

Thermodynamic consistency in modeling of SLE and VLE in aqueous alkanolamine solutions

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Outline

- ❑ Introduction
- ❑ Theory
 - VLE (Vapor-Liquid Equilibrium)
 - SLE (Solid-Liquid Equilibrium)
- ❑ Modeling : NRTL Framework as an example
- ❑ Results
 - MEA+H₂O
 - DEEA+H₂O
 - AMP+H₂O
- ❑ Conclusions

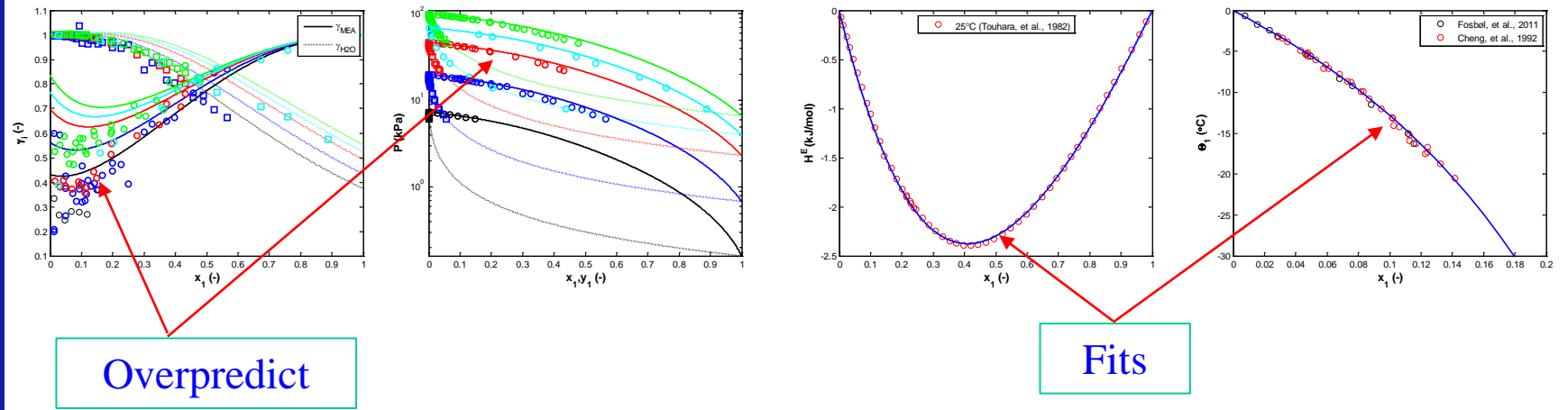
Introduction

- ❑ Rigorous thermodynamic models based on excess Gibbs energy (eNRTL and eUNIQUAC) are capable of representing both Solid-Liquid-Equilibria (SLE) and Vapor-Liquid-Equilibria (VLE) in aqueous alkanolamine solutions
- ❑ A robust and accurate modeling relies on the quality and type of data used to regress the parameters to get the best representation of the data.
- ❑ Different apparatuses provide different equilibrium data:
 - Ebulliometer experiments usually generate PT_{xy} data which can be used to determine the activity coefficient for both amine and water.
 - A calorimetric measurement can provide excess enthalpy of mixing and reaction as well heat capacity
 - Freezing point depression measurements provide SLE and water activity data .
- ❑ When comparing activity coefficients of water from VLE and SLE data often inconsistencies are seen: e.g.
 - the excess enthalpies calculated were slightly skewed toward higher amine concentrations when a best fit to freezing point depressions was achieved .
 - the minimum value of the excess enthalpy was fitted optimally but the freezing point depression was found to be under-predicted, in particular at higher concentrations.

Examples: MEA + H₂O

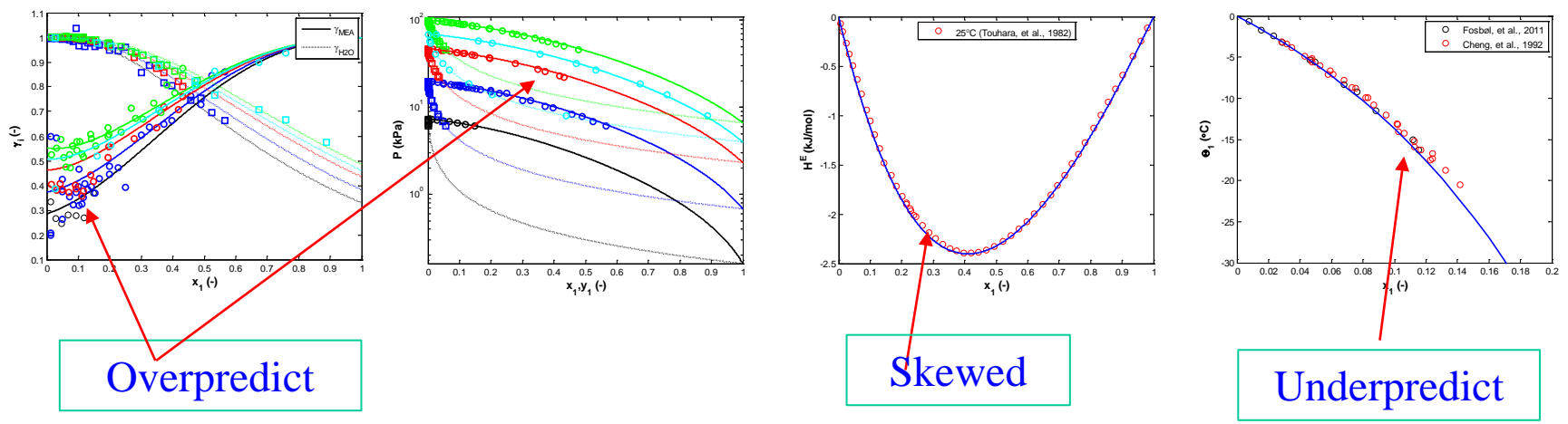
Posey, 1996

VLE (P-T-x and P-T-x-y), Excess Enthalpy and Freezing Point.



Schmidt, et al., 2007

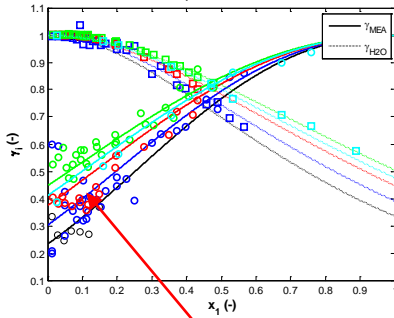
VLE (P-T-x and P-T-x-y) and Excess Enthalpy.



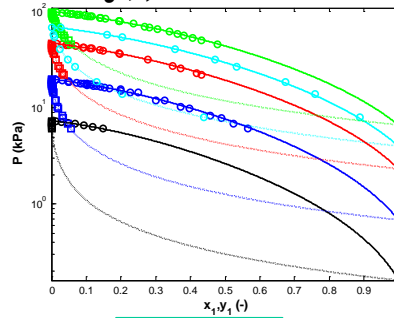
Examples:

Hessen, et al., 2010

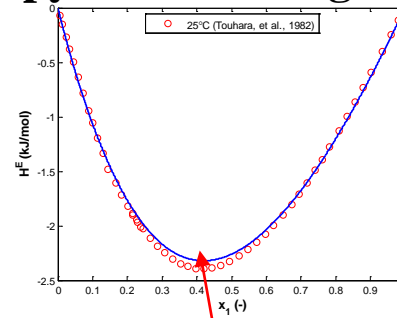
VLE (P-T-x and P-T-x-y), Excess Enthalpy and Freezing Point.



