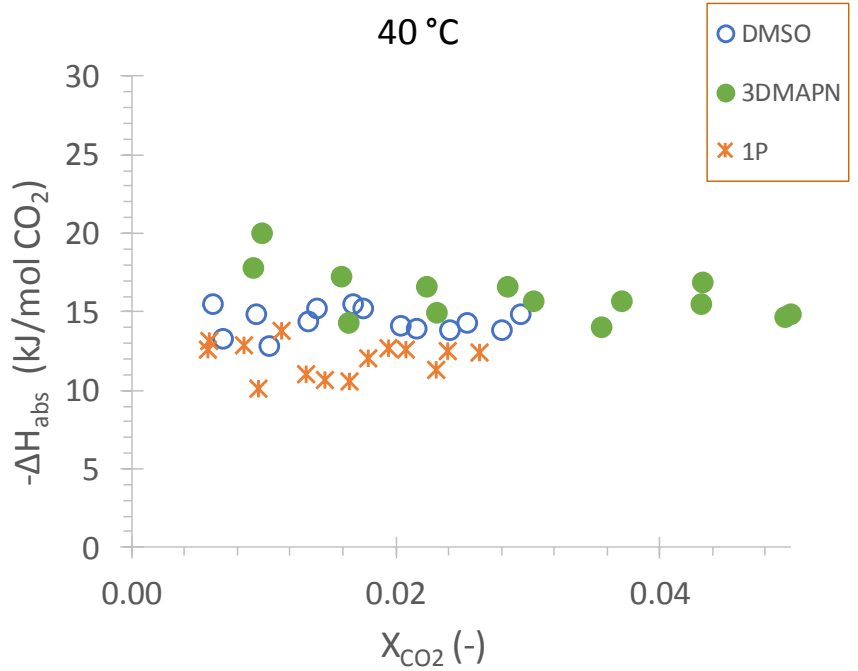
3DMAPN > NMP > DMSO > 1P > H_2O

*Svensson et al. 2014 Int. J. Greenh. Gas Control 27, 247–254.
**Karlsson et al. 2018. 14th Greenhouse Gas Control Technologies Conference Melbourne .SSRN, pp. 1–7.
ASPEN 2017

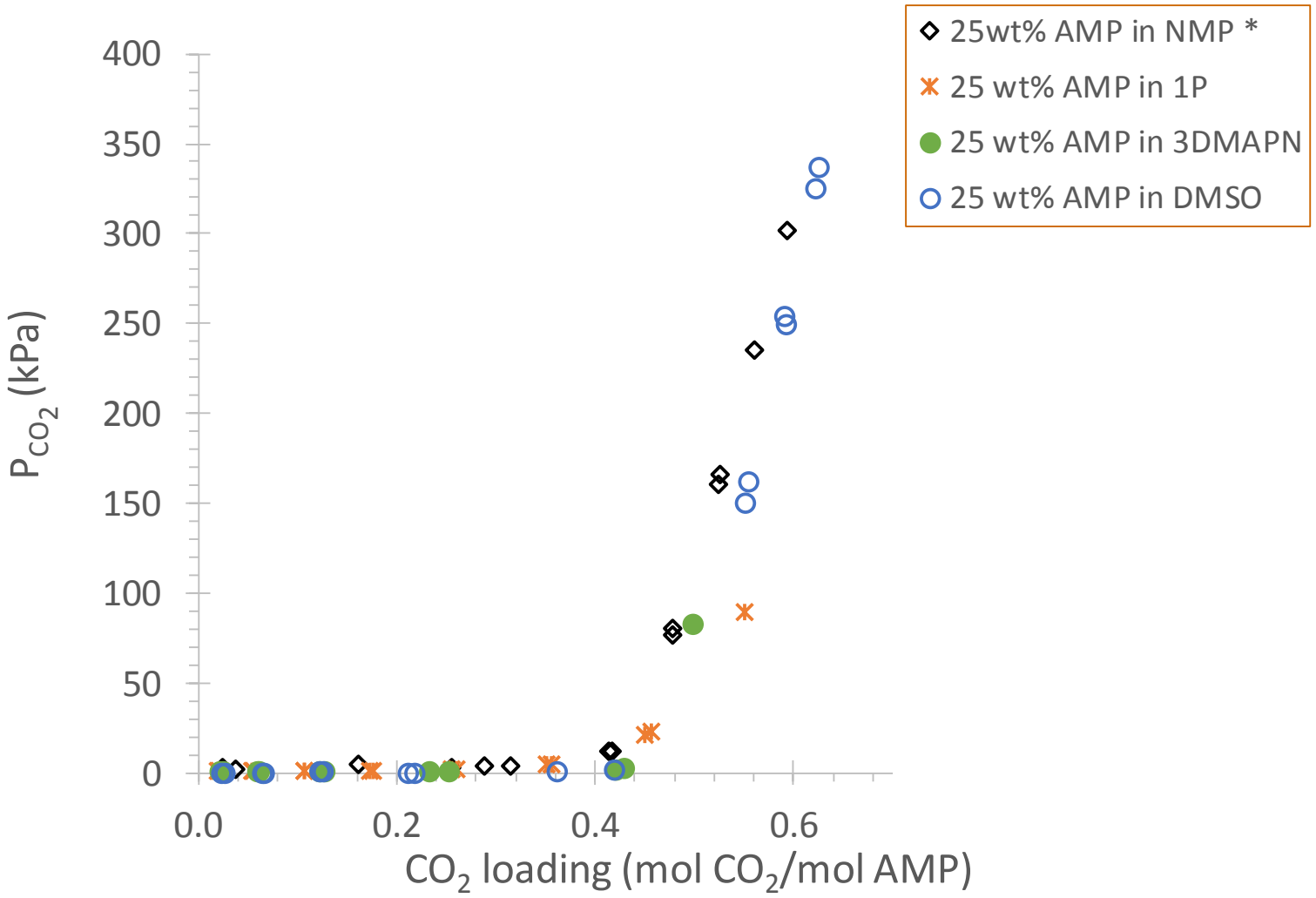
H_{abs} – pure solvents

	$-\Delta H_{abs}$ (kJ/mol CO_2)		
Solvent	**25 °C**	**40 °C**	**Average**
DMSO	14.2	14.4	14.3
3DMAPN	17.1	16.0	16.6
1P	10.9	12.0	11.5





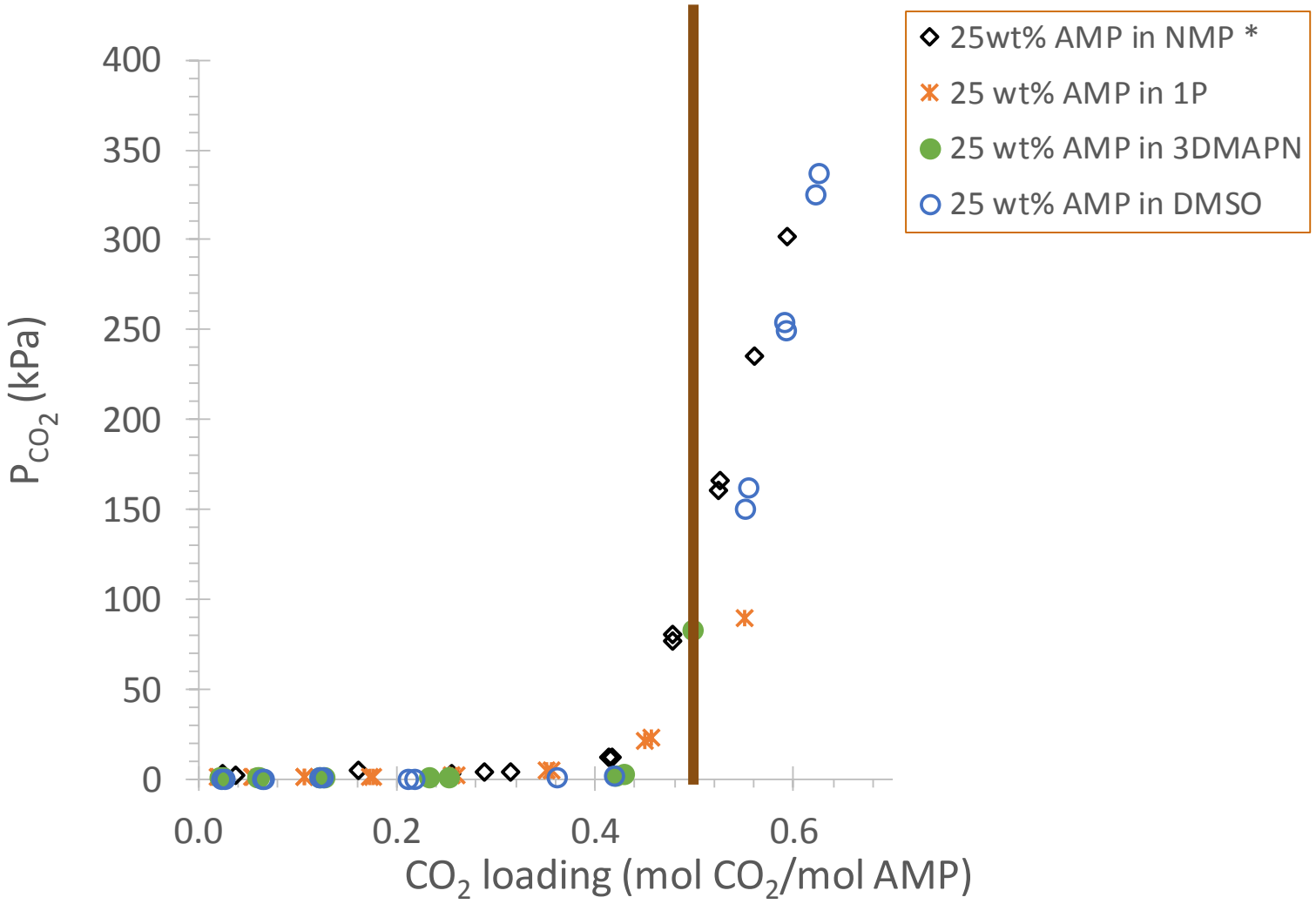
CO_2 solubility – amine mix 25°C



25 wt% AMP in	Loading (mol CO_2/mol AMP) 25 °C Run 1	Run 2
DMSO	0.21	0.22
3DMAPN	0.02	0.02
1P	0.11	0.11
NMP	0.26*	0.29*

*Svensson et al. 2014 Int. J. Greenh. Gas Control 27, 247–254.

