Captage du CO_2 dans un mélange de solvants

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Prométhée Procédés hydrométallurgiques pour la gestion intégrée des ressources primaires et secondaires

JOURNÉES SCIENTIFIQUES
23 et 24 mai 2024,
IFPEN, Rueil-Malmaison

ifp Energies nouvelles

INTRODUCTION

fives

Sustainable mobility | New energies | Responsible oil and gas

EleTher 2

Ele-Ther:

e-Thermodynamics Joint Industrial Project (JIP)

An Industrial Community on Electrolyte Thermodynamics

User community

ifp Energies nouvelles

Software community

NESTE

BASF We create chemistry

BAYER

orano

covestro

SOLVAY

aspentech

Hafnium Labs

fives

ProSim

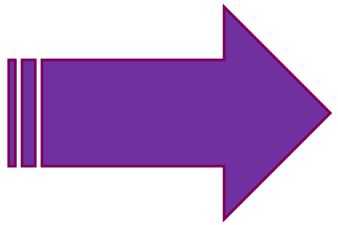
INTRODUCTION

ELECTROLYTE THERMODYNAMICS
REACTIVE SYSTEMS WITH MIXED SOLVENTS

Industrial & Technical context

New processes involve electrolytic systems including ionic species and chemical reactions

- Transformation of biomass
- Battery
- CO_2 capture
- Geothermal context
- Metal purification and recycling
- ….



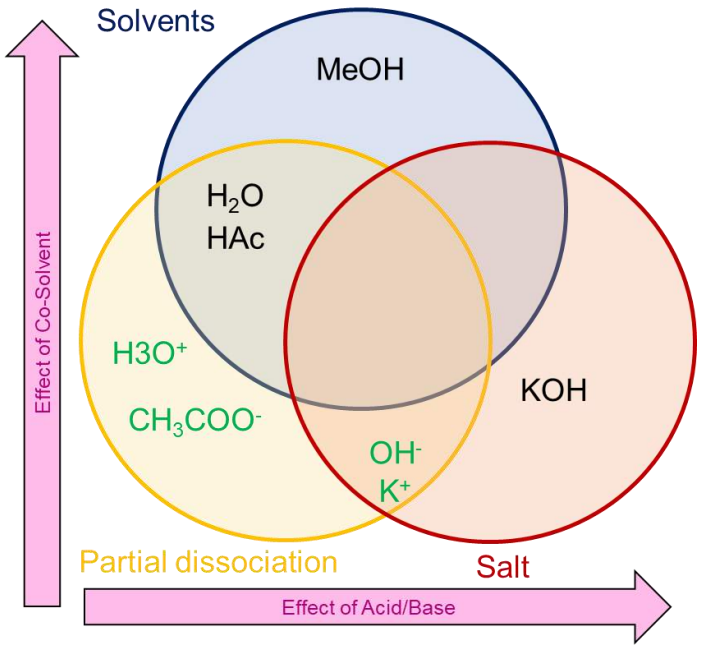
Needs:
- Reaction constants
- Non-ideality model
- Algorithm to compute equilibrium

Need of methodologies and benchmark of process solutions
➔ proposal of the JIP Elether2

INTRODUCTION

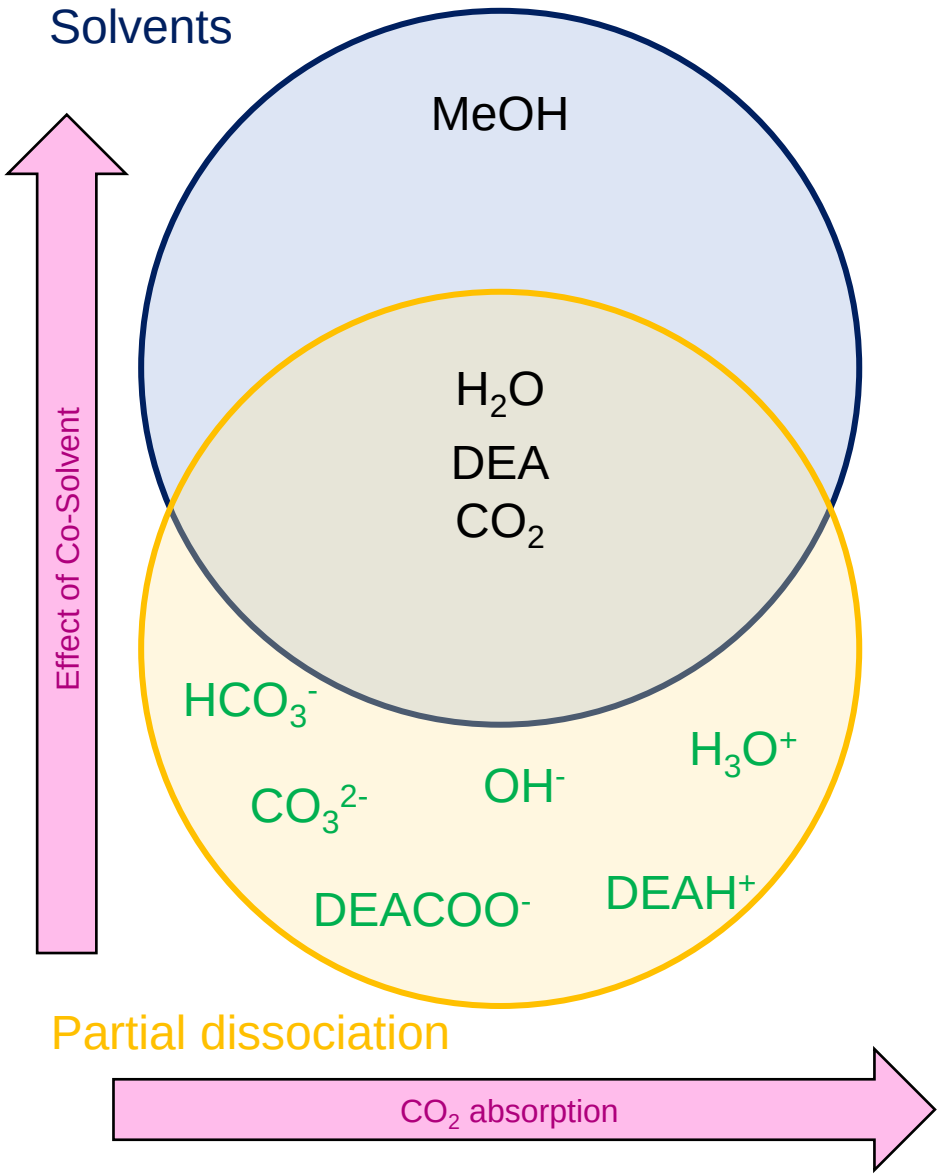
fives

CASE STUDY N° 1



CASE STUDY N° 2

e-NRTL



INTRODUCTION

FIVES-PROSIM TOOLS

Simulis Thermodynamics® →
- VLLSE / Thermo. Prop. Calcl. In MS Excel
- Large Thermo. Models Library
- Pure comp. Database

+

Reactive Models Editor →
- Edit Reaction constants, BIP, TIP for electrolyte models

+

Simulis Parameters Identification →
- VBA Macro. to adjust Electrolyte models parameters

+

Simulis Numerics® →
- Numerical method to adjust parameters

CONTENTS

H_2O / DEA / MeOH / CO_2 PARAM. REG. USING e-NRTL

01 Thermodynamic Model

1. 1. eNRTL AND VLE CALCULATIONS

- eNRTL formulation in Simulis Thermodynamics®
  - ln γNRTL: Tsanas 2022 / **Song 2009** / Bollas 2008

$$\frac{1}{\tau_c}\ln\gamma_c^{lc} = \sum_m \frac{X_m G_{cm}}{\sum_l X_l G_{lm}}\left(\tau_{cm} - \frac{\sum_l X_l G_{lm}\tau_{lm}}{\sum_l X_l G_{lm}}\right) + \frac{\sum_{l\neq c} X_l G_{lc}\tau_{lc}}{\sum_{l\neq c} X_l G_{lc}} + \sum_a \frac{X_a G_{ca}}{\sum_{l\neq a} X_l G_{la}}\left(\tau_{ca} - \frac{\sum_{l\neq a} X_l G_{la}\tau_{la}}{\sum_{l\neq a} X_l G_{la}}\right)$$

$$\ln\gamma_k^{NRTL} = Z_k\left[R_k + \sum_j \frac{X_j G_{kj}\left(\tau_{kj} - R_j\right)}{S_j}\right]$$