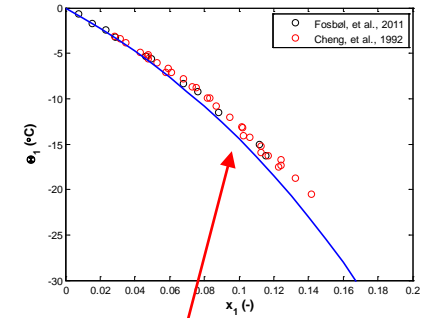
Overpredict



Fits



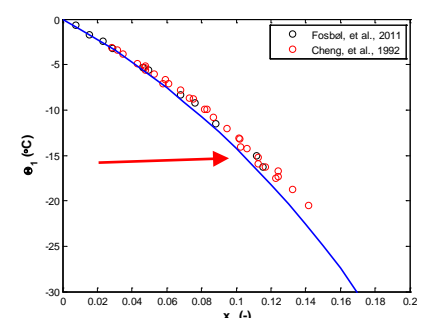
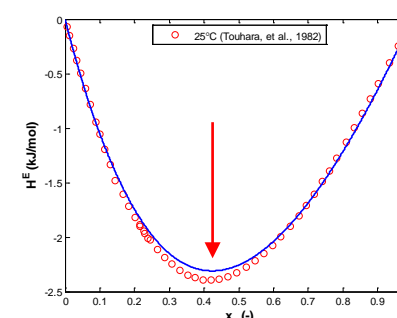
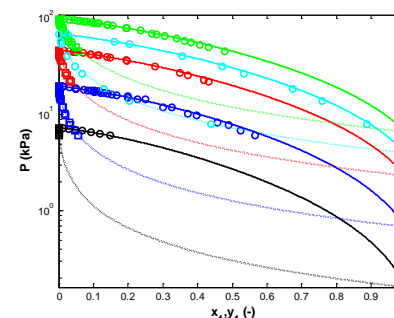
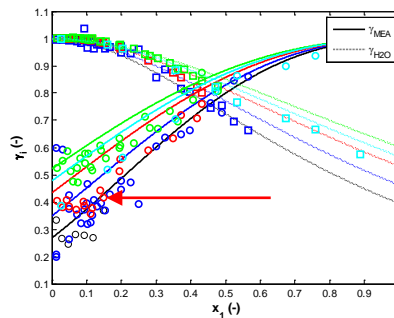
Overpredict



Underpredict

Zhang, et al., 2011

VLE (P-T-x and P-T-x-y), Excess Enthalpy and Heat Capacity.



AIM:

To find the origin of the discrepancy between measured data used for the thermodynamic modeling of the activity coefficient of water.

Theory

VLE

$$\begin{aligned}
 m_l(T, p) &= m_v(T, p) \\
 m_l(T, p) &= m_l^s(T, p) + RT \ln f_i^l \\
 m_v(T, p) &= m_v^s(T, p) + RT \ln f_i^v \\
 f_i^l &= f_i^v \\
 x_i g_i x_i^P &= P y_i x_i^F
 \end{aligned}$$

$$F_i^o \frac{f_i^l}{f_i^v} \exp\left[-\frac{V_i^l(P - P_i^o)}{RT}\right] \gg 1$$

$$\ln g_i = \frac{\int_{P_i^o}^P (nG^E/RT) dP}{P_i^o - P}$$

$$-\frac{H^E}{RT^2} = \frac{\int_{P_i^o}^P (G^E/RT) dP}{P_i^o - P}$$

$$C_P^E = \frac{\int_{P_i^o}^P H^E dP}{P_i^o - P}$$

SLE

$$\begin{aligned}
 m_l(T, p) &= m_s(T, p) \\
 m_l(T, p) &= m_l^s(T, p) + RT \ln f_i^l \\
 m_s(T, p) &= m_s^s(T, p) + RT \ln f_i^s \\
 DG &= RT \ln \frac{f_i^l}{f_i^s} = -RT \ln a_i
 \end{aligned}$$

$$-RT \ln x_i g_i = DG$$

$$-\ln x_i g_i = \frac{DH_f^o}{RT} - \frac{DS_f^o}{R} + \frac{1}{RT} \int_{T_f}^T DC_P dT - \frac{1}{R} \int_{T_f}^T \frac{DC_P}{T} dT$$

$$DH_f^o = T_f DS_f^o$$

$$-\ln x_i g_i = \frac{DH_f^o}{RT_f} (T_R - 1) + \frac{1}{RT_f} \int_{T_f}^T DC_P dT - \frac{1}{R} \int_{T_f}^T \frac{DC_P}{T} dT$$

$$\begin{aligned}
 DG &= DH - TDS \\
 DH &= DH_f^o + \int_{T_f}^T DC_P dT \\
 DS &= DS_f^o + \int_{T_f}^T \frac{DC_P}{T} dT \\
 DC_P &= C_P^l - C_P^s
 \end{aligned}$$

$$- \ln x_i g_i = \frac{DH_f^\circ}{RT_f} (T_R - 1) + \frac{1}{RT_f} \int_{T_f}^T DC_P dT - \frac{1}{R} \int_{T_f}^T \frac{DC_P}{T} dT$$

Case 1

$$\frac{1}{RT_f} \int_{T_f}^T DC_P dT \approx \frac{1}{R} \int_{T_f}^T \frac{DC_P}{T} dT$$

$$\ln x_i g_i = \frac{DH_f^\circ}{RT_f} (1 - T_R)$$

$$T_R = \frac{T_f}{T}$$

□ Posey (1996), Cheng et al. (1993) and Hessen, et al. (2010)

Case 2

$$DC_P \approx DS_f^\circ$$

$$- \ln x_i g_i = \frac{DH_f^\circ}{RT_f} \ln T_R$$

Case 3

$$DC_P \approx k_{T_f}$$

$$- \ln x_i g_i = \frac{DH_f^\circ}{RT_f} (T_R - 1) + \frac{DC_P}{RT} (1 + \ln T_R - T_R)$$

$$- \ln x_i g_i = \frac{DH_f^\circ}{RT_f} (T_R - 1) + \frac{1}{RT_f} \int_{T_f}^T DC_p dT - \frac{1}{R} \int_{T_f}^T \frac{DC_p}{T} dT$$

Case 4

$$DC_p = a + bT$$

$$- \ln x_i g_i = \frac{DH_f^\circ}{RT_f} (T_R - 1) + \frac{a}{R} (1 + \ln T_R - T_R) + \frac{bT_f}{2R} (T_R^2 - T_f^2) - \frac{1}{R} \left(\frac{1}{T_R} - \frac{1}{T_f} \right)$$

□ Ge and Wang (2009) and Hartono, et al. (2013)