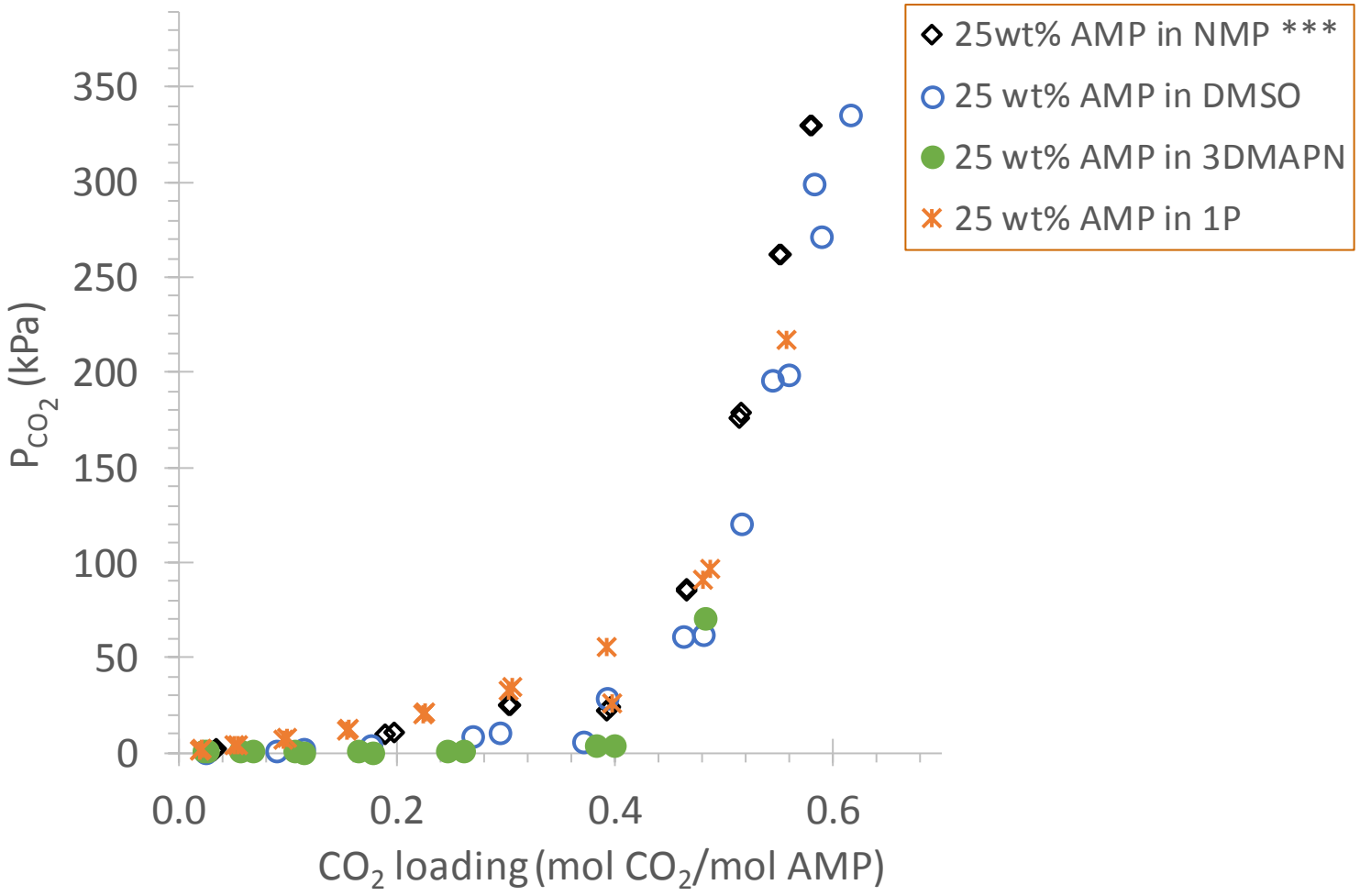
CO_2 solubility – amine mix 25°C



25 wt% AMP in	Loading (mol CO_2/mol AMP) 25 °C Run 1	Run 2
DMSO	0.21	0.22
3DMAPN	0.02	0.02
1P	0.11	0.11
NMP	0.26*	0.29*

*Svensson et al. 2014 Int. J. Greenh. Gas Control 27, 247–254.

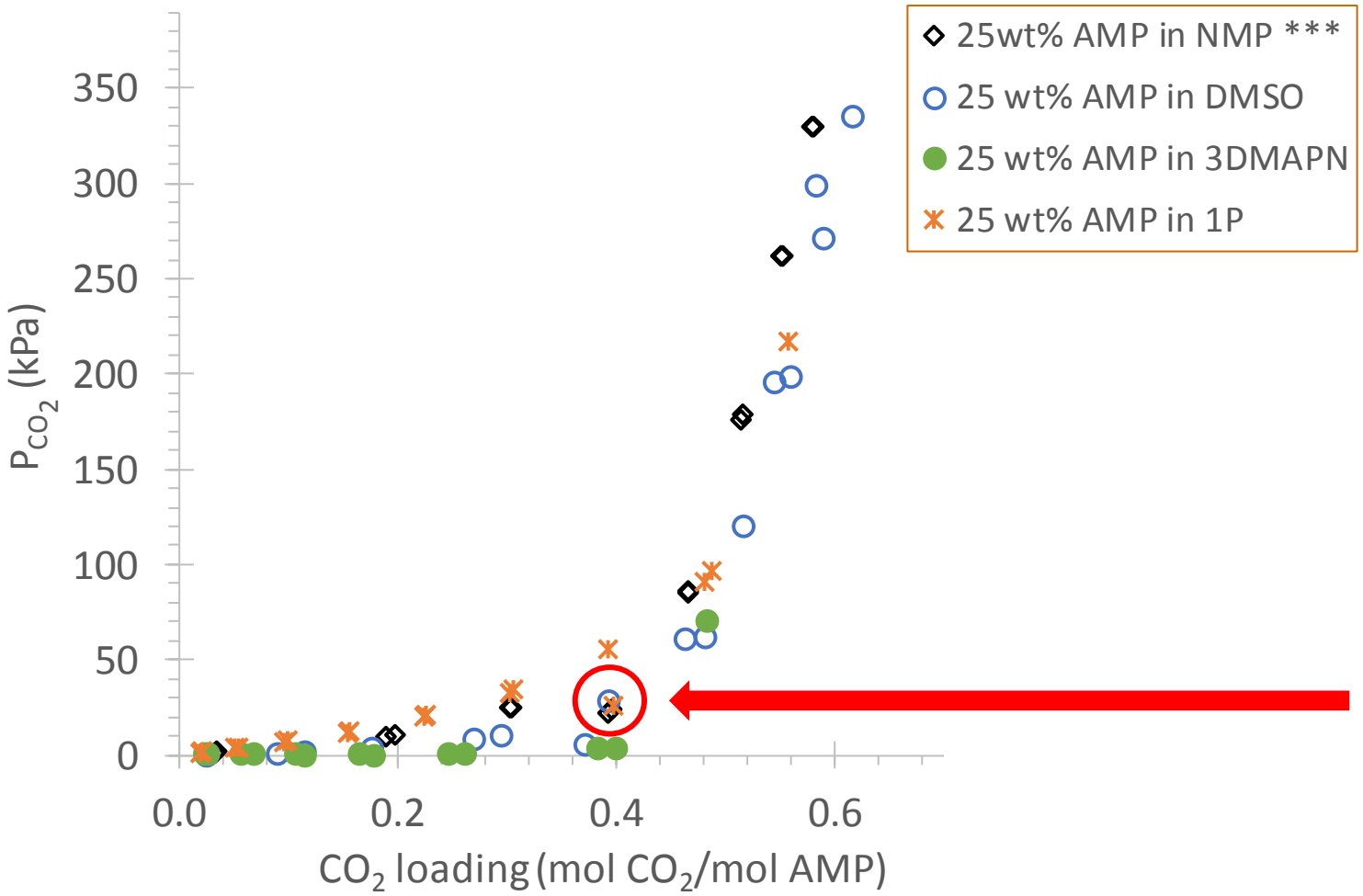
CO_2 solubility – amine mix 40°C



25 wt% AMP in	Loading (mol CO_2/mol AMP)	
	40 °C	
	Run 1	Run 2
DMSO	0.37	0.52
3DMAPN	0.03	0.02
1P	X	0.40
NMP	0.39***	0.40***