  - Born & PDH terms

$$\ln\gamma_i^{Born} = \frac{N_A Q_e^2}{2RT}\cdot\frac{z_i^2}{\mathbf{r_i}}\cdot\left(\frac{1}{\boldsymbol{\varepsilon}} - \frac{1}{\boldsymbol{\varepsilon_w}}\right)10^{-2}$$

$$\ln\gamma_i^{PDH} = f(A_\varphi)$$

$$A_\varphi = \frac{1}{3}\cdot\left(\frac{2\pi N_A}{\mathbf{v}}\right)^{1/2}\cdot\left(\frac{Q_e^2}{\boldsymbol{\varepsilon} k_B T}\right)^{3/2}$$

  - Chemical reaction constant: Molality scale + Symetric Ref. State
  - VLE

$$P\cdot y_j^{app}\varphi_j^{vap}(y^{app},T,P) = \mathbf{f_j^{0,l}(T,P)}\cdot x_j^{app}\cdot\gamma_j(T,P,x^{app})$$

$$\ln\frac{H_{CO_2}^{MS}(T,x^{app})}{\gamma_{CO_2}^{\infty,MS}(T,P,x^{app})} = \sum_s w_s(x^{app})\ln\frac{\mathbf{H_{CO_2}^s(T)}}{\gamma_{CO_2}^{\infty,s}(T,P)}$$

$$w_i = \frac{x_i\left(\mathbf{v_{CO_2,i}^\infty}\right)^{2/3}}{\sum_s x_s\left(\mathbf{v_{CO_2,s}^\infty}\right)^{2/3}}$$

→ Solute gas: $\mathbf{H_{j,solvant}(T)}\cdot\Pi_j(T,P)$ → Multisolvent

→ Other: $\mathbf{P_j^{sat}(T)}\cdot\Pi_j(T,P)$

1. 2. NUMBER OF ADJUSTABLE PARAMETERS

Classification		Signification	Concerned	Number of parameters
Pure comp. param.	ε_i	Dielectrique constant	Solvent	NSolvent
Pure comp. param.	V_i	Molar volume	Solvent	NSolvent
Pure comp. param.	R_i	Born radius	Ions	NIons
Pure comp. param.	$\mathbf{H_i}$	Henry law constant	Gas solute	NGas x Nsolvent
Pure comp. param.	$\mathbf{P_i^{sat}}$	Sat. Pressure	Solvent	NConst - NGas
χ Reaction	$\mathbf{K_j}$	χ Reaction constant	χ Reaction	NReac
e-NRTL param.	τ	Non-symetric parameters	Molecule/ion pairs	[NConstxNIon_pairs + NConst(NConst-1)/2] x 2
e-NRTL param.	α	Symetric parameters	Molecule/ion pairs	NConstxNIon_pairs + NConst(NConst-1)/2

$$N_{param} = 2 \cdot N_{solvent} + N_{ions} + N_{gas} \cdot (N_{solvent} - 1) + N_{comp} + N_{react} + 3 \cdot \left[N_{comp} \cdot N_{ion\ pairs} + \frac{N_{comp}(N_{comp}-1)}{2} \right]$$

$$\mathbf{N_{param} = 137}$$

1. 2. NUMBER OF ADJUSTABLE PARAMETERS

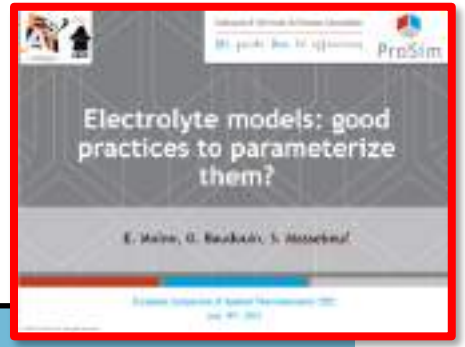
Classification		Signification	Concerned	Number of parameters
Pure comp. param.	ε_i	Dielectrique constant	Solvent	NSolvent
Pure comp. param.	V_i	Molar volume	Solvent	NSolvent
Pure comp. param.	R_i	Born radius	Ions	NIons
Pure comp. param.	$\mathbf{H_i}$	Henry law constant	Gas solute	NGas x Nsolvent
Pure comp. param.	$\mathbf{P_i^{sat}}$	Sat. Pressure	Solvent	NConst - NGas
χ Reaction	$\mathbf{K_j}$	χ Reaction constant	χ Reaction	NReac
e-NRTL param.	τ	Non-symetric parameters	Molecule/ion pairs	[NConstxNIon_pairs + NConst(NConst-1)/2] x 2
e-NRTL param.	α	Symetric parameters	Molecule/ion pairs	NConstxNIon_pairs + NConst(NConst-1)/2

$$N_{param} = 2 \cdot N_{solvent} + N_{ions} + N_{gas} \cdot (N_{solvent} - 1) + N_{comp} + N_{react} + 3 \cdot \left[N_{comp} \cdot N_{ion\ pairs} + \frac{N_{comp}(N_{comp}-1)}{2} \right]$$

$$N_{param} = 3 \cdot \left[N_{comp} \cdot N_{ion\ pairs} + \frac{N_{comp}(N_{comp}-1)}{2} \right]$$

$$\mathbf{N_{param} = 114}$$

1. 2. NUMBER OF ADJUSTABLE PARAMETERS



Classification		Signification	Concerned	Number of parameters
Pure comp. param.	ε_i	Dielectrique constant	Solvent	NSolvent
Pure comp. param.	V_i	Molar volume	Solvent	NSolvent
Pure comp. param.	R_i	Born radius	Ions	NIons
Pure comp. param.	$\mathbf{H_i}$	Henry law constant	Gas solute	NGas x Nsolvent
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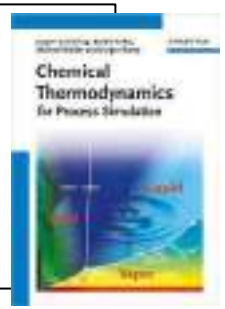
e-NRTL param.	τ	Non-symetric parameters	Molecule/ion pairs	[NConstxNIon_pairs + NConst(NConst-1)/2] x 2
e-NRTL param.	α	Symetric parameters	Molecule/ion pairs	NConstxNIon_pairs + NConst(NConst-1)/2

Lack of experimental data:

- ε_i
- H_i

No database for r_i

- Gmehling 3Å
- From Charge + Born constant
- High influence

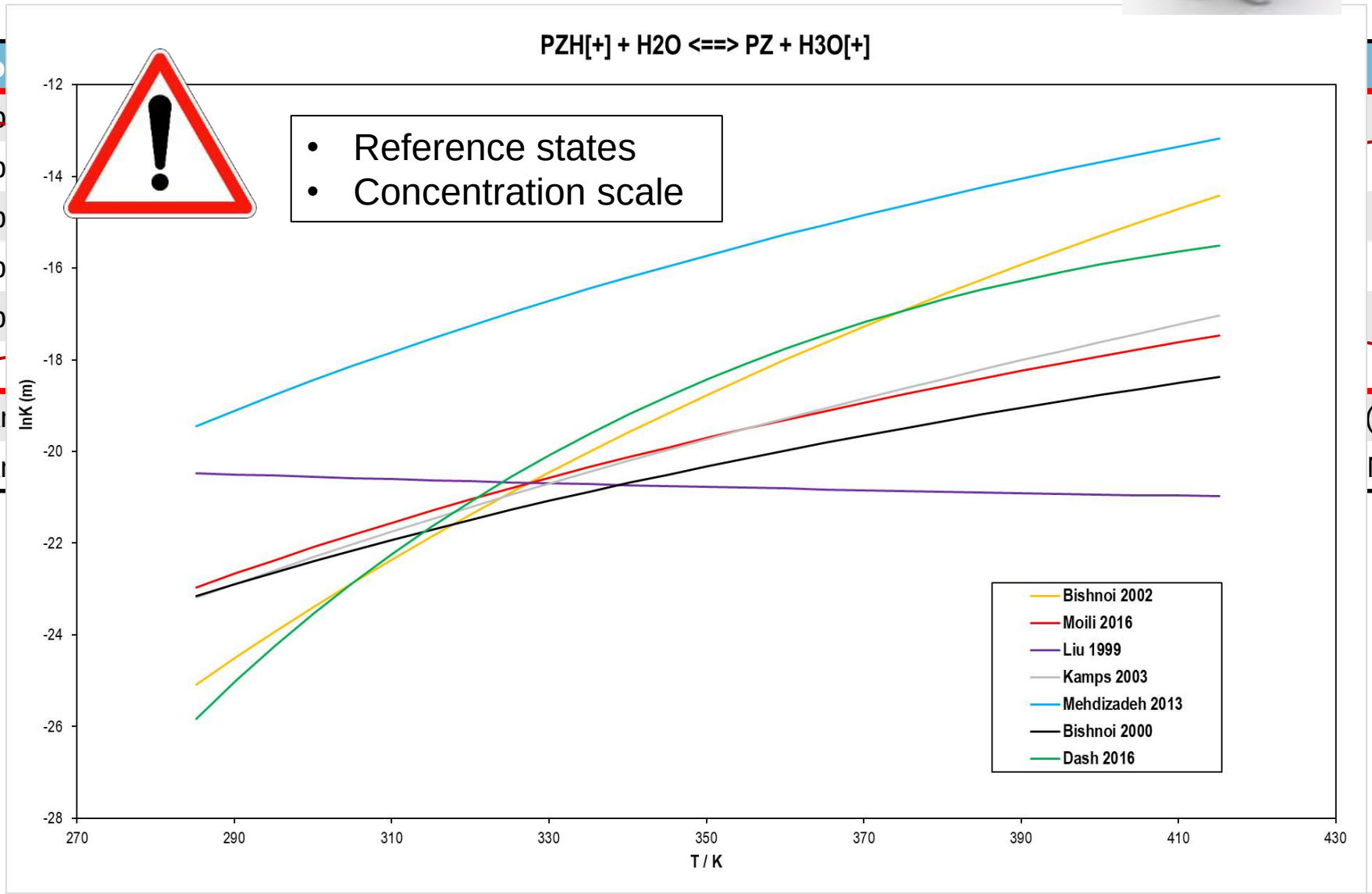


Chemical reaction constants

- Obviously dependent on activity coefficients
- From $\Delta_f G^{ig}_{298,15}$, $\Delta_f H^{ig}_{298,15}$, $\Delta_f G^{\infty,aq}_{298,15}$, $\Delta_f H^{\infty,aq}_{298,15}$, $C^{\infty,aq}_{p,i}$
  → New experimental data required
- Already established in publication

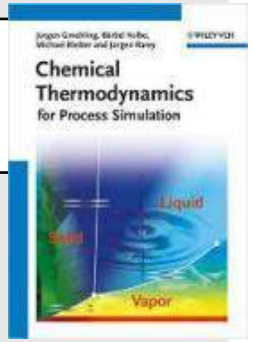
1. 2. NUMBER OF ADJUSTABLE PARAMETERS

Classificatio	
Pure comp. p	
Pure comp. p	
Pure comp. p	
Pure comp. p	
Pure comp. p	
χ Reaction	
e-NRTL parar	(NConst-1)/2] x 2
e-NRTL parar	NConst-1)/2



1. 2. NUMBER OF ADJUSTABLE PARAMETERS

Classification		Signification	Concerned	Methods to fix parameters
Pure comp. param.	ε_i	Dielectric constant	Solvent	• DEA = MDEA [ZHA11] • MeOH [SON09]
Pure comp. param.	v_i	Molar volume	Solvent	• DIPPR
Pure comp. param.	R_i	Born radius	Ions	• 3 Å • From Charge + Born Constant (SW)
Pure comp. param.	$\mathbf{H_i}$	Henry law constant	Gas solute	• CO_2/H_2O [AUS91] • CO_2/MeOH [SCH08] • CO_2/DEA = CO_2/MDEA [ZHA11]
Pure comp. param.	$\mathbf{P_i^{sat}}$	Sat. Pressure	Solvent	• DIPPR
χ Reaction	$\mathbf{K_j}$	χ Reaction constant	χ Reaction	• [AUS91]



02

Regression procedure

2. REGRESSION PROCEDURE

- Binary systems → Ternary systems → Quaternary system
- At each step (binary, ternary, quaternary), identify the parameters that may affect the results of earlier steps.
- Using a sensitivity analysis and speciation data, have a look at which parameters can be adjusted for the considered step

Legend

	Regressed parameters at the current step
	Regressed parameters on sub-systems already studied
	Default parameters
	Parameters that cannot be regressed without affecting results on previously studied sub-systems

2. 1. BINARY SYSTEM

- H_2O/MeOH → OK – EleTher 1
- H_2O/DEA

Reaction (molality scale)	
$2\ H_2O \Leftrightarrow H_3O^+ + OH^-$	[AUS91]
$DEAH^+ \Leftrightarrow DEA + H_3O^+$	[AUS91]

BIP	H_2O	DEA
H_2O		T-dep param.
DEA	T-dep param.	

Reg. NRTL to eNRTL

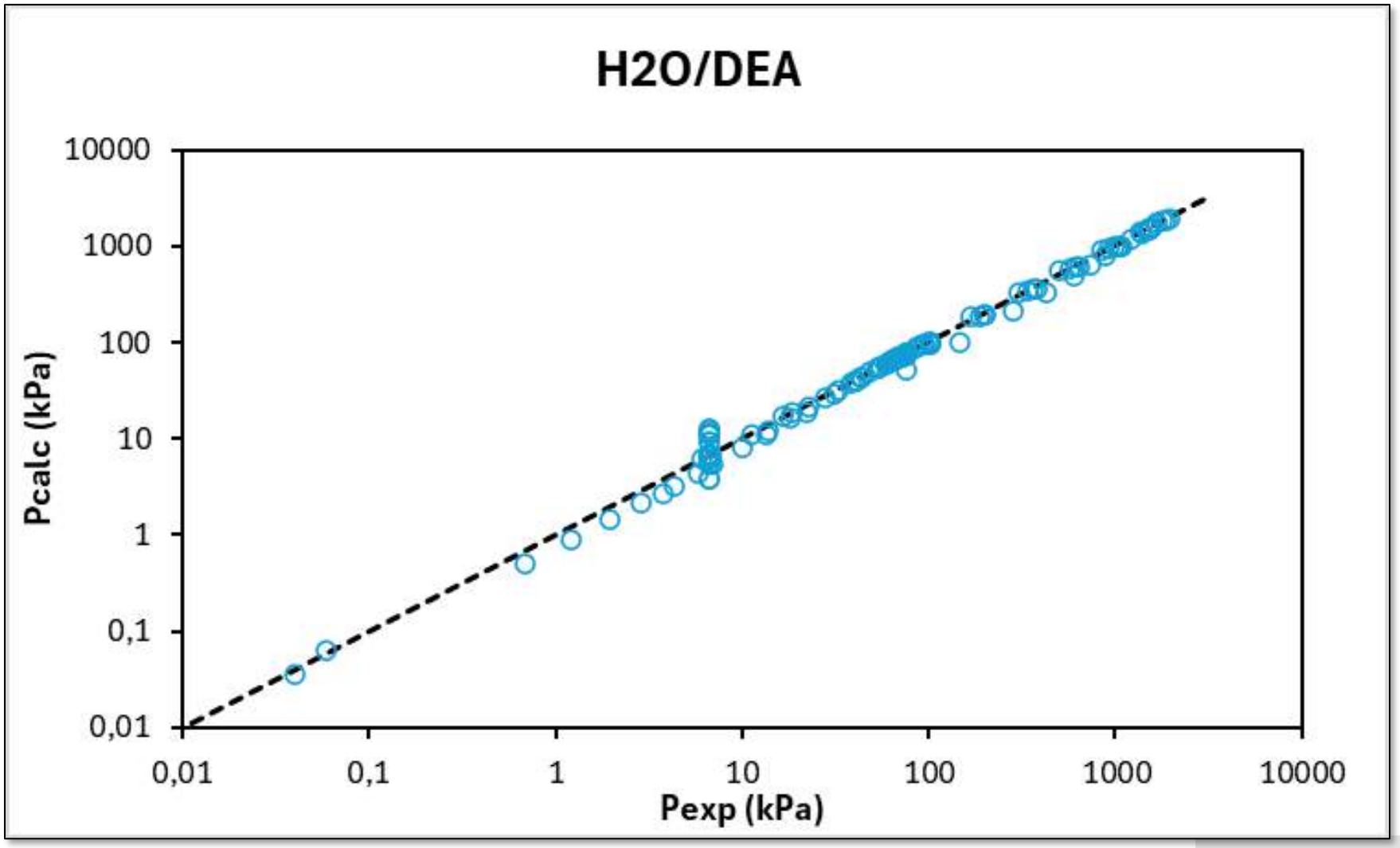
TIP	$(H_3O^+;OH^-)$	$(DEAH^+;OH^-)$
H_2O	Default	Default
DEA	Default	Default

$$\begin{cases} \tau = p_1 + \frac{p_2}{T} + \frac{p_3}{T^2} + p_4 \ln T + \ p_5 \cdot T \\ \alpha = p_1 + p_2 \cdot T + p_3 \cdot T^2 \end{cases}$$

	current step
	already regressed
	Default
	No regression available

2. 1. BINARY SYSTEM

- H_2O/MeOH → OK – EleTher 1
- H_2O/DEA



[KEN84]
[WIL91]
[CAI96a]
[CAI96b]
[HOR02]