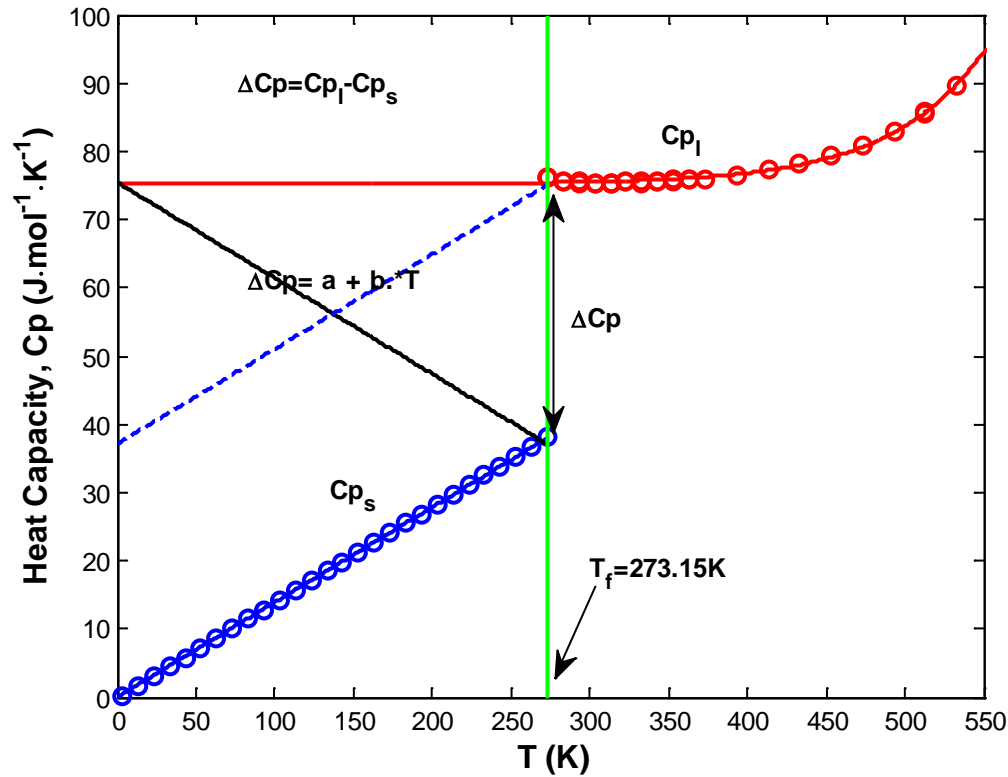
Case 5

$$DC_p = a + bT + \frac{c}{(T - T_Q)}$$

$$- \ln x_i g_i = \frac{DH_f^\circ}{RT_f} (T_R - 1) + \frac{a}{R} (1 + \ln T_R - T_R) + \frac{bT_f}{2R} (T - T_f)^2 + c \left[\frac{(T - 1)}{T} \ln \frac{T - T_Q}{T_f - T_Q} - \ln T_R \right]$$

□ Fosbøl, et al. (2009 and 2011)

Thermo physical property of water as solvent



$$DH_f^\circ = 6009.4 \frac{J}{mol}$$

$$DC_p = 37.97 \frac{J}{K \cdot mol}$$

$$DC_p = 75.929 - 0.1405 \cdot T \frac{J}{K \cdot mol}$$

$$DC_p = 75.929 - 0.1405 \cdot T - \frac{2.45634 \cdot 10^{-4}}{(T - 200)} \frac{J}{K \cdot mol}$$

Modeling

$$OF = \sum_{i=1}^n \frac{(g_i^{Exp} - g_i^{calc})^2}{g_i^{Exp}} + \sum_{i=1}^n \frac{(P_{Sol}^{Exp} - P_{Sol}^{calc})^2}{P_{Sol}^{Exp}} + \sum_{i=1}^n \frac{((H_{Sol}^E)^{Exp} - (H_{Sol}^E)^{calc})^2}{(H_{Sol}^E)^{Exp}} + \sum_{i=1}^n \frac{((Q_{Sol}^F)^{Exp} - (Q_{Sol}^F)^{calc})^2}{(Q_{Sol}^F)^{Exp}}$$

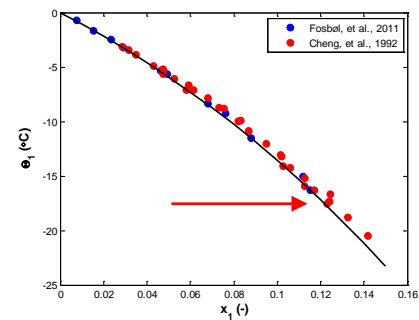
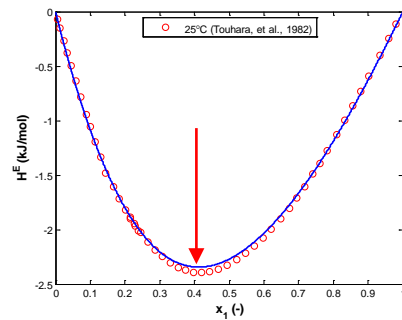
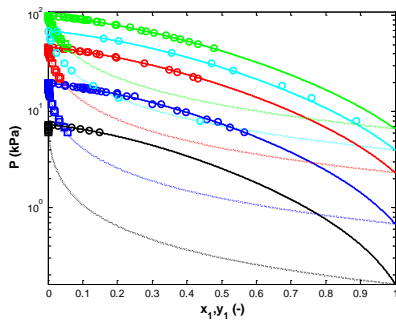
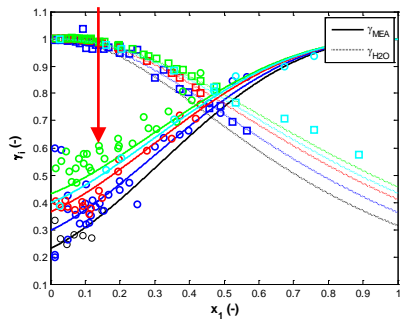
$$AARD = \frac{1}{n} \sum_{i=1}^n \frac{|\hat{A}_{model} - \hat{A}_{exp}|}{\hat{A}_{exp}}$$

Species	Melting/ Freezing Point (°C)
Water	0
MEA	10.3
AMP	67
DEEA	-70

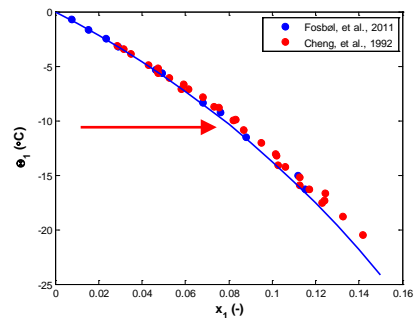
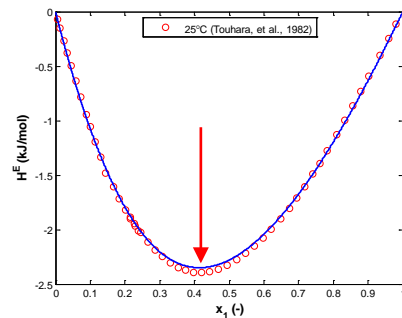
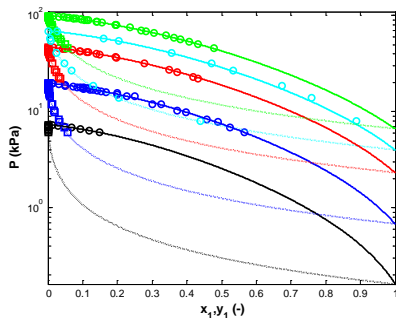
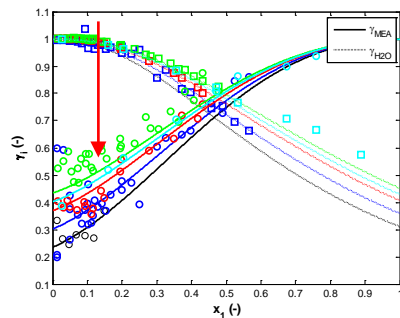
Results