***Svensson et al. 2018. 14th Greenhouse Gas Control Technologies Conference Melbourne. SSRN, pp. 1–8.

CO_2 solubility – amine mix 40°C

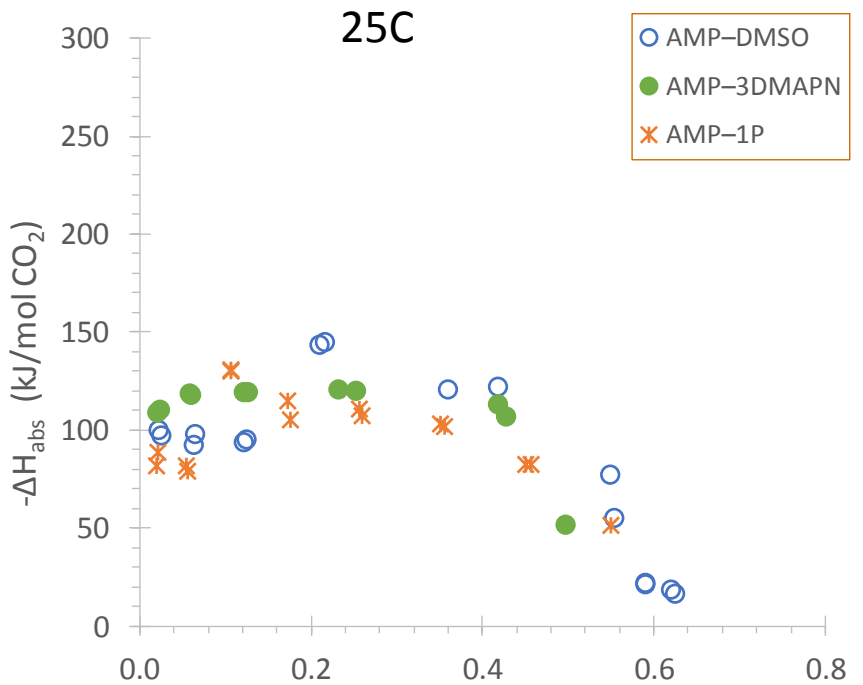


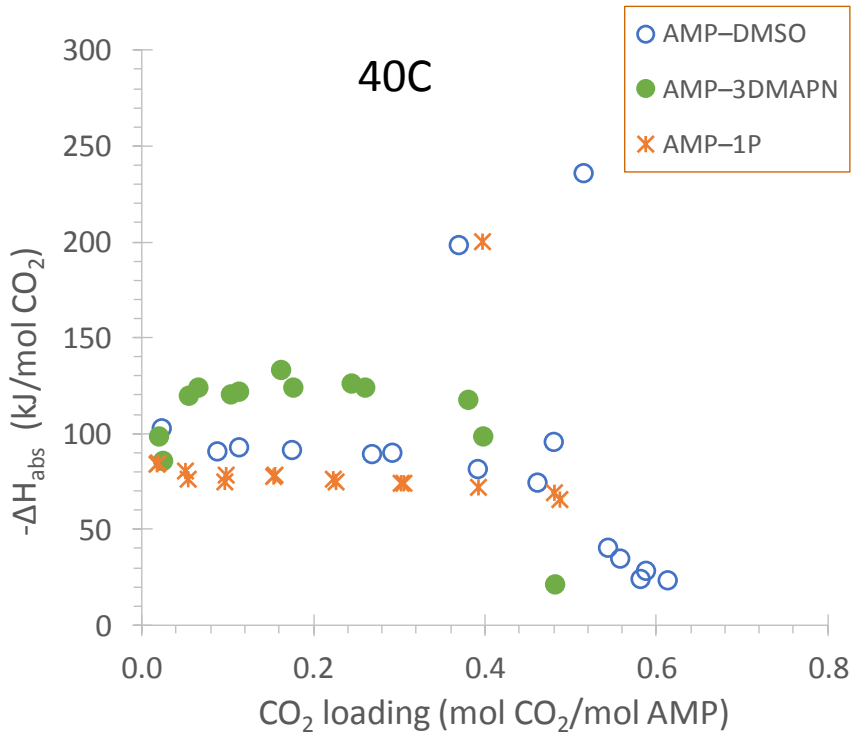
25 wt% AMP in	Loading (mol CO_2/mol AMP)	
	40 °C	
	Run 1	Run 2
DMSO	0.37	0.52
3DMAPN	0.03	0.02
1P	X	0.40
NMP	0.39***	0.40***

***Svensson et al. 2018. 14th Greenhouse Gas Control Technologies Conference Melbourne. SSRN, pp. 1–8.

H_{abs} – amine mix

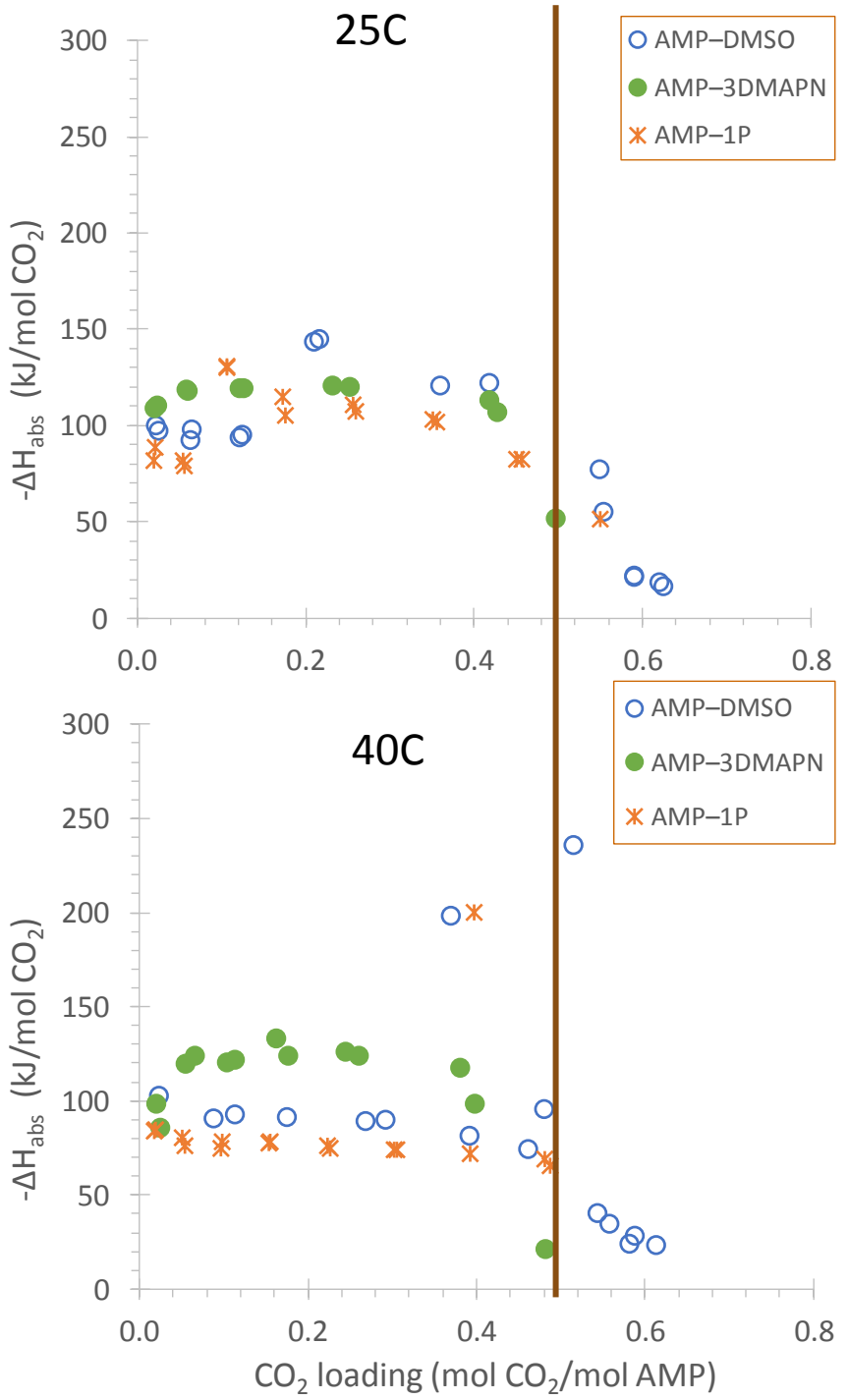
- Heat of absorption higher with reaction
- Heat of absorption gets lower as loading increases towards maximum loading (0.5)