2. 1. BINARY SYSTEM

- H_2O/MeOH → OK – EleTher 1
- H_2O/DEA → OK – Reg.
- H_2O/CO_2

Reaction (molality scale)	
$2\ H_2O \Leftrightarrow H_3O^+ + OH^-$	[AUS91]
$CO_2 + H_2O \Leftrightarrow HCO_3^- + H_3O^+$	[AUS91]
$HCO_3^- + H_2O \Leftrightarrow CO_3^{2-} + H_3O^+$	[AUS91]

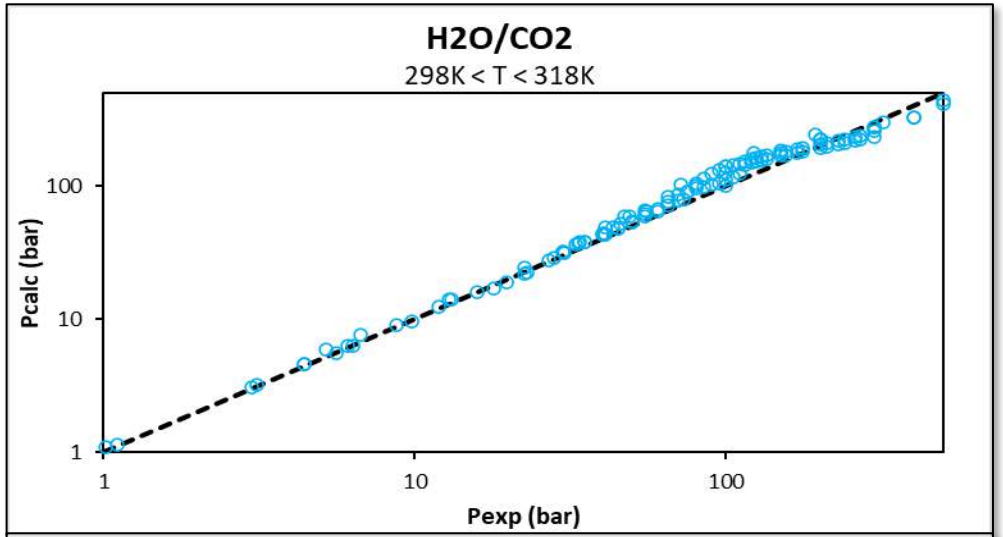
BIP	H_2O	CO_2
H_2O		T-dep param.
CO_2	T-dep param.	

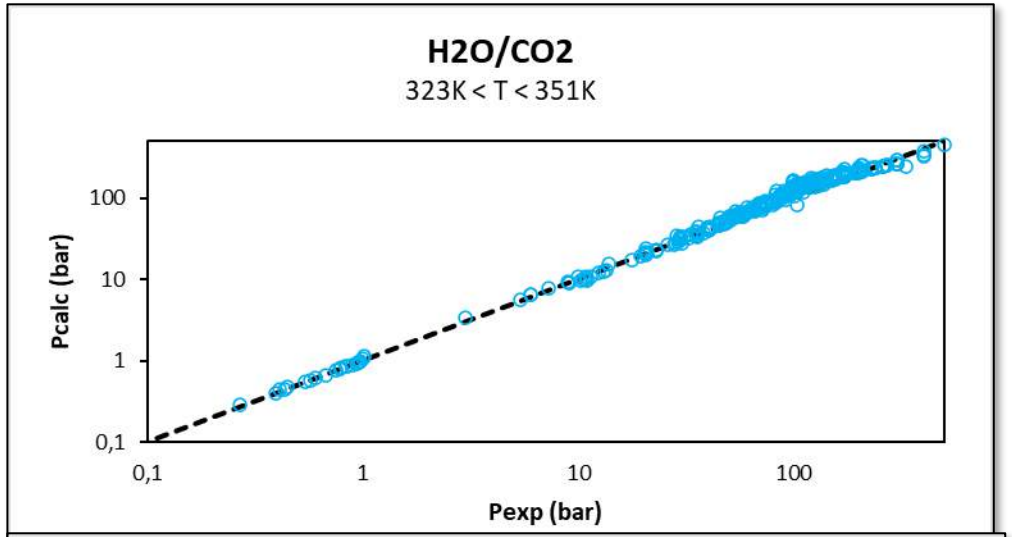
Reg.

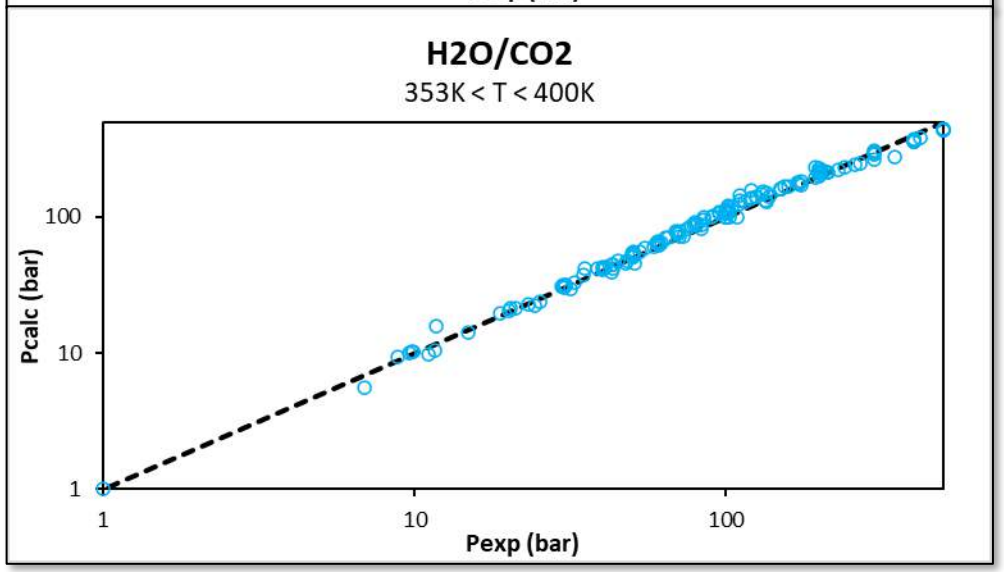
TIP	$(H_3O^+;OH^-)$	$(H_3O^+;CO_3^{2-})$	$(H_3O^+;HCO_3^-)$
H_2O	Default	Default	Default
CO_2	Default	Default	Default