□ MEA+H₂O

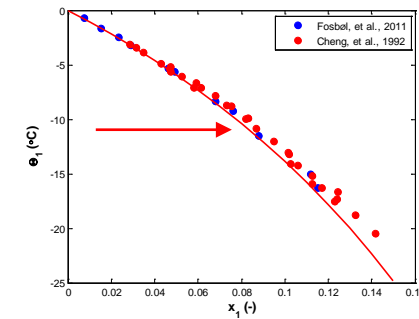
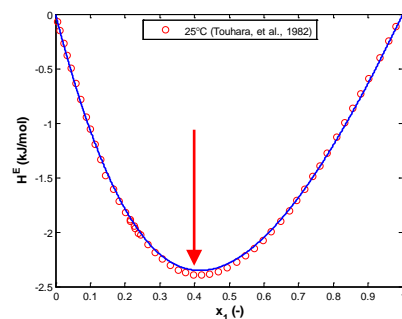
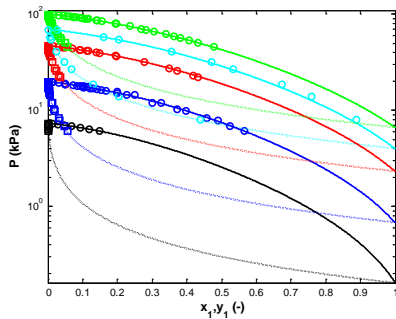
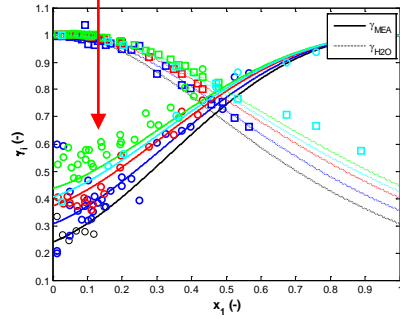
□ Case 1



□ Case 2

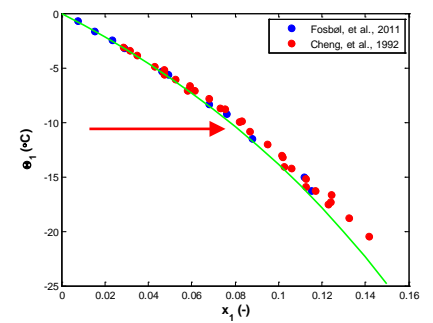
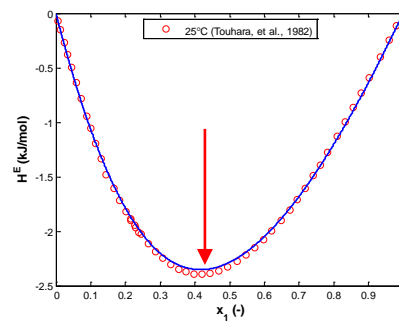
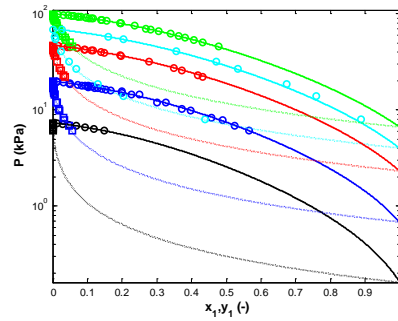
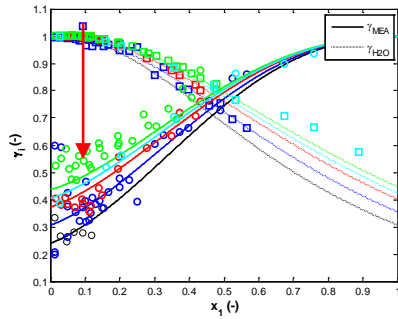


□ Case 3

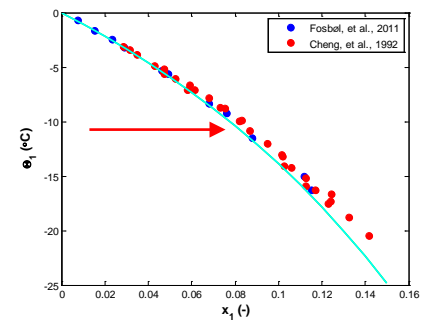
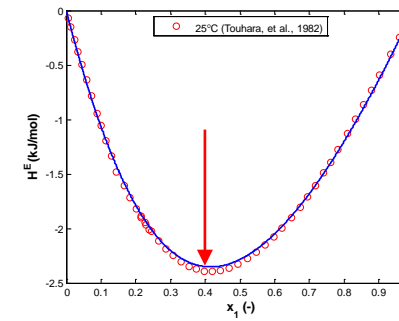
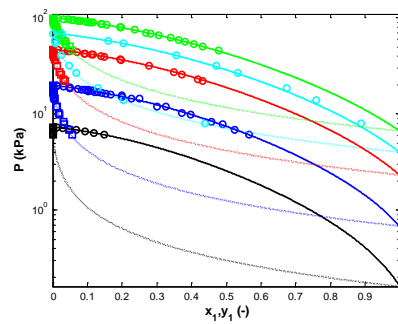
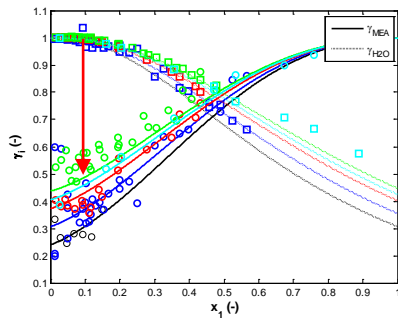


MEA+H₂O

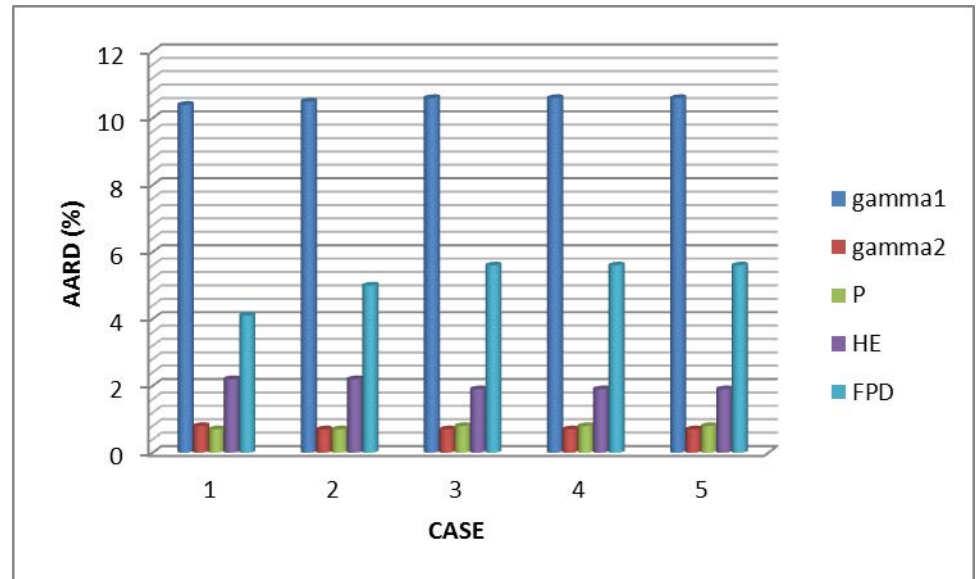
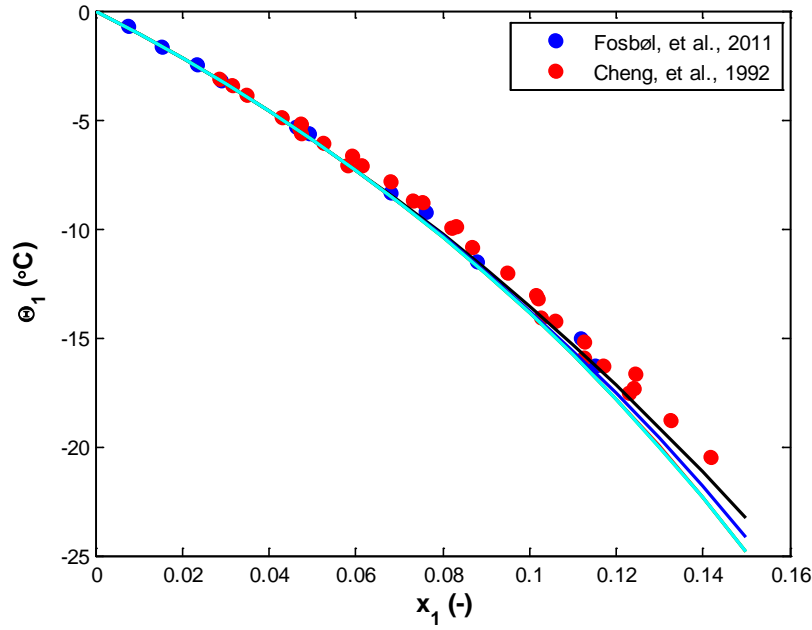
Case 4