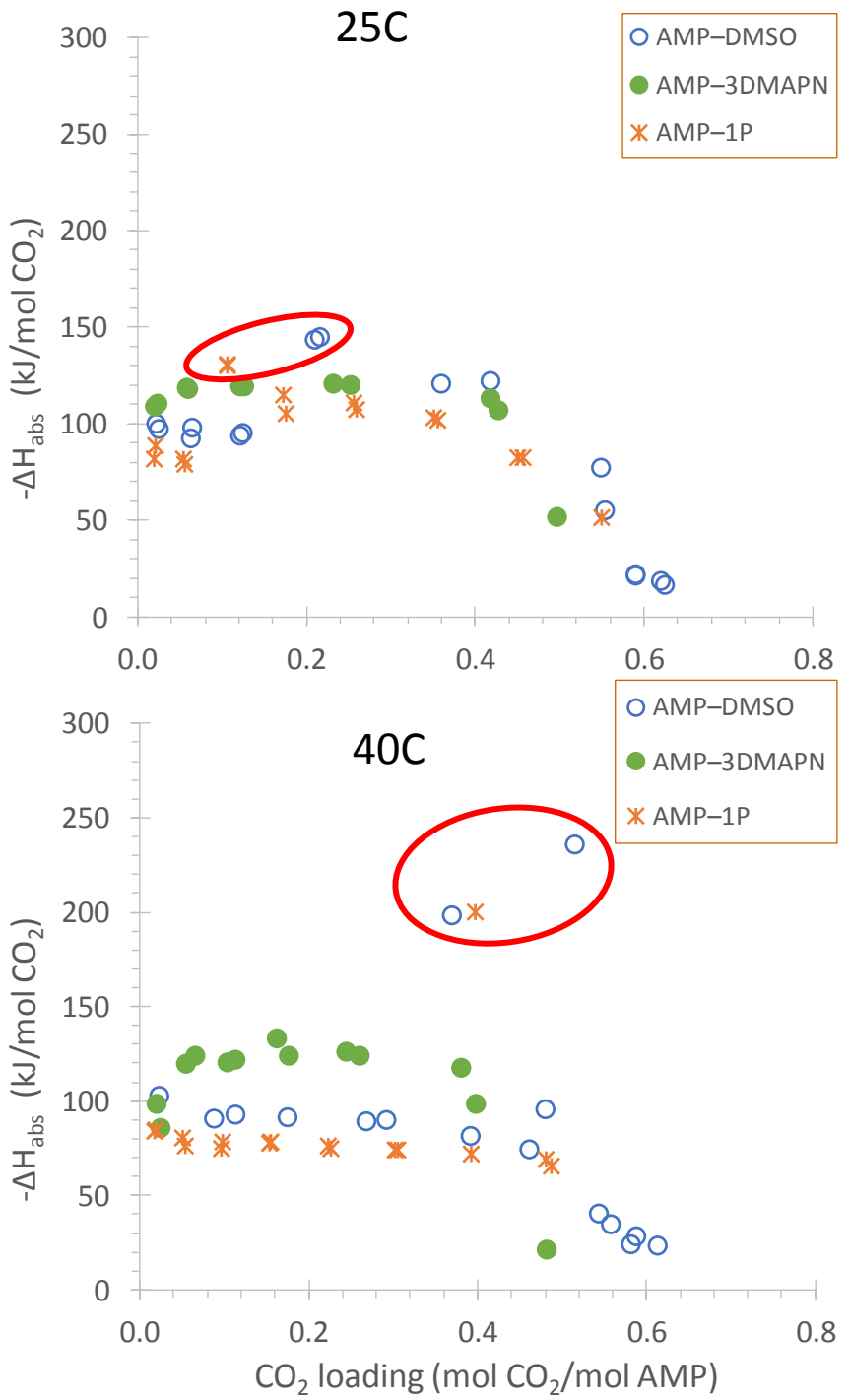
H_{abs} – amine mix

- Heat of absorption higher with reaction
- Heat of absorption gets lower as loading increases towards maximum loading (0.5)



H_{abs} – amine mix

- Heat of absorption higher with reaction
- Heat of absorption gets lower as loading increases towards maximum loading (0.5)
- Precipitation point gives significantly higher heat of absorption – solution is supersaturated



Summary and conclusions

- Solvents evaluated for non-aqueous precipitating absorption solutions with AMP
  - ✓3 promising solvents DMSO, 1-Pentanol and 3-DMAPN

- Physical solubility (Henry's constant) and heat of absorption for pure solvent
  - ✓High CO_2 solubility in the tested solvents

- CO_2-solubility in mixtures with 25 wt% AMP
  - ✓Limited to loadings of 0.5
- Heat of absorption for mixtures with 25 wt% AMP
  - ✓Similar trends as for AMP in NMP

Zwitterion reaction mechanism?

THANK YOU FOR YOUR ATTENTION!

hanna.karlsson@chemeng.lth.se

or

helena.svensson@chemeng.lth.se

LUND UNIVERSITY

EXTRA SLIDES

References

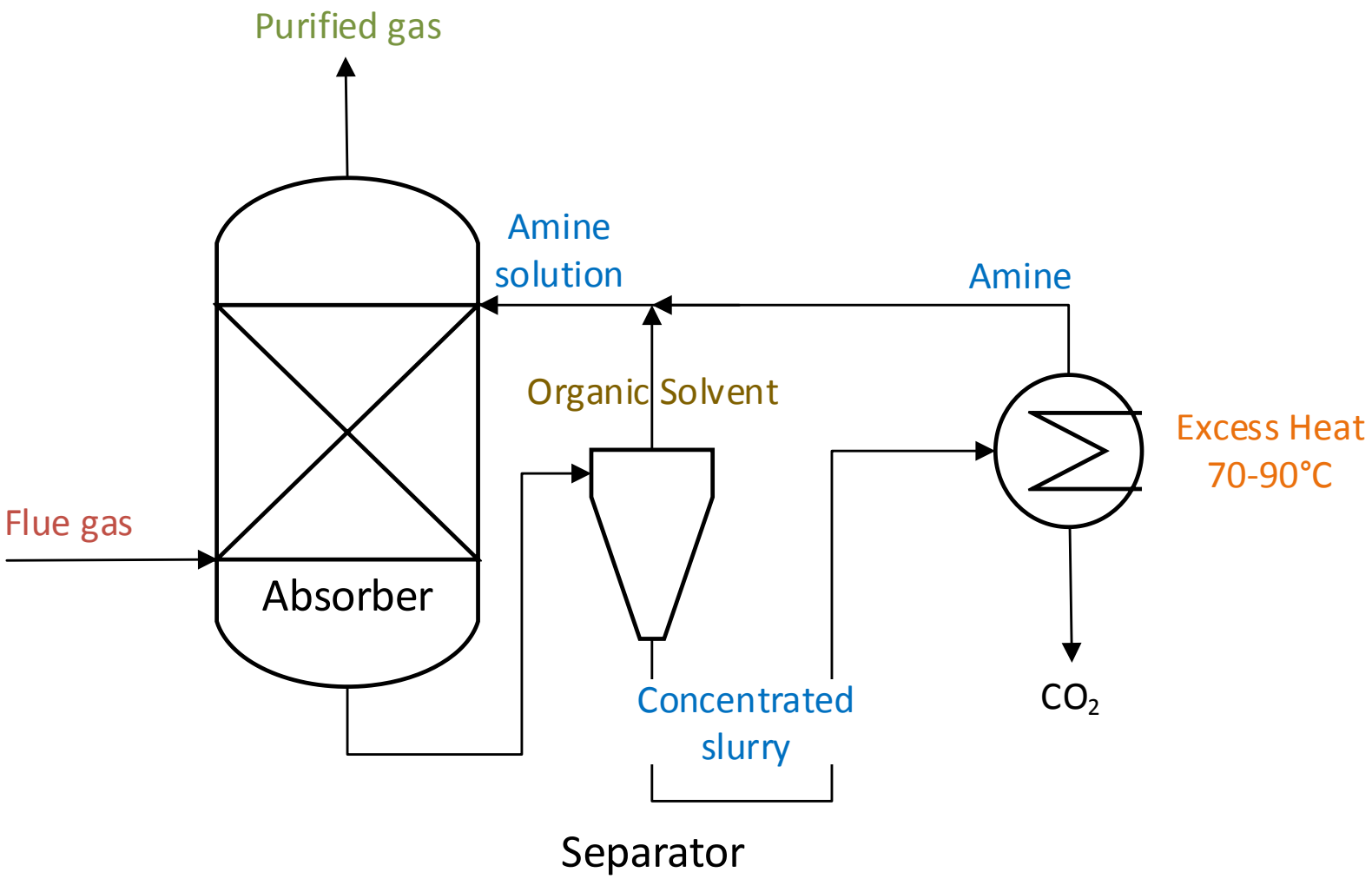
*Svensson, H., Edfeldt, J., Zejnullahu Velasco, V., Hulteberg, C., Karlsson, H.T., 2014a. Solubility of carbon dioxide in mixtures of 2-amino-2-methyl-1-propanol and organic solvents. Int. J. Greenh. Gas Control 27, 247–254. https://doi.org/10.1016/j.ijggc.2014.06.004