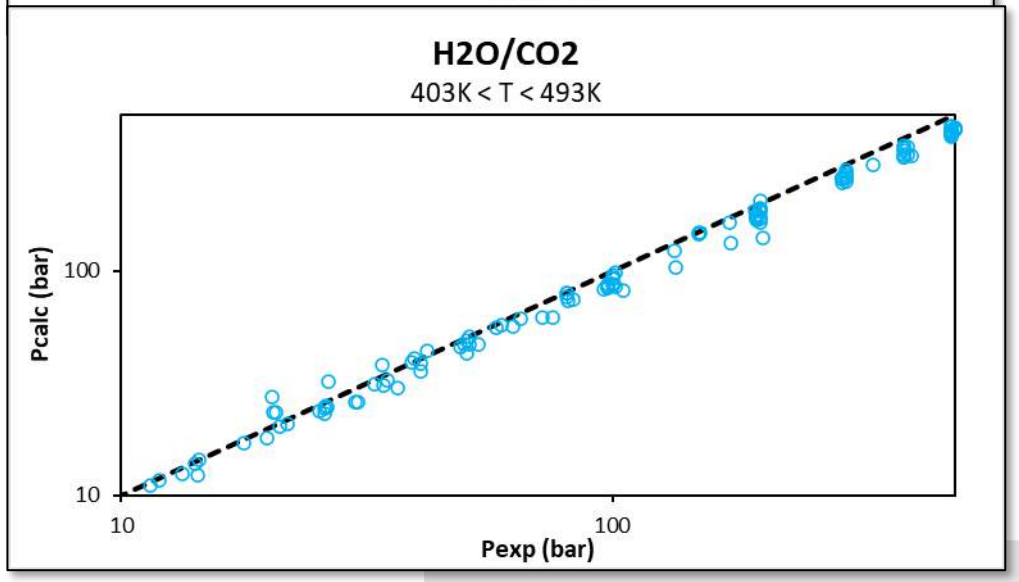
2. 1. BINARY SYSTEM

- H_2O/MeOH → OK – EleTher 1
- H_2O/DEA → OK – Reg.
- H_2O/CO_2







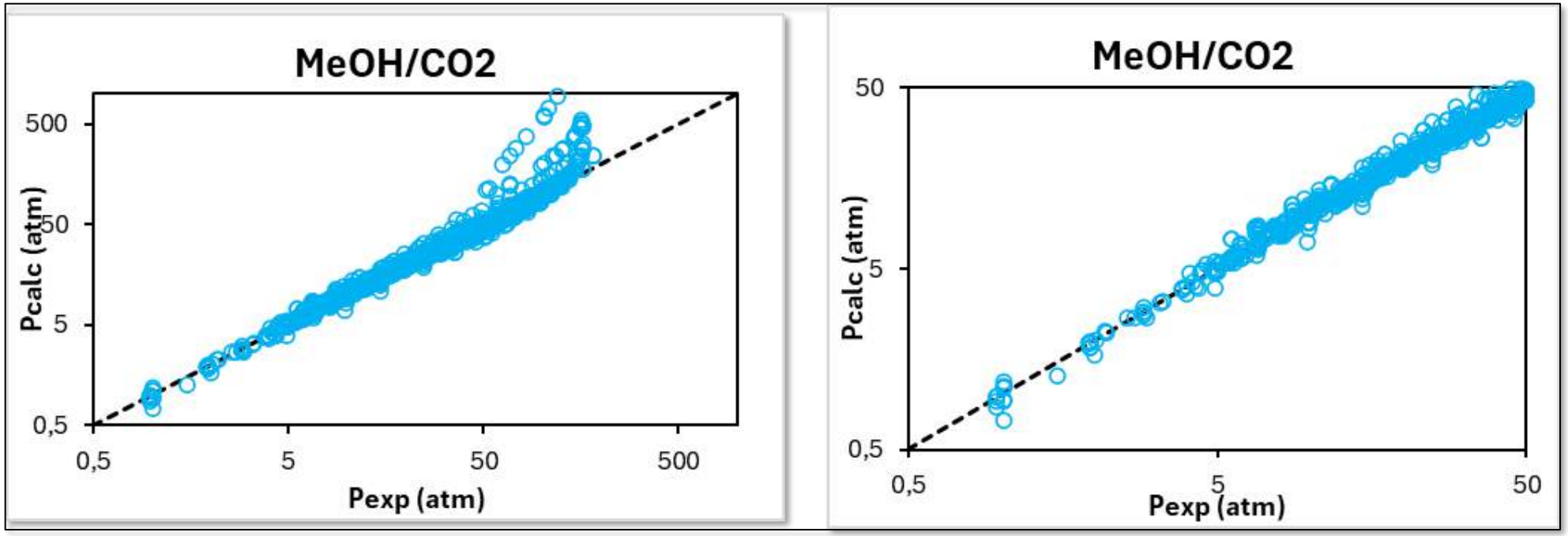


2. 1. BINARY SYSTEM

- H_2O/MeOH → OK – EleTher 1
- H_2O/DEA → OK – Reg.
- H_2O/CO_2 → OK – Reg.
- MeOH/CO_2

BIP	MeOH	CO_2
MeOH		T-dep param.
CO_2	T-dep param.	

Reg. NRTL → eNRTL



2. 2. TERNARY SYSTEMS

- H_2O/MeOH/DEA

Reaction (molality scale)	
$2\ H_2O \Leftrightarrow H_3O^+ + OH^-$	[AUS91]
$DEAH^+ \Leftrightarrow DEA + H_3O^+$	[AUS91]

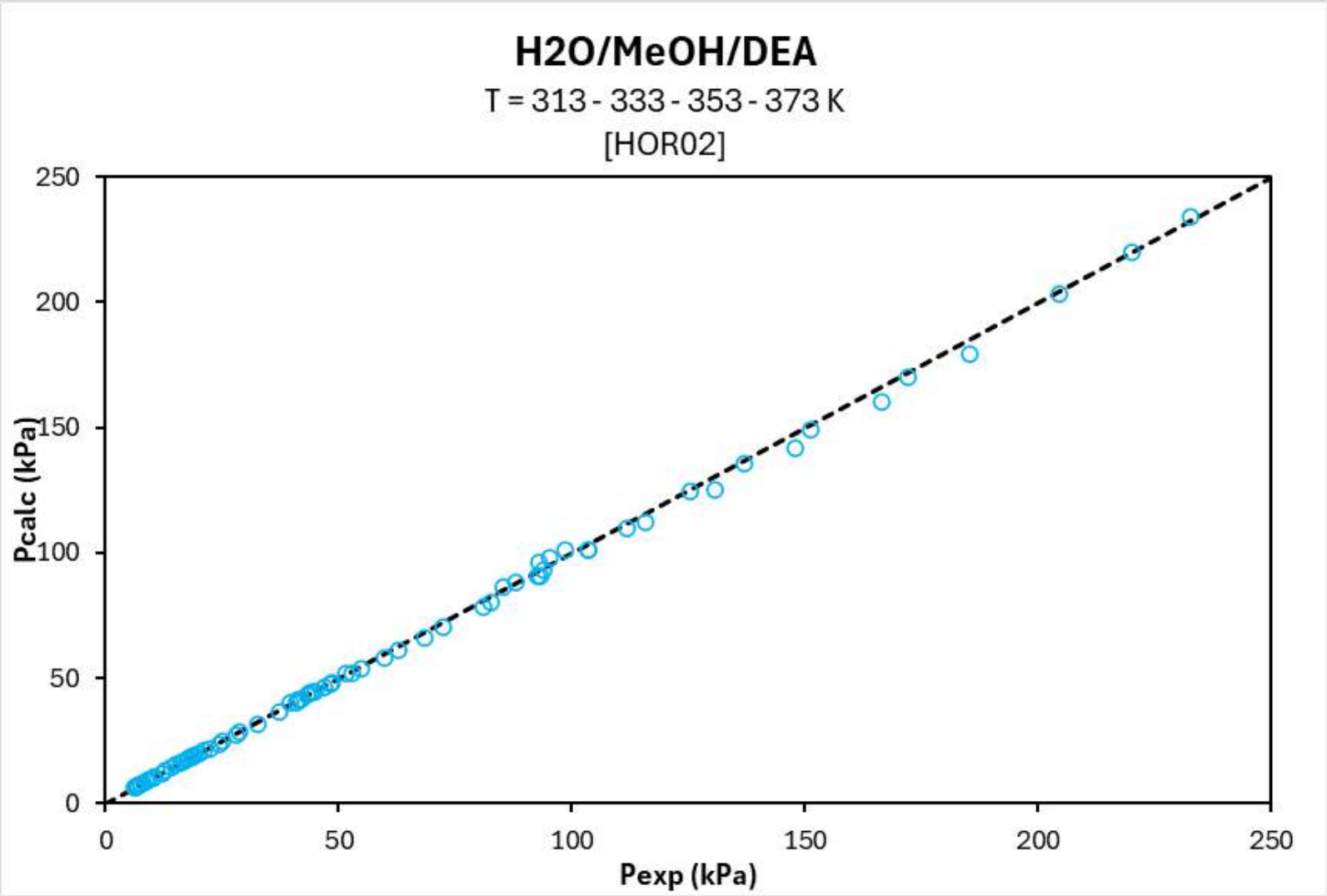
BIP	H_2O	DEA	MeOH
H_2O		T-dep param.	EleTher 1
DEA	T-dep param.		
MeOH	EleTher 1		

TIP	$(H_3O^+;OH^-)$	$(DEAH^+;OH^-)$
H_2O		
DEA		
MeOH		

	current step
	already regressed
	Default
	No regression available

2. 2. TERNARY SYSTEMS

- H_2O/MeOH/DEA



2. 2. TERNARY SYSTEMS

- H_2O/DEA/CO_2

Reaction (molality scale)	
$2\ H_2O \Leftrightarrow H_3O^+ + OH^-$	[AUS91]
$CO_2 + H_2O \Leftrightarrow HCO_3^- + H_3O^+$	
$HCO_3^- + H_2O \Leftrightarrow CO_3^{2-} + H_3O^+$	
$DEAH^+ + H_2O \Leftrightarrow DEA + H_3O^+$	
$DEACOO^- + H_2O \Leftrightarrow DEA + HCO_3^-$	