Case 5

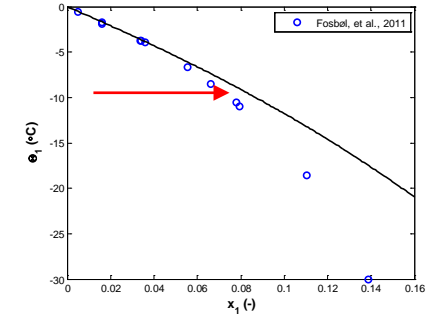
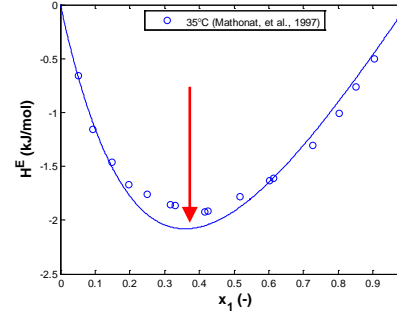
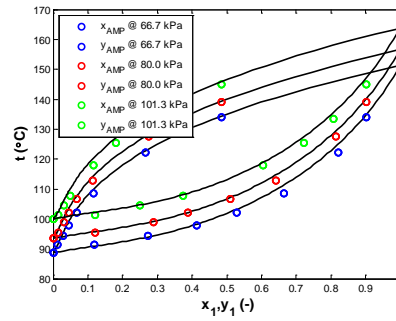
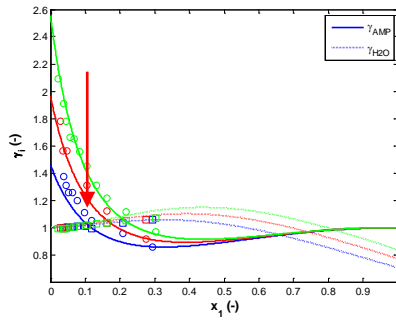


MEA+H₂O

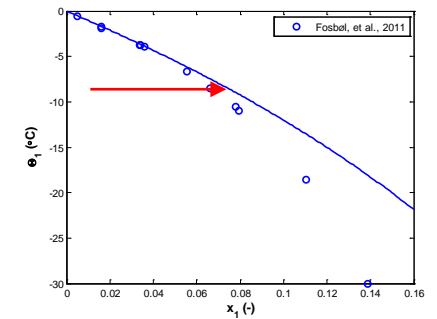
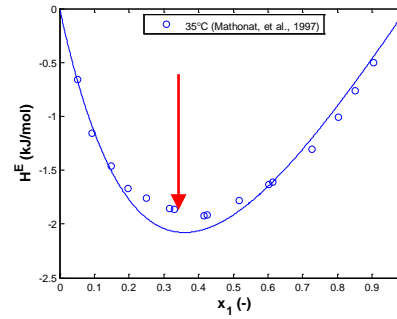
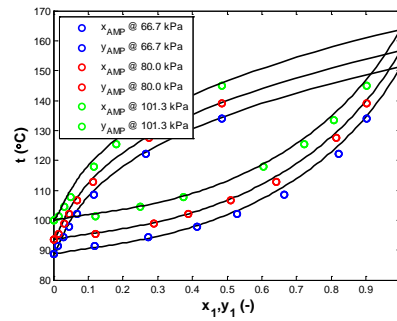
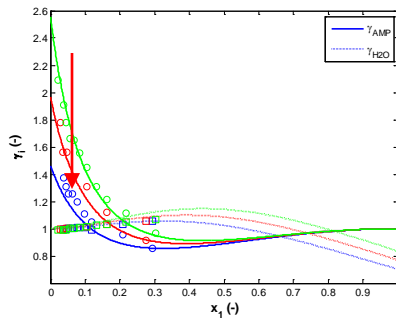


AMP+H₂O

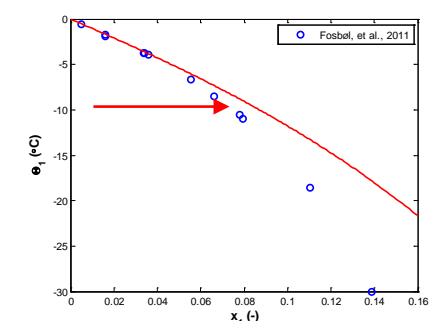
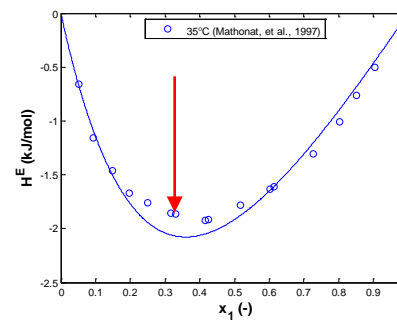
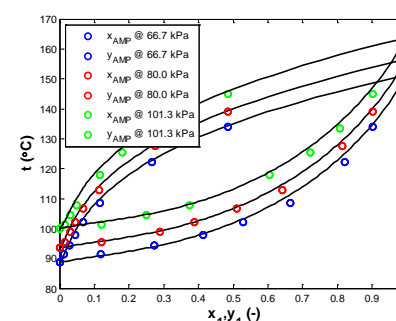
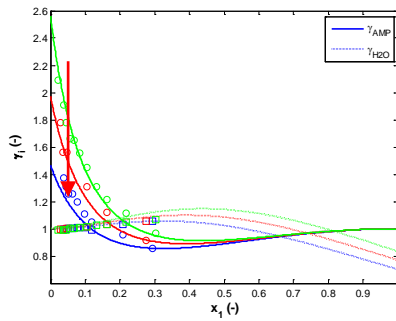
Case 1



Case 2

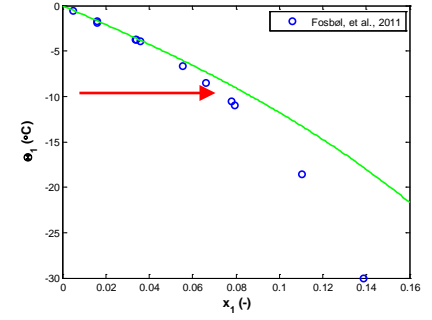
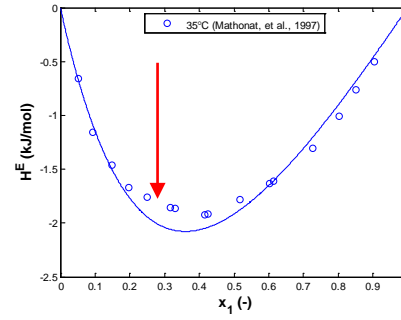
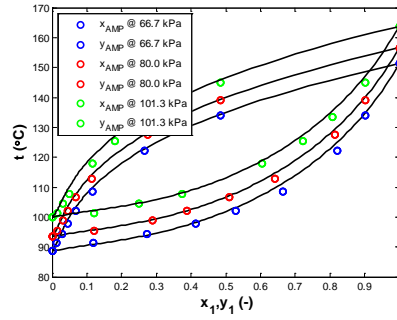
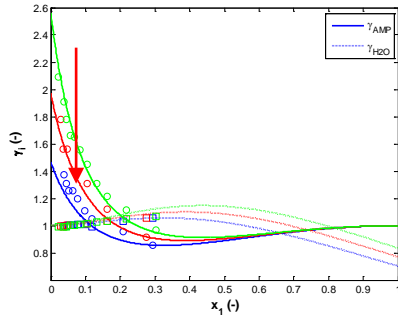