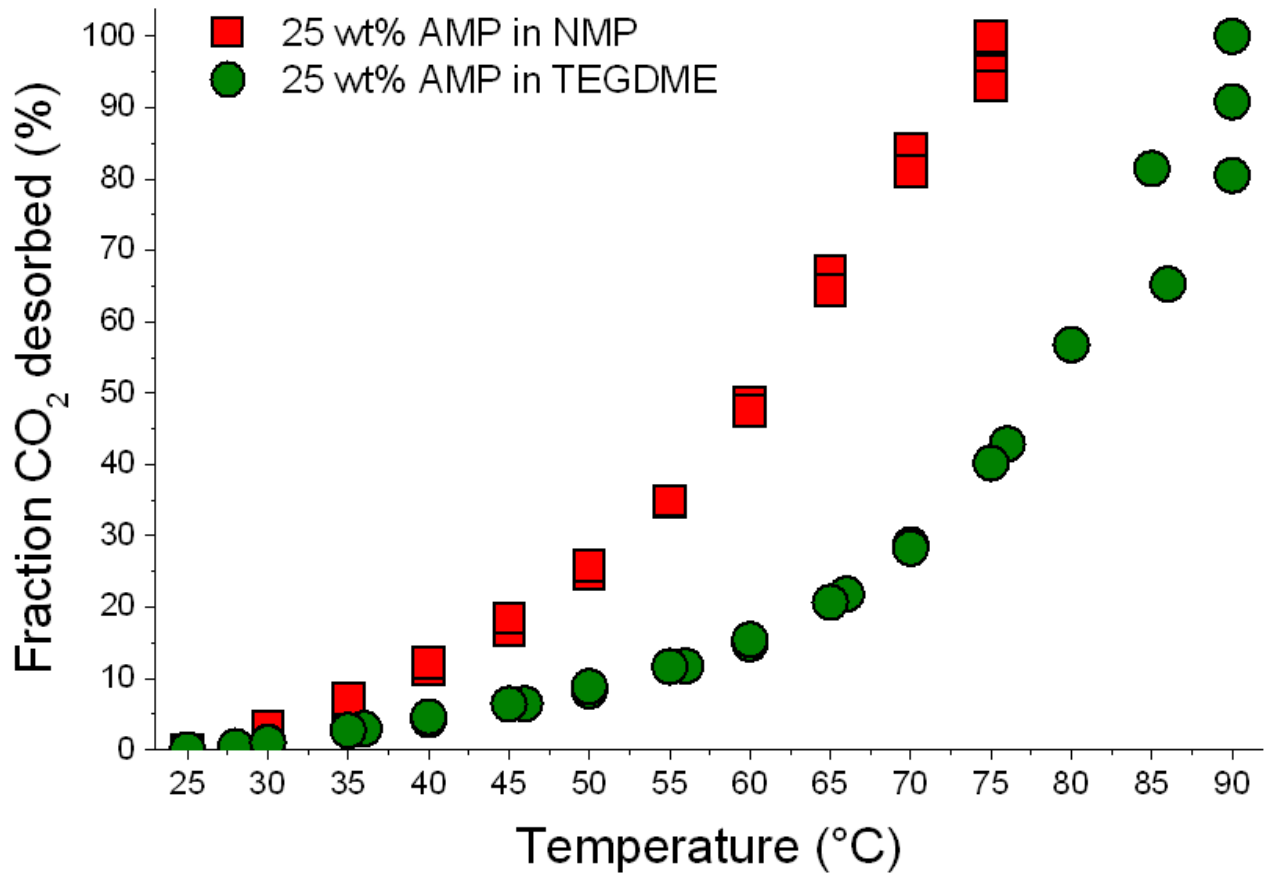
**Karlsson, H., Svensson, H., 2018. Physical properties of the 2-amino-2-methyl-1-propanol and N-methyl-2-pyrrolidone system, in: 14th Greenhouse Gas Control Technologies Conference Melbourne 21-26 October 2018 (GHGT-14). SSRN, pp. 1–7.

***Svensson, H., Karlsson, H.K., 2018. Solubility of carbon dioxide in mixtures of 2-amino-2-methyl-1-propanol and N-methyl2-pyrrolidone at absorption and desorption conditions, in: 14th Greenhouse Gas Control Technologies Conference Melbourne 21-26 October 2018 (GHGT-14). SSRN, pp. 1–8.

ASPEN, 2017. Aspen Technology Inc., Aspen Plus, V8.8 ed. AspenTech.

Process design




25 wt% AMP in NMP
25 wt% AMP in TEGDME
Fraction CO_2 desorbed (%)
Temperature (°C)
0
10
20
30
40
50
60
70
80
90
100
25
30
35
40
45
50
55
60
65
70
75
80
85
90

Solvent	T_b (°C)	η (mPas)	T_{exp} (°C)
1-Pentanol (1P)*	136	3.44[a]	25, 40
Propylene Carbonate (PC)*	240	2.76[b]	25
4-Heptanone (4H)*	145	0.74[b] [5]	25
Cyclohexanol (CH)*	160	32.4[c]	40
3(Dimethylamino)propionitrile (3DMAPN)*	171	1.4[b]	25, 40
Dimethyl sulfoxide (DMSO)*	189	2.14[b]	25, 40
1-Methylimidazole (1MIMI)	198	1.89[b]	25

*Precipitation of the AMP-carbamate occurred at 25 °C (40 °C for CH) in mixtures with 25 wt% AMP.
[a]25 °C, [b]20 °C, [c]35 °C

SÄKERHETSDATABLAD

enligt Förordning (EG) nr 1907/2006
Version 6.5 Revisionsdatum 15.03.2018
Tryckdatum 17.04.2018

AVSNITT 1: Namnet på ämnet/blandningen och bolaget/företaget

1.1 Produktbeteckningar

Produktnamn : N-metyl-2-pyrrolidon

Produktnummer : 328634
Märke : Sigma-Aldrich
INDEX-nr : 606-021-00-7
REACH Nr. : 01-2119472430-46-XXXX
CAS-nr. : 872-50-4

1.2 Relevanta identifierade användningar av ämnet eller blandningen och användningar som det avråds från

Identifierade användningar : Laboratoriekemikalier, Tillverkning av ämnen

1.3 Närmare upplysningar om den som tillhandahåller säkerhetsdatablad

Företag : Sigma-Aldrich Sweden AB
Solkraftsvagen 14C
S-135 70 STOCKHOLM

Telefon : +46 (0)8-742-4200
Fax : +46 (0)8-742-4243
E-postadress : eurtechserv@sial.com

1.4 Telefonnummer för nödsituationer

Nödtelefon # +(46)-852503403 (CHEMTREC)
Vid akut fara för liv, egendom eller miljö - 112

AVSNITT 2: Farliga egenskaper

2.1 Klassificering av ämnet eller blandningen

Klassificering enligt förordning (EC) Nr 1272/2008
Irriterande på huden (Kategori 2), H315
Ögonirritation (Kategori 2), H319
Reproduktionstoxicitet (Kategori 1B), H360D
Specifik organtoxicitet - enstaka exponering (Kategori 3), Andningsorgan, H335

Se avsnitt 16 för den fullständiga lydelsen av H-(faro-)angivelserna nämnda i detta avsnitt.

AVSNITT 8: Begränsning av exponeringen/personligt skydd

8.1 Kontrollparametrar

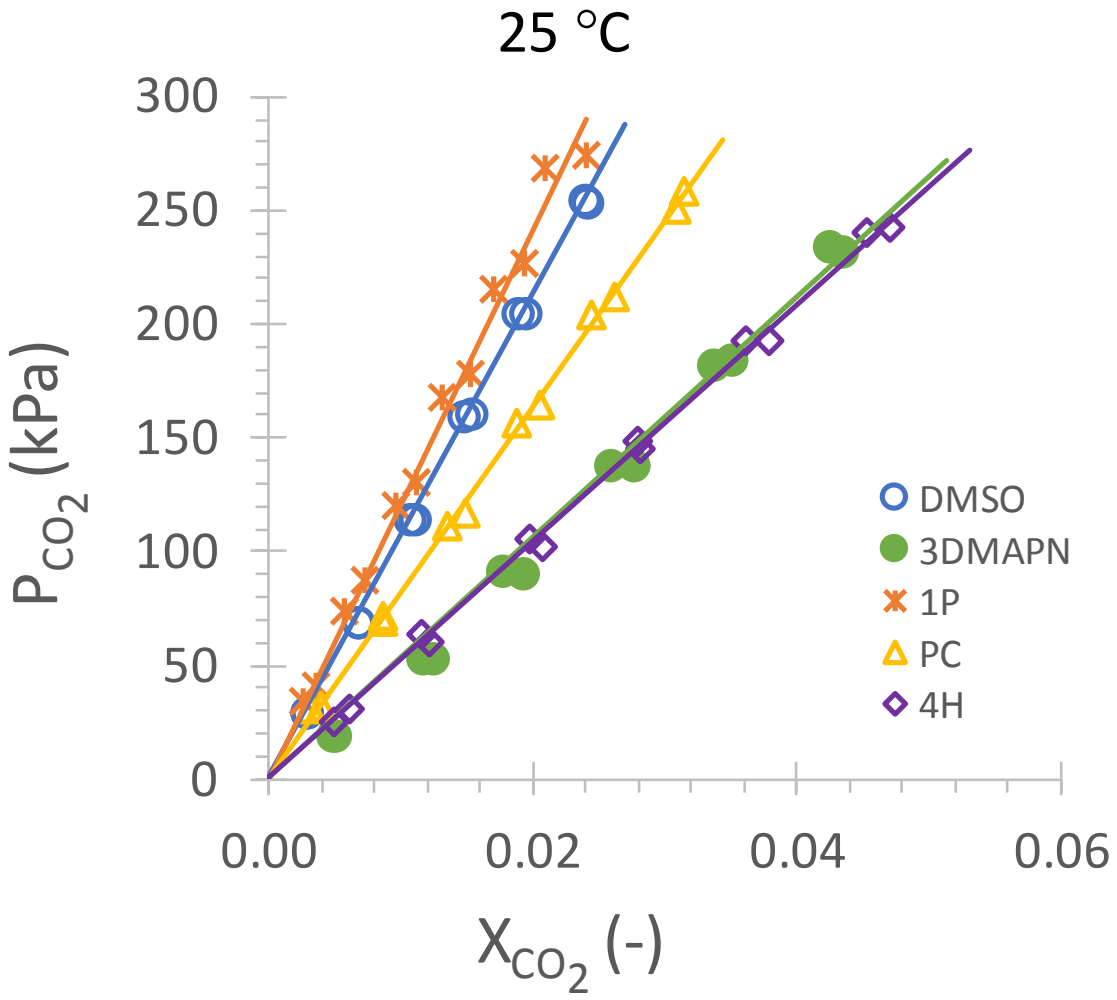
Beståndsdelar med arbetsplatsrelaterade gränsvärden att beakta