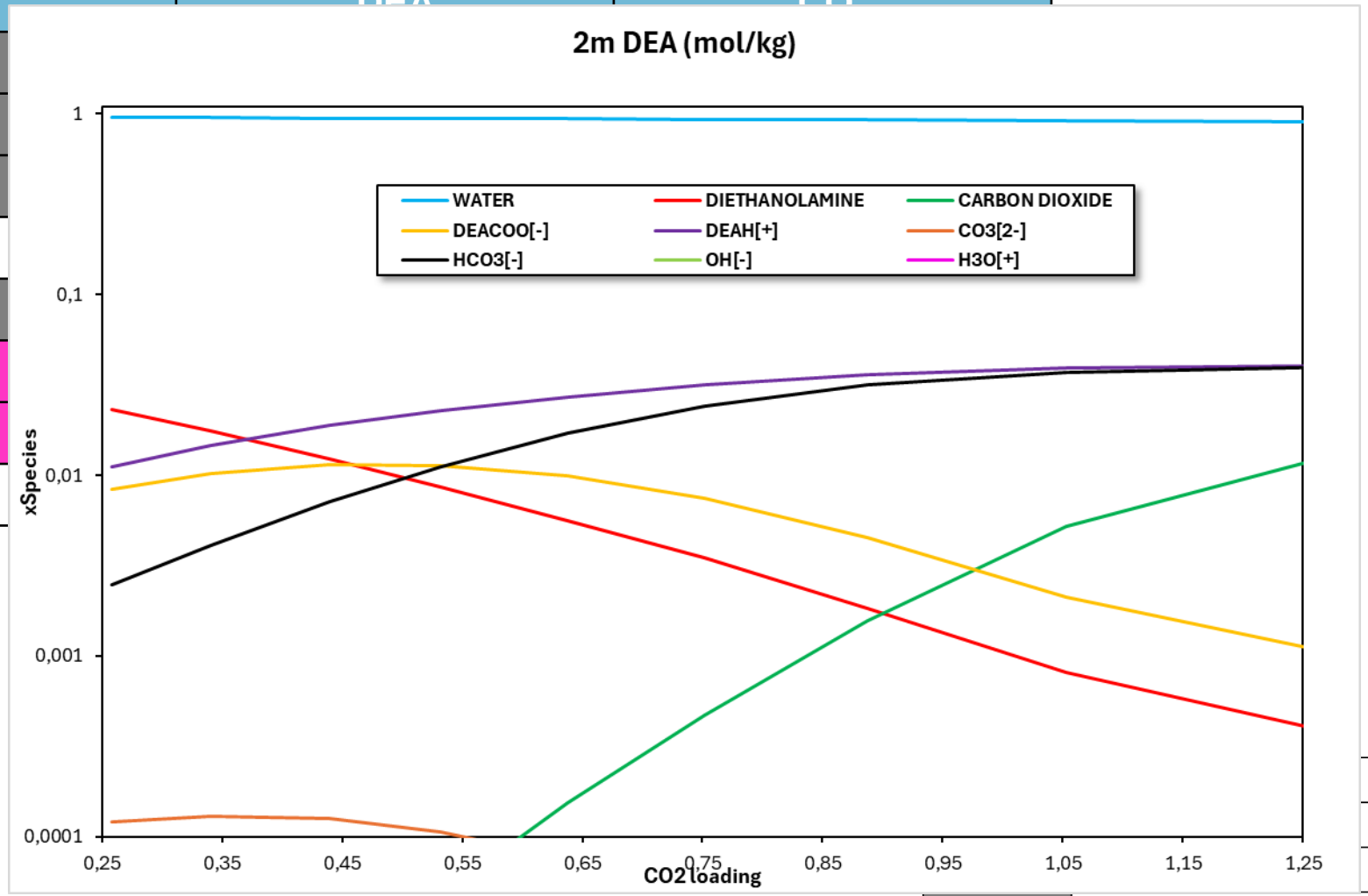
BIP	H_2O	DEA	CO_2
H_2O		T-dep param.	T-dep param.
DEA	T-dep param.		
CO_2	T-dep param.		

	current step
	already regressed
	Default
	No regression available

2. 2. TERNARY SYSTEMS

- $H_2O/DEA/CO_2$

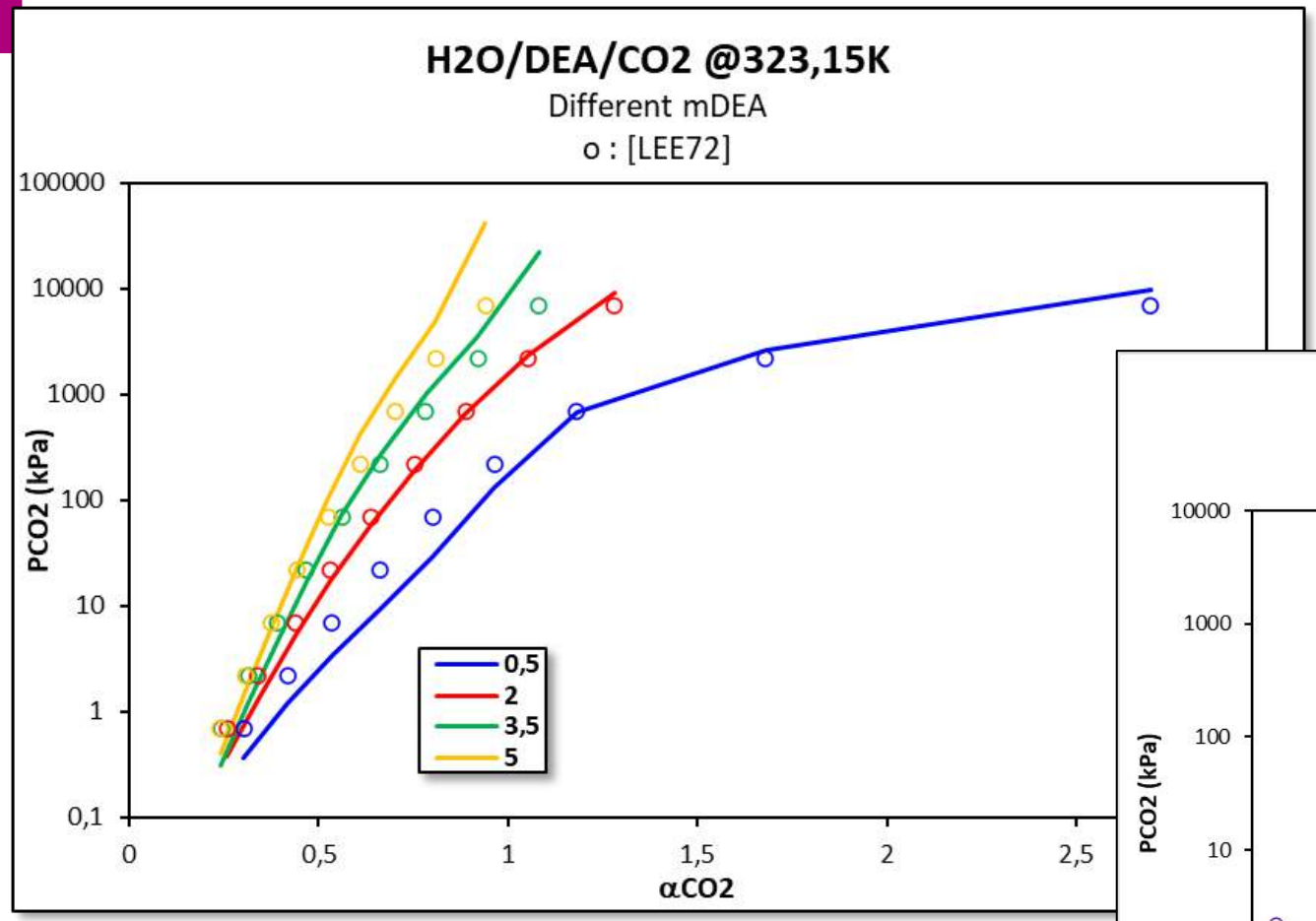
TIP	H2O	DEA	CO
$(H_3O^+;OH^-)$			
$(H_3O^+;CO_3^{2-})$			
$(H_3O^+;HCO_3^-)$			
$(H_3O^+;DEACOO^-)$			
$(DEAH^+;OH^-)$			
$(DEAH^+;CO_3^{2-})$			
$(DEAH^+;HCO_3^-)$			
$(DEAH^+;DEACOO^-)$			