Case 3

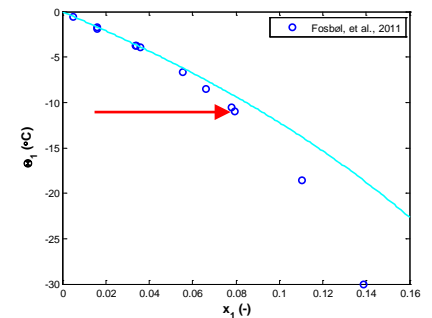
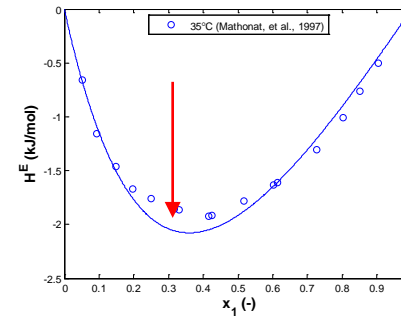
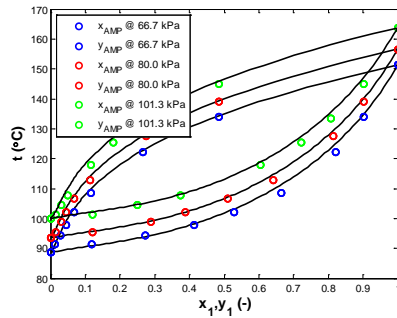
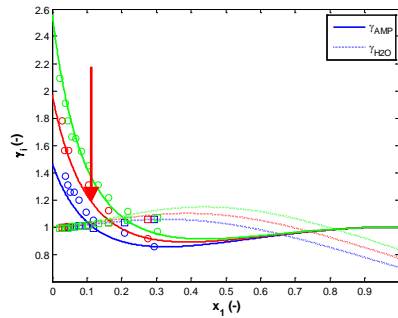


AMP+H₂O

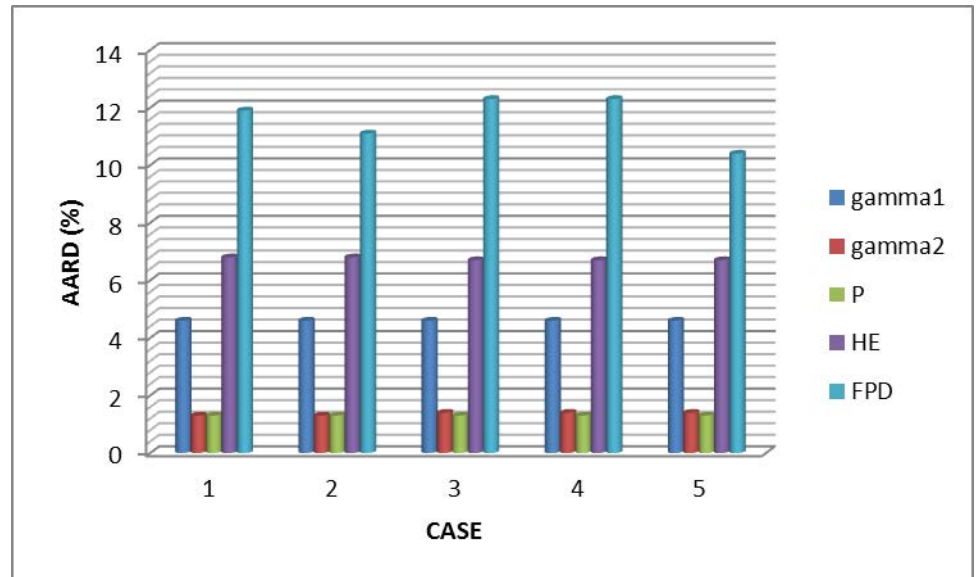
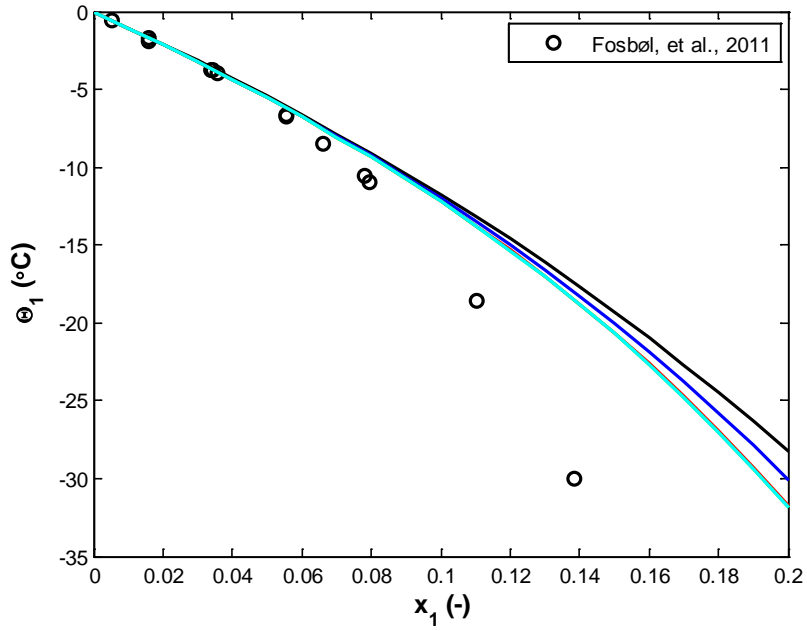
Case 4



Case 5

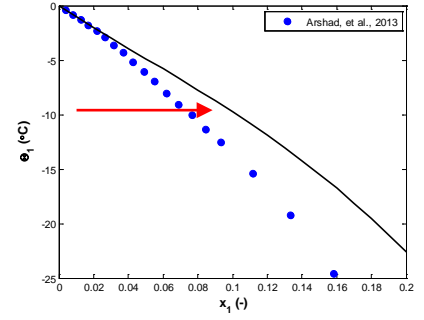
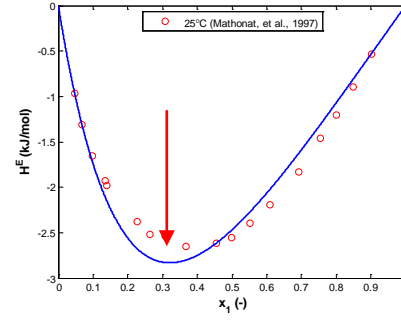
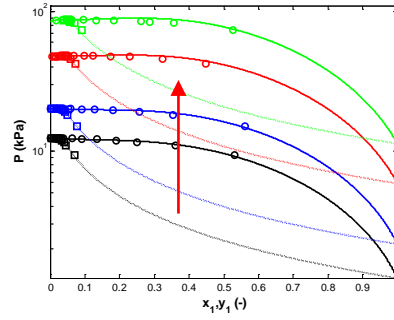
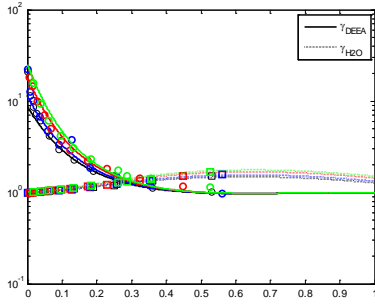