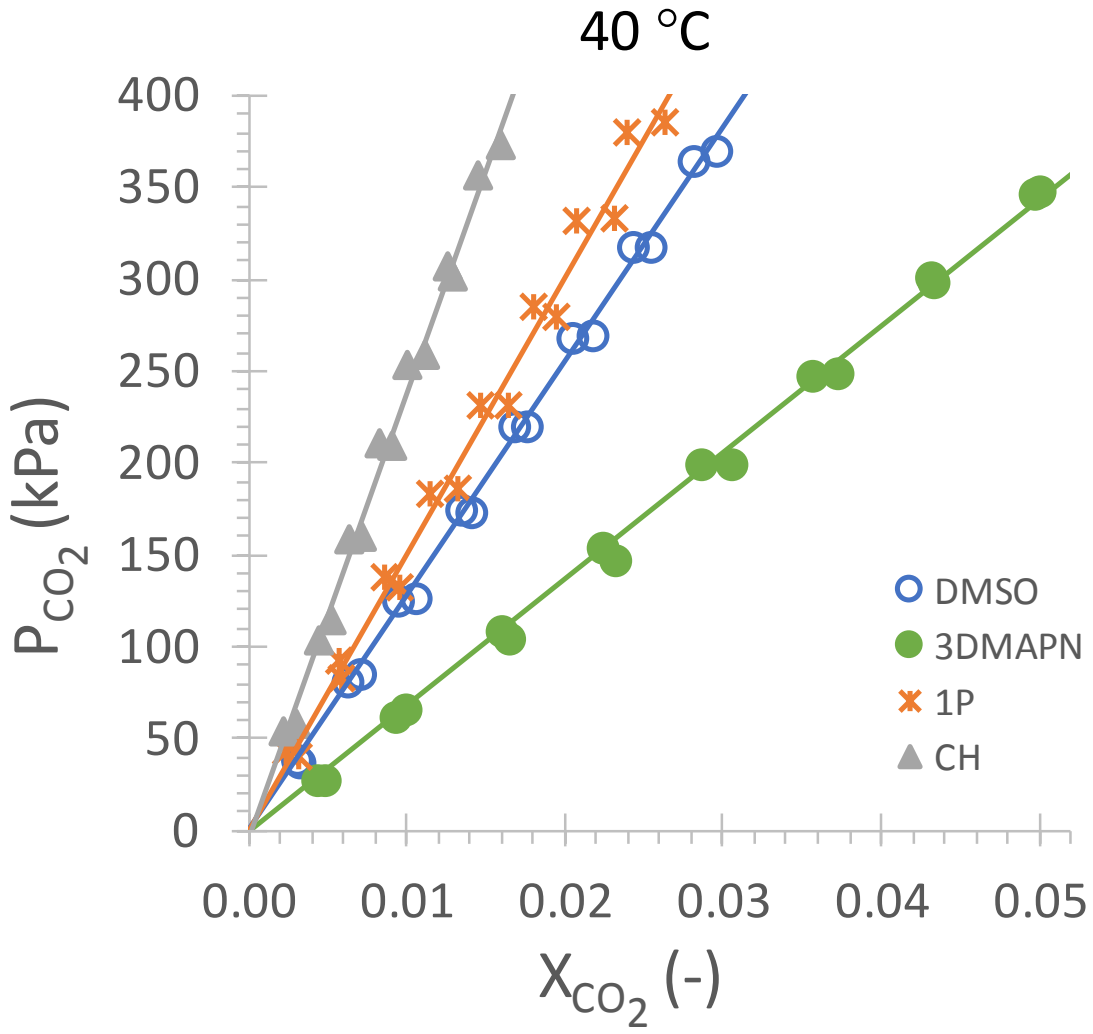
Beståndsdel	CAS-nr.	VärdeExponeringssätt	Kontrollparametrar	Grundval
N-methyl-2-pyrrolidone	872-50-4	TWA	10 ppm 40 mg/m3	Europa. KOMMISSIONENS DIREKTIV 2009/161/EU om upprättande av en tredje förteckning över indikativa yrkeshygieniska gränsvärden enligt rådets direktiv 98/24/EG och om ändring av kommissionens direktiv 2000/39/EG
	Anmärkning	Fastställer möjligheten av betydande upptag genom huden Vägledande		
		STEL	20 ppm 80 mg/m3	Europa. KOMMISSIONENS DIREKTIV 2009/161/EU om upprättande av en tredje förteckning över indikativa yrkeshygieniska gränsvärden enligt rådets direktiv 98/24/EG och om ändring av kommissionens direktiv 2000/39/EG
		Fastställer möjligheten av betydande upptag genom huden Vägledande		
		KTV	20 ppm 80 mg/m3	Hygieniska gränsvärden - Gränsvärdeslista
		Ämnet kan lätt upptas genom huden. Ämnet är reproduktionsstörande.		
		NGV	10 ppm 40 mg/m3	Hygieniska gränsvärden - Gränsvärdeslista
		Ämnet kan lätt upptas genom huden. Ämnet är reproduktionsstörande.		

Härledd nolleffektnivå (DNEL)

Tillämpningsområde	Exponeringsväg	Hälsoeffekt	Värde
Arbetstagare	Hudkontakt	Akut - systemiska effekter	208mg/kg kroppsvikt/d
Arbetstagare	Inandning	Akut - systemiska effekter	80 mg/m3
Arbetstagare	Hudkontakt	Långtids - systemiska effekter	19,8mg/kg kroppsvikt/d
Arbetstagare	Inandning	Långtids - systemiska effekter	40 mg/m3

Physical Solubility – pure solvents





Henry's Constant

25 °C

Solvent	H_{CO2} (MPa)
4H	5.2
3DMAPN	5.29
NMP	6.97*
PC	8.17
DMSO	10.7
1P	12.1
H_2O	163#

40 °C

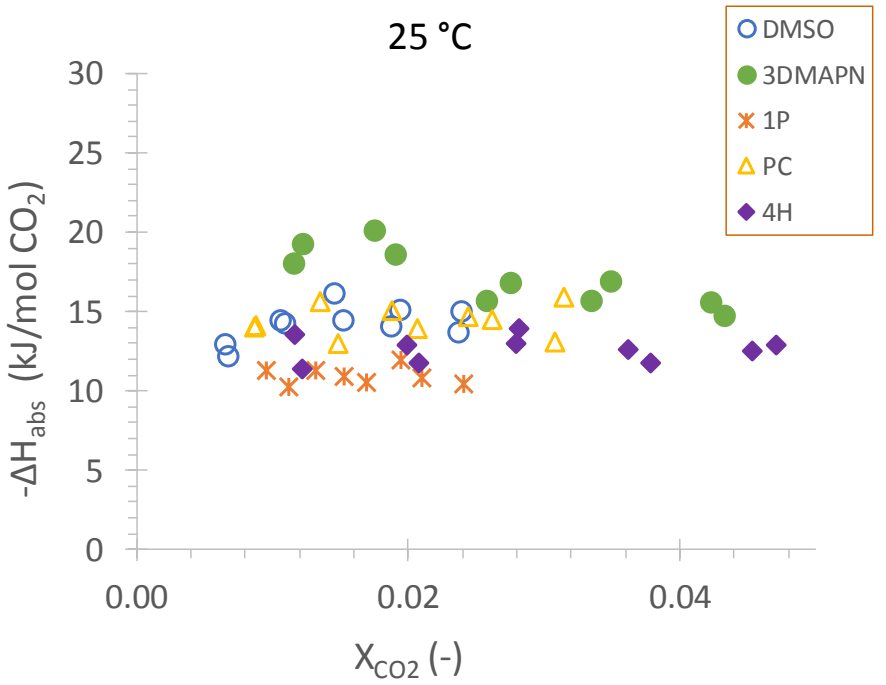
Solvent	H_{CO2} (MPa)
3DMAPN	6.87
NMP	8.85**
DMSO	12.8
1P	15.1
CH	23.87
H_2O	325#