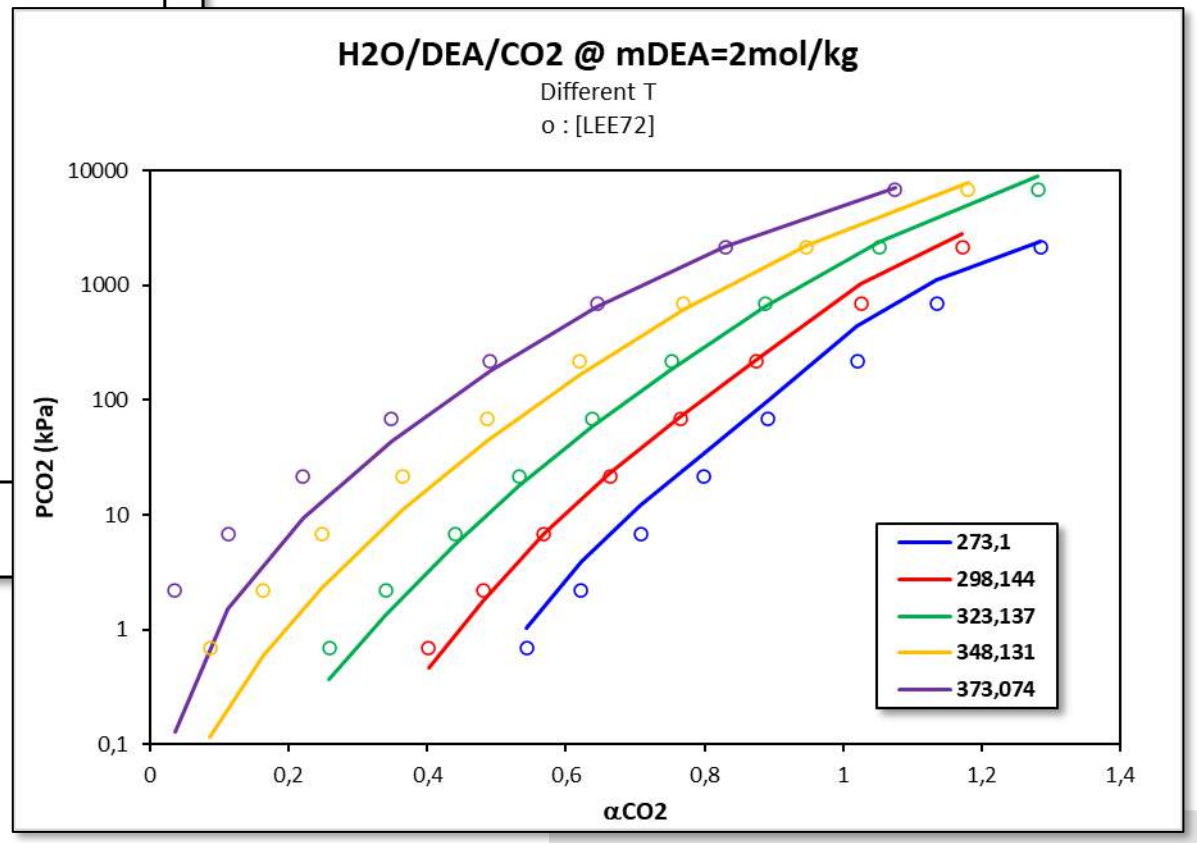


No regression available

2. 2. TERNARY SYSTEMS

- $H_2O/DEA/CO_2$





2. 3. QUATERNARY SYSTEM

- H_2O/DEA/MeOH/CO_2

Reaction (molality scale)	
$2\ H_2O \Leftrightarrow H_3O^+ + OH^-$	[AUS91]
$CO_2 + H_2O \Leftrightarrow HCO_3^- + H_3O^+$	
$HCO_3^- + H_2O \Leftrightarrow CO_3^{2-} + H_3O^+$	
$DEAH^+ + H_2O \Leftrightarrow DEA + H_3O^+$	
$DEACOO^- + H_2O \Leftrightarrow DEA + HCO_3^-$	

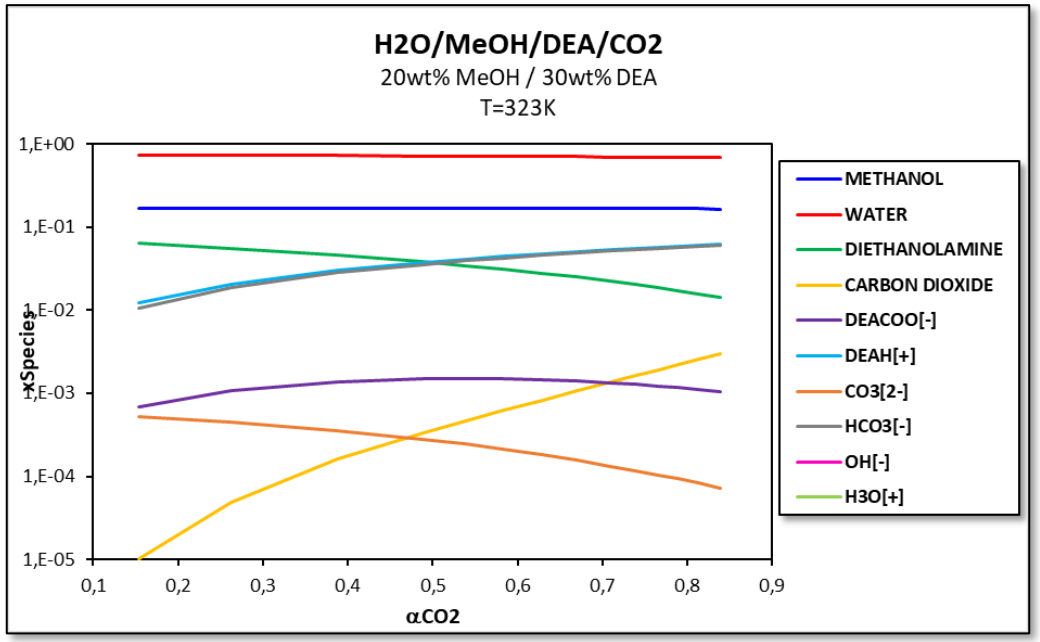
BIP	H_2O	DEA	CO_2	MeOH
H_2O		T-dep param.	T-dep param.	T-dep param.
DEA	T-dep param.			
CO_2	T-dep param.			T-dep param.
MeOH	T-dep param.		T-dep param.	

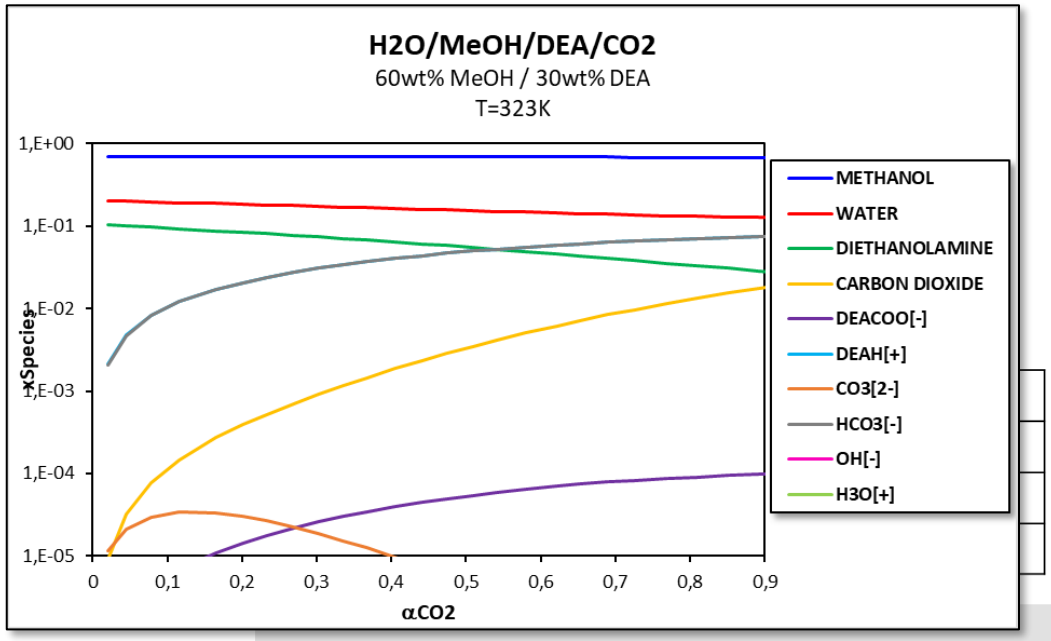
	current step
	already regressed
	Default
	No regression available