AMP+H₂O

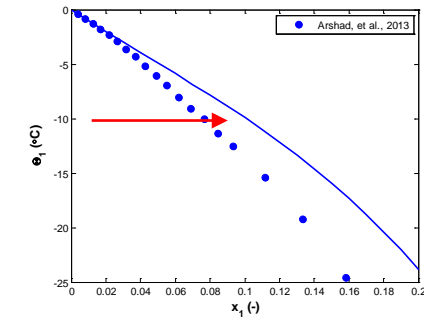
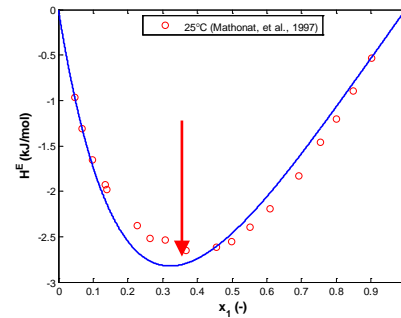
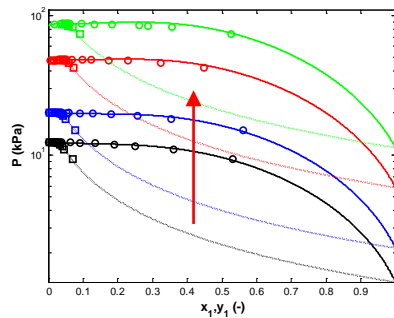
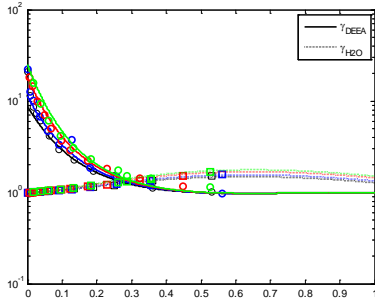


DEEA+H₂O

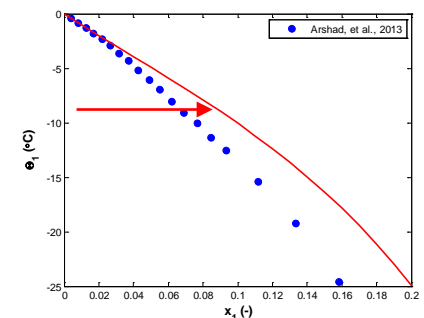
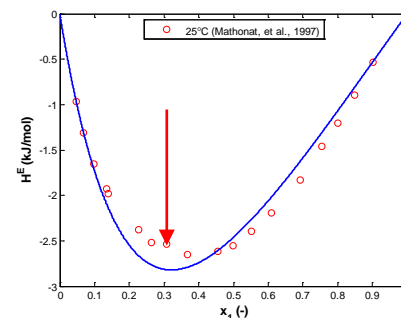
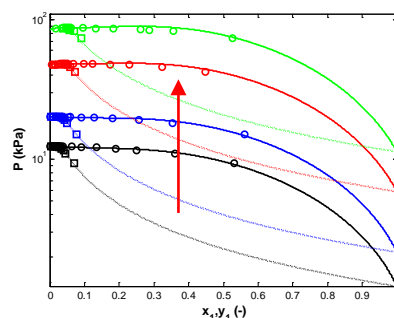
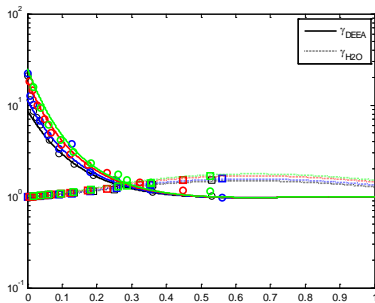
Case 1



Case 2

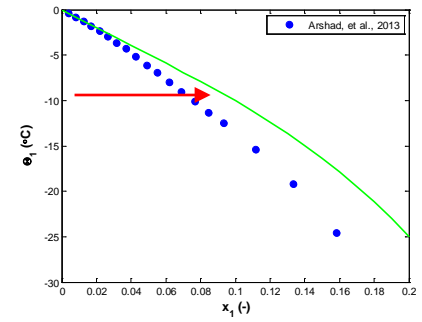
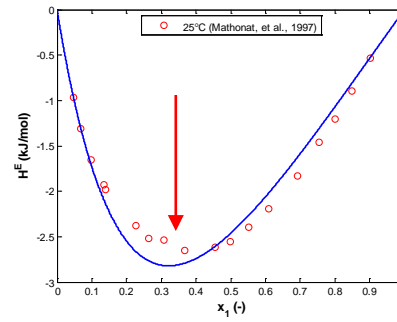
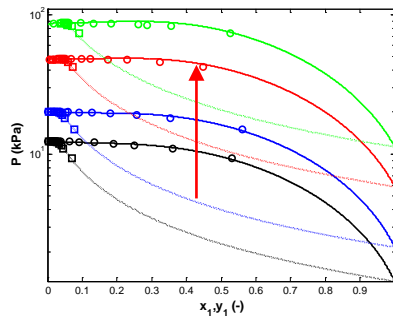
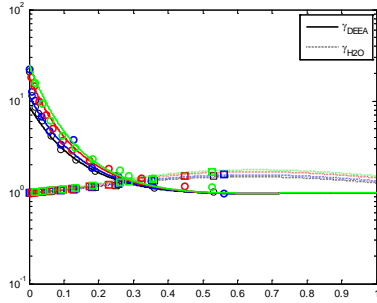


Case 3

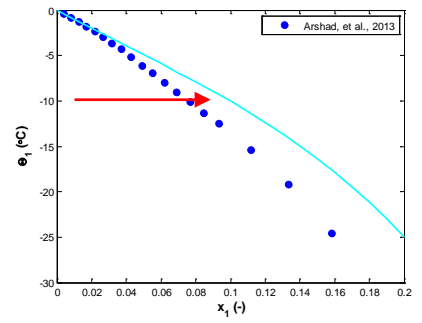
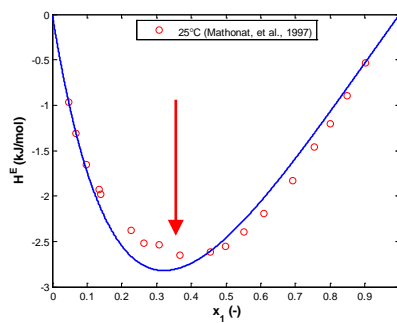
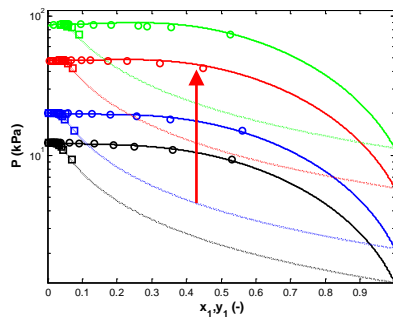
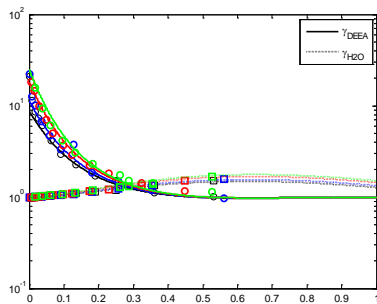