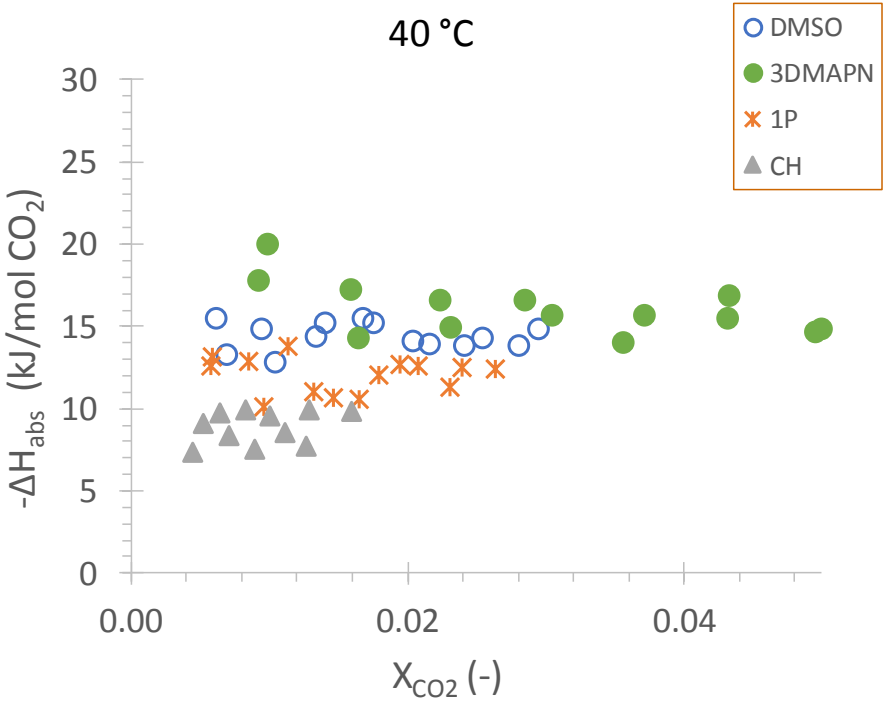
CO_2 solubility:

4H > 3DMAPN > NMP > PC > DMSO > 1P > CH > H_2O

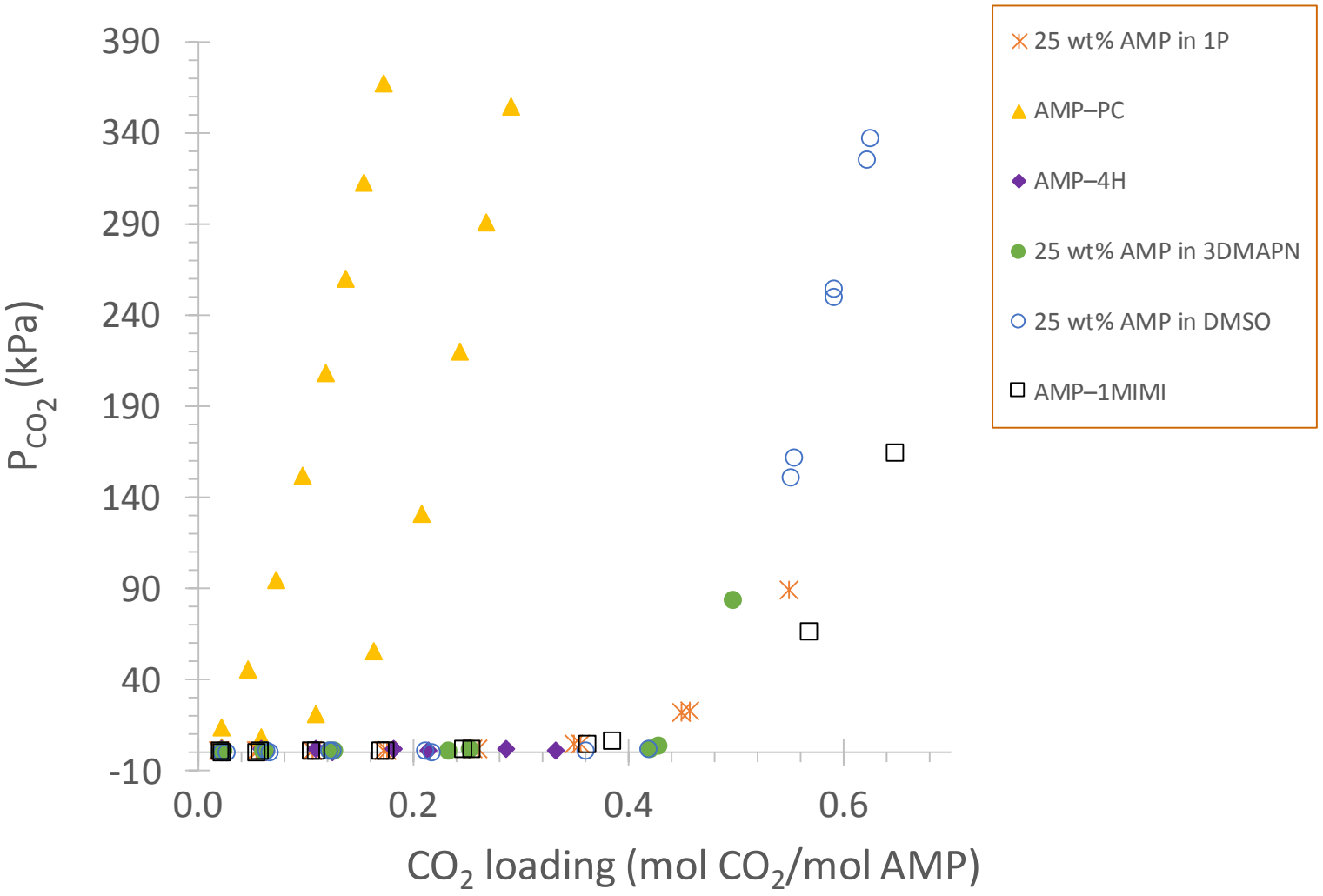
H_{abs} – pure solvents

	$-\Delta H_{abs}$ (kJ/mol CO_2)		
Solvent	**25 °C**	**40 °C**	**Average**
DMSO	14.2	14.4	14.3
3DMAPN	17.1	16.0	16.6
1P	10.9	12.0	11.5
PC	14.4	-	-
4H	12.6	-	-
CH	-	8.9	-





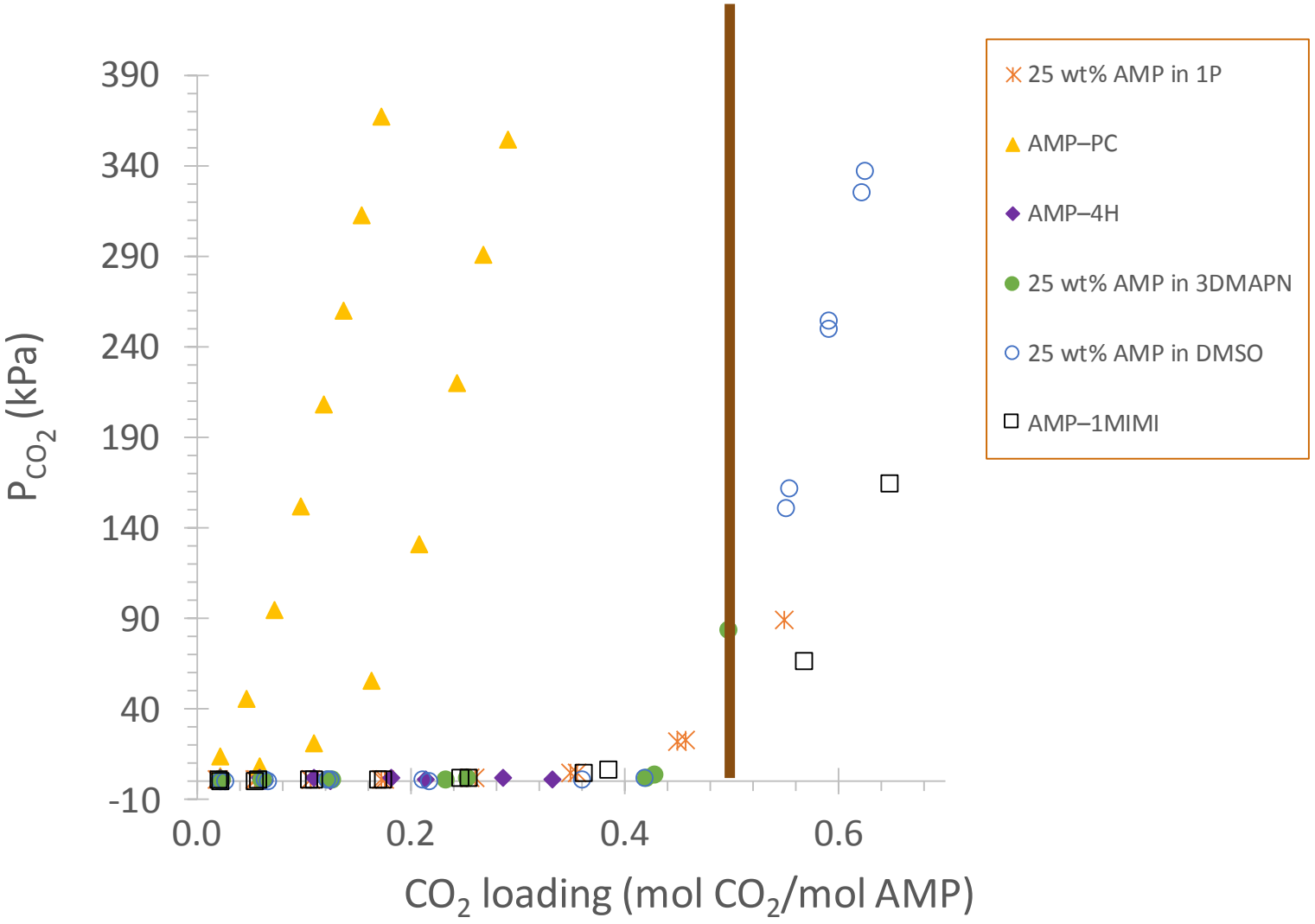
CO_2 solubility – amine mix 25°C



25 wt% AMP in	Loading (mol CO_2/mol AMP) 25 °C Run 1	Run 2
DMSO	0.21	0.22
3DMAPN	0.02	0.02
1P	0.11	0.11
PC	0.16	X
4H	0.02	0.02
1MIMI	X	X
CH	-	-
NMP	0.26*	0.29*