2. 3. QUATERNARY SYSTEM

- H_2O/DEA/MeOH/CO_2

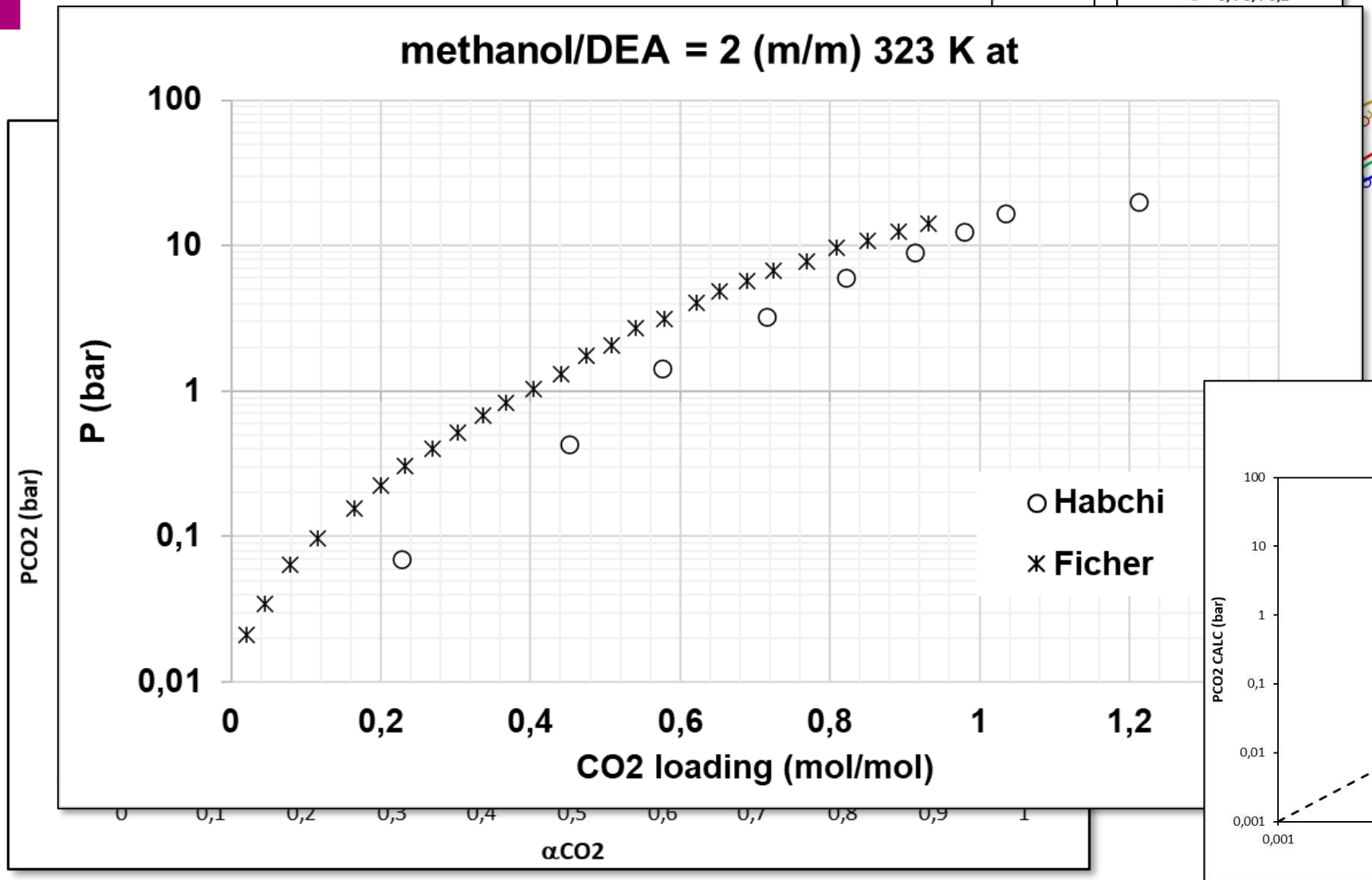
TIP	H2O	DEA	CO_2	MeOH
(H_3O^+;OH^-)				
(H_3O^+;CO_3^{2-})				
(H_3O^+;HCO_3^-)				
(H_3O^+;$DEACOO^-$)				
($DEAH^+$;OH^-)				
($DEAH^+$;CO_3^{2-})				
($DEAH^+$;HCO_3^-)				T-dep Param.
($DEAH^+$;$DEACOO^-$)				

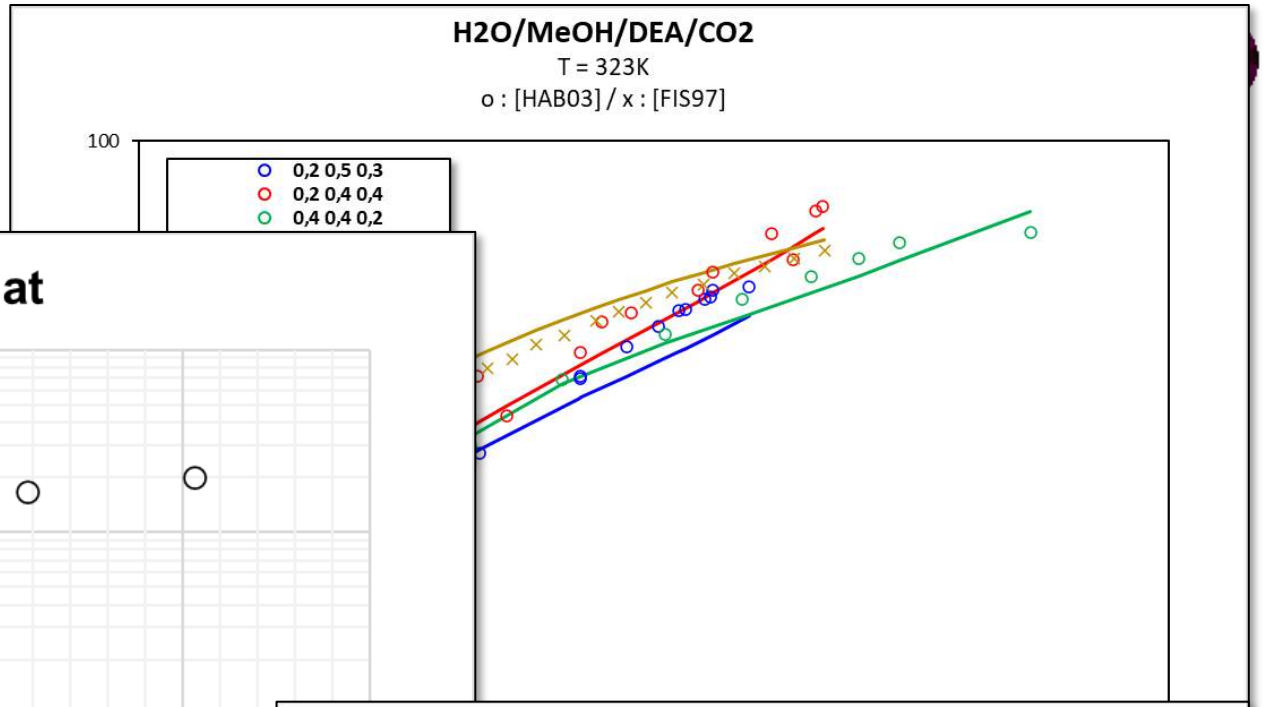


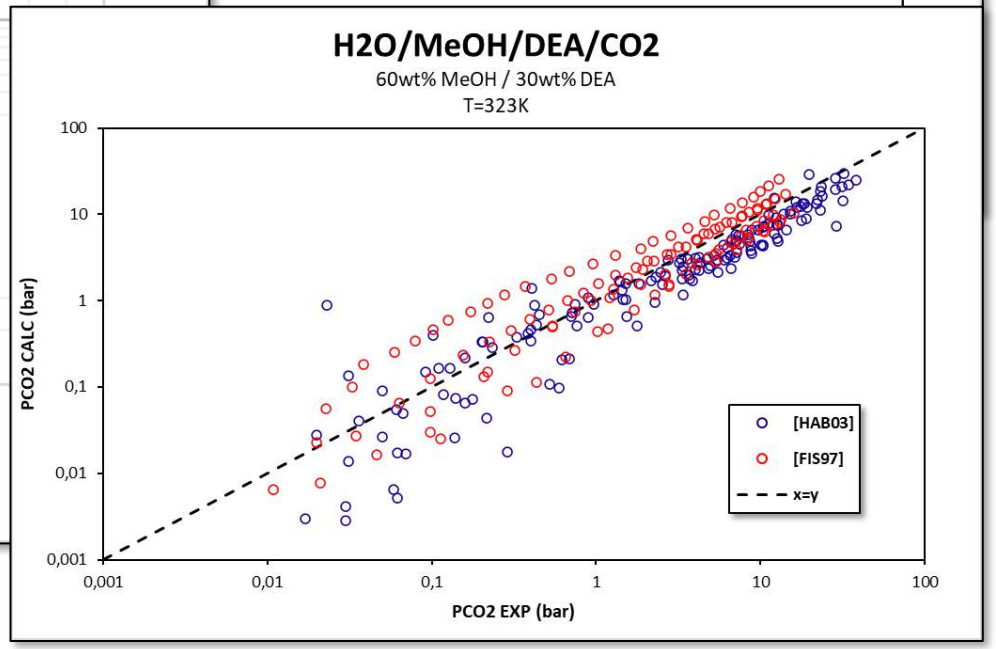


2. 3. QUATERNARY SYSTEM

- H_2O/DEA/MeOH/CO_2







CONCLUSION

- Wide disparity in experimental data → Sort or establish new data
- **Several sets of parameters can be found**
- A set that better reproduces low CO2 composition (low PCO2) and high temperatures can be found.
  - A sensitivity analysis using tools such as LAGUN should be used
- Model?
  - Is the Born term suitable for taking account of the co-solvent phenomenon?
  - ε_{DEA} ?
  - R_{born} ?
  - $H_{CO2/DEA}$?
  - Is eNRTL the best model for this application?

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