□ DEEA+H₂O

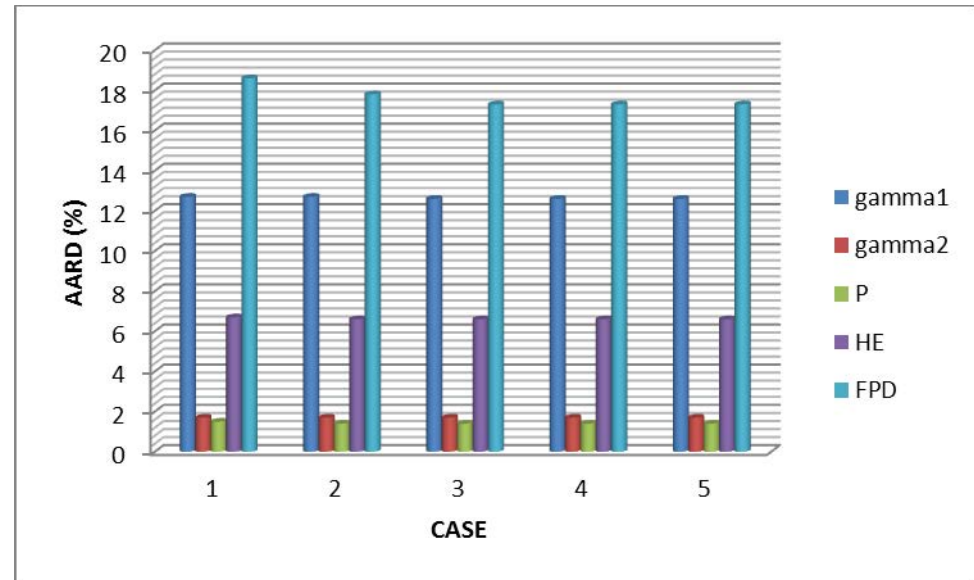
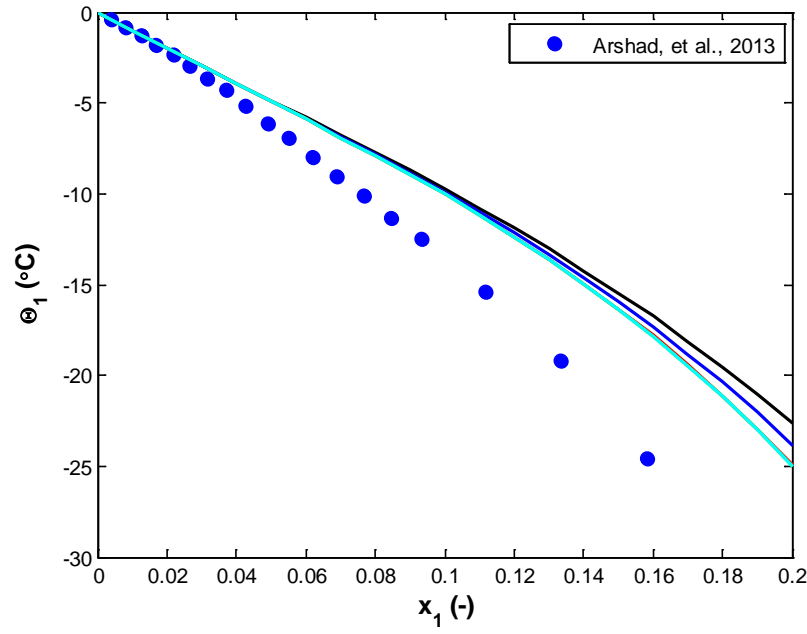
□ Case 4



□ Case 5



□ DEEA+H₂O

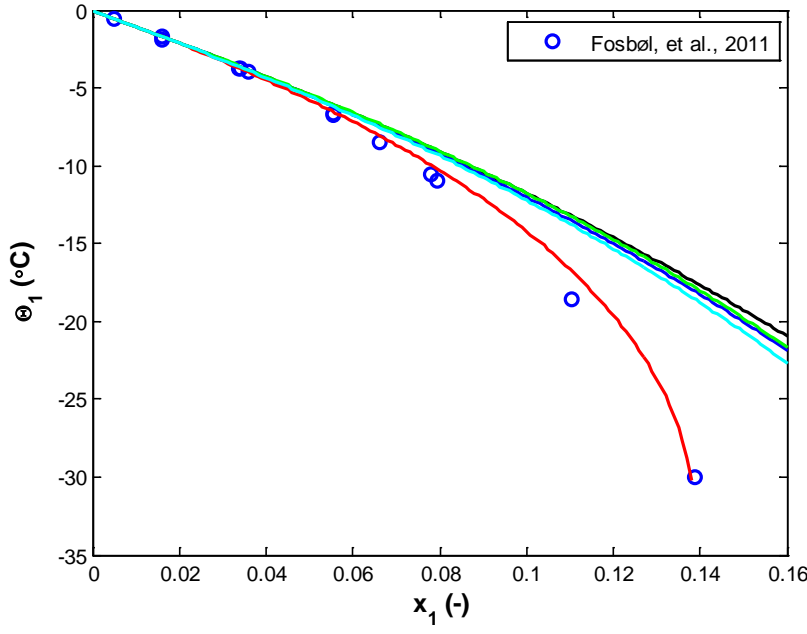


Conclusions

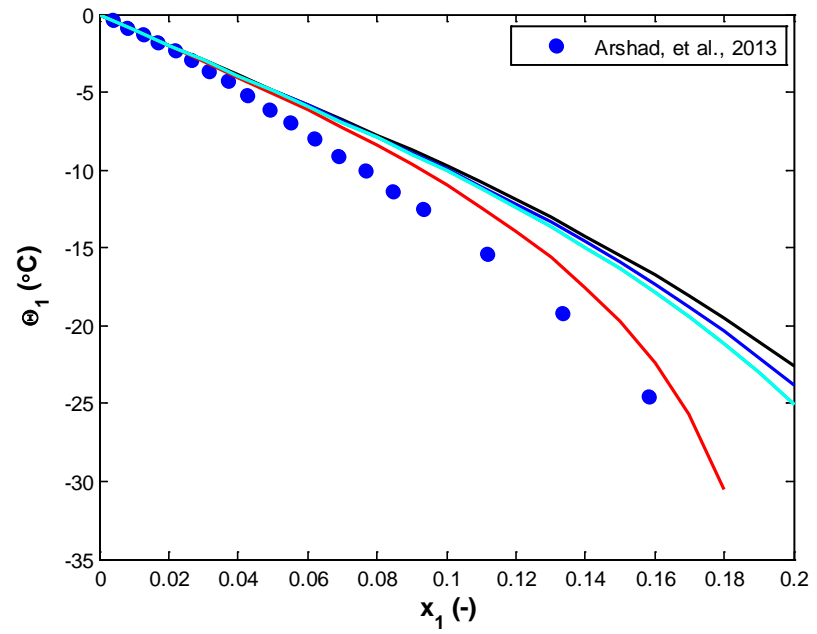
- ❑ 5 different cases to estimate the freezing point depression were tested for aqueous MEA, DEEA and AMP solutions.
- ❑ Physical/ thermo physical properties of Water/Ice were only used.
- ❑ When the freezing point differences between solute (alkanolamine) and solvent (water) is larger, none of the suggested cases were able to predict the data.
- ❑ A systematic error in the measurements ??
- ❑ Challenge to the selected thermodynamic model??
- ❑ The required thermal and physical properties should be from the alkanolamines solution??

Future Work

AMP + H₂O



DEEA + H₂O



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Thank you!

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