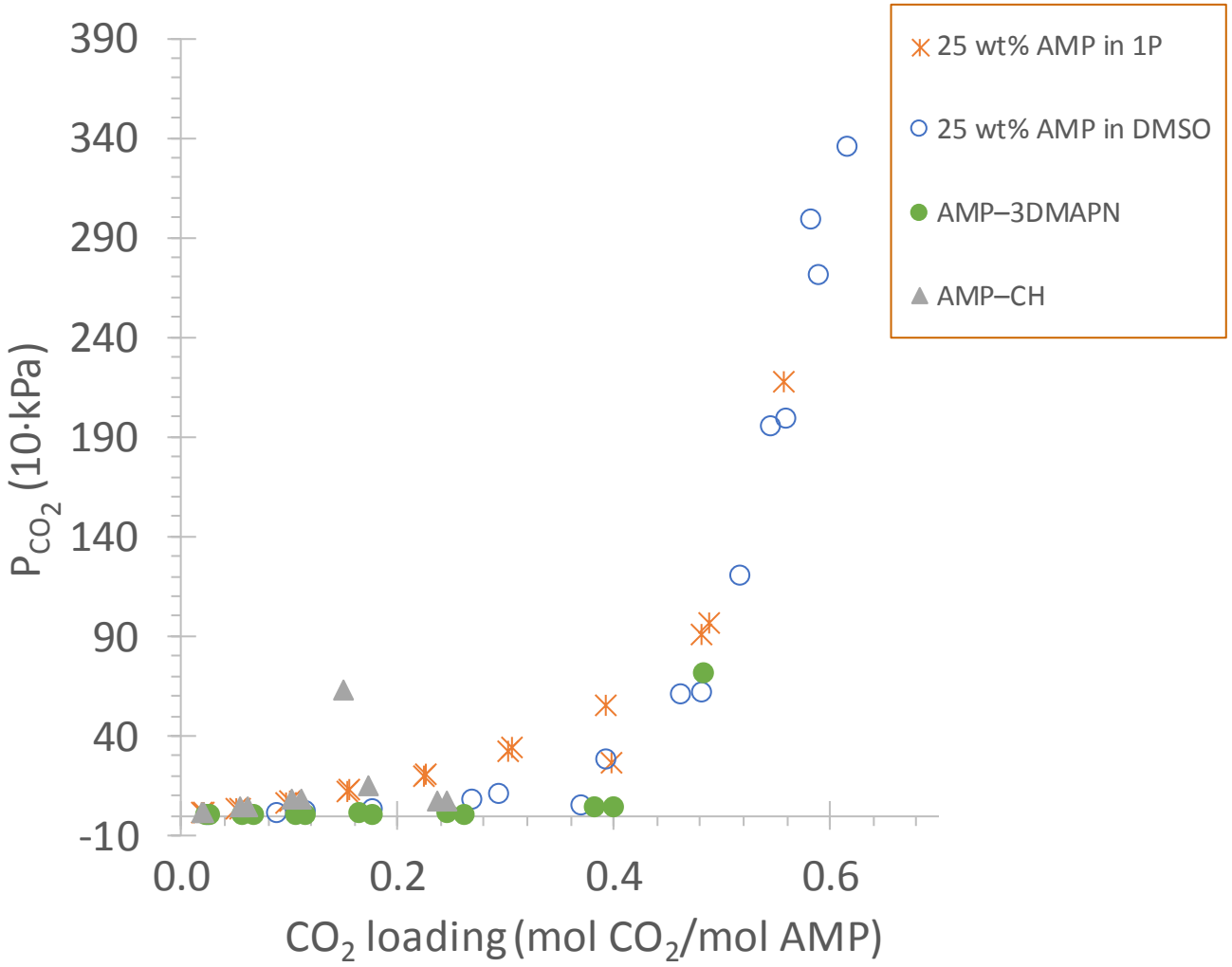
CO_2 solubility – amine mix

25°C



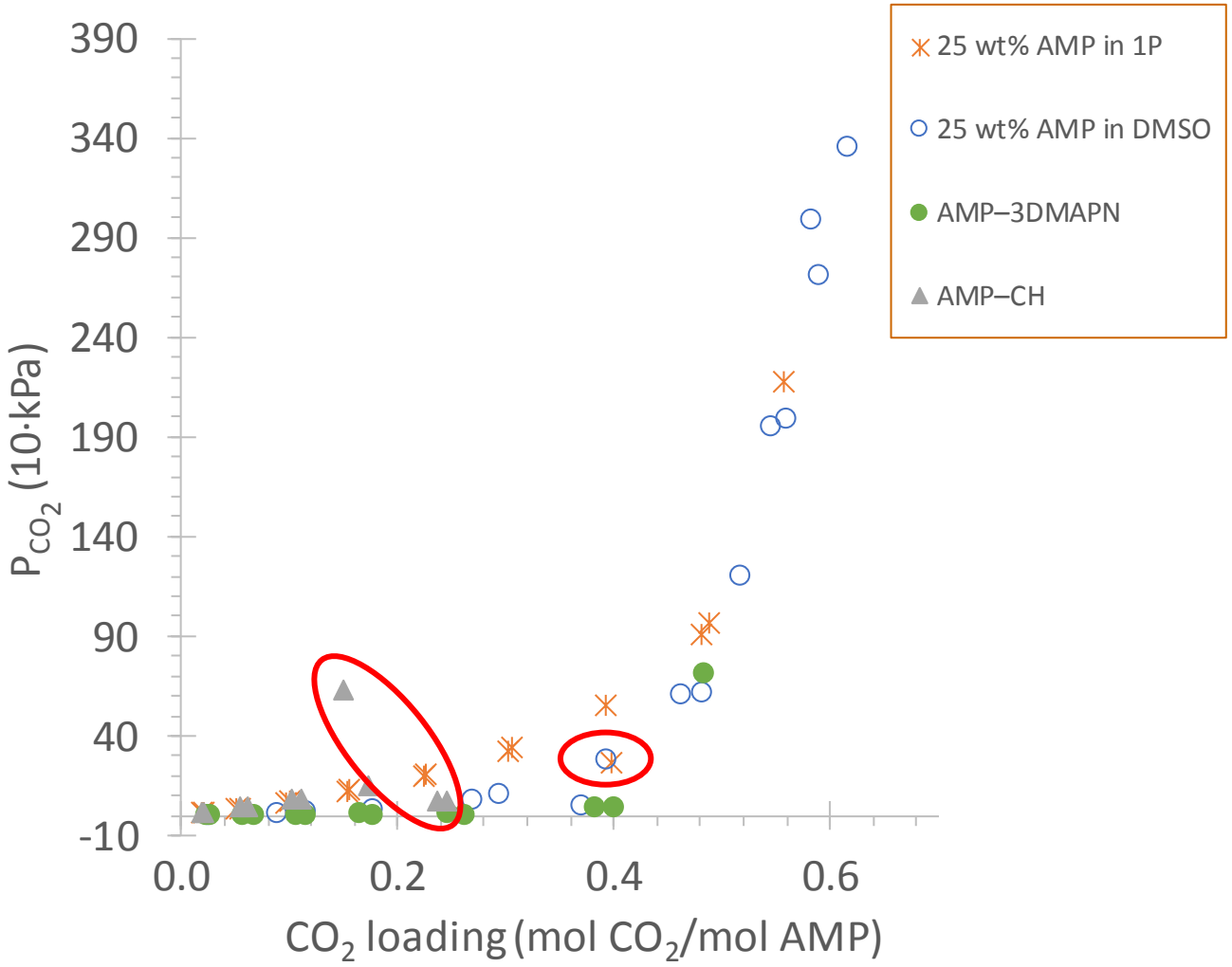
25 wt% AMP in	Loading (mol CO_2/mol AMP) 25 °C Run 1	Run 2
DMSO	0.21	0.22
3DMAPN	0.02	0.02
1P	0.11	0.11
PC	0.16	X
4H	0.02	0.02
1MIMI	X	X
CH	-	-
NMP	0.26*	0.29*

CO_2 solubility – amine mix 40°C



25 wt% AMP in	Loading (mol CO_2/mol AMP) 40 °C Run 1	Run 2
DMSO	0.37	0.52
3DMAPN	0.03	0.02
1P	X	0.40
PC	-	-
4H	-	-
1MIMI	-	-
CH	0.24	0.25
NMP	0.39**	0.40**

CO_2 solubility – amine mix 40°C



25 wt% AMP in	Loading (mol CO_2/mol AMP) 40 °C Run 1	Run 2
DMSO	0.37	0.52
3DMAPN	0.03	0.02
1P	X	0.40
PC	-	-
4H	-	-
1MIMI	-	-
CH	0.24	0.25
NMP	0.39**	0.40**

LUND
UNIVERSITY