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Alkane solubilities in aqueous alkanolamine solutions with CPA EoS

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Abstract

Absorption with aqueous alkanolamine solution is often used for acid gas removal processes. Thermodynamic model is very important to predict phase behaviour for designing and optimizing acid gas absorption units. To estimate alkanes losses in these processes, the knowledge of alkanes solubility in aqueous alkanolamine solutions is essential. In the present work, Cubic-Plus-Association Equation of State (CPA EoS) was applied to represent alkanes solubility in aqueous alkanolamine. The Average Relative Deviation on alkanes solubility in aqueous alkanolamine solution is less than 15%. Due to our model, the temperature of alkanes minimum solubility in pure water and alkanolamine solutions are correctly predicted. Water content is also well predicted at Vapour Liquid Equilibrium condition.

Keywords: phase equilibria, data treatment, modelling, parameter determination

1. Introduction

Among fossil fuels, natural gas is the cleanest, in terms of CO₂ emission, burn efficiency and amount of air pollutant [1]. Methane is the prevailing element of natural gas. However, there are a variety of impurities in the natural gas reservoir. Usually, natural gas contains considerable amounts of acid gas (CO₂, H₂S). With the presence of water, acid gas can lead to corrosion in equipments and pipelines. The presence of acid gas can also reduce the heating value of gas and make more air pollution. Acid gas is needed to be removed until acceptable standard is achieved: not greater than 4 ppm for H₂S and less than 280 ppm for CO₂ [2]. For this purpose, different acid gas removal processes have been developed in recent decades, such as absorption [3], adsorption [4], low temperature separation processes (CFZ [5] and Sprex [6] processes) and membrane separation [7]. Chemical absorption with aqueous alkanolamines solutions is the most established and used technology for efficient removal of acid gas. As alkanolamines, we can cite monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA). After absorption step, solvent is regenerated into a second column by heating. During the operation, a part of alkanes can be absorbed as well. It is essential to estimate the losses of alkanes in the process design and simulation. For this reason, it is necessary to develop thermodynamic models in order to predict the solubilities of different alkanes in alkanolamine solutions.

Due to the presence of associating molecules like alkanolamine and water, it is better to consider molecular models or an Equation of State (EoS) containing an association term. In the beginning of 80s, Wertheim [8] has developed a model for association molecules. This model is used in the Statistical Associating Fluid Theory EoS [9]. In 1996, Kontogeorgis et al. [10] has proposed to combine Wertheim's model and Cubic EoS. This model is called Cubic Plus Association EoS (CPA EoS). This EoS can easily consider the presence of hydrogen bonding. In this study, we have considered the Peng-Robinson (PR)-CPA EoS. It takes advantage of PR EoS for non-associating components as well. In 2015, Hajiw et al. [11] have developed a Group Contribution (GC) version of this model. In previous studies, Avlund et al. [12,13] have applied CPA EoS to describe the phase equilibria of alkanolamine-water binary systems, and claimed that the results are satisfactory overall with an ARD less than 30%. Folas et al. [14] and Oliveira et al. [15] have used CPA EoS to study water-alkane binary systems. They have considered no temperature dependant Binary Interaction Parameters (BIPs). They claimed that the model has good performance for both alkane solubilities in water and water content in alkane. Since they found that the Average Relative Deviation is smaller than 30 % and 25 % respectively.

The aim of this study is to describe alkanes (methane, ethane, propane, n-butane, i-butane, n-propane and hexane) solubility in aqueous MDEA, MEA and DEA solutions by using PR-CPA EoS. In the present work, pure compounds parameters are fitted with CPA EoS from experimental vapour pressure and liquid density. Then, for the water-alkane and water-alkanolamine binary systems, their BIPs are adjusted from experimental binary data. The above experimental data are taken from ThermoData Engine [16]. However, due to the lack of

experimental data concerning alkane-alkanolamine binary systems, it is impossible to directly adjust their BIPs. We have determined the missing parameters from alkane-water-alkanolamine ternary systems experimental data. Because a large number of Vapour-Liquid-Equilibrium (VLE), Liquid-Liquid-Equilibrium (LLE) and Vapour-Liquid-Liquid-Equilibrium (VLLE) experimental data of these ternary systems are available in the open literature (as examples these two GPA research reports: Mokraoui et al. [17] and Valtz et al. [18]).

To the best of our knowledge, only the paper of Carroll et al. [19] has allowed us to compare water content and MDEA vapour compositions. With optimized BIPs, solubilities of pure alkanes and mixtures of alkanes in aqueous alkanolamine solutions are predicted. These mixtures [17] are composed by ethane, propane, n-butane, i-butane, n-propane and hexane.

2. The PR-CPA EoS

The CPA EoS has an explicit part to account for hydrogen bonding, making it well suited to describe water- alkanolamines-alkanes systems, where water and alkanolamines molecules form hydrogen bonds between them and themselves (self and cross associations). PR-CPA EoS takes a cubic EoS as the basis and adds a correction for hydrogen bonding [10]. Here, the cubic part is the PR EoS [20] and the association part is from Wertheim [8] (Eq. 1).

$$P = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b) + b(V_m - b)} - \frac{1}{2} \frac{RT}{V_m} \left(1 + \rho \frac{\partial \ln g_r}{\partial \rho} \right) \sum_i x_i \sum_{A_i} (1 - X_{A_i}) \quad (1)$$

The model is detailed in the appendix A. For LLE and VLE, liquid and vapour compositions were calculated by two phase flash using algorithm of Michelsen et al. [21]. For VLLE, all three phase compositions were calculated by multi-phases flash method (Michelsen [22]) with stability analysis (Michelsen [23]).

3. Results

3.1. Pure components

Alkanes do not form any hydrogen bond between themselves, the parameters of association term (ϵ^{AiBj} and β^{AiBj}) are set to zero. Cubic pure component parameters (a_0 , b , c_1) were calculated from critical pressure, critical temperature and acentric factor by using Eq A 9-12 from Appendix A. The values of pure components critical properties (T_c and P_c) and acentric factors (ω) are taken from Thermo Data Engine [16] (Table 1).

Table 1. Pure components critical properties and acentric factors from Thermo Data Engine [16].

Compound	T_c /K	P_c /Mpa	ω
Methane	190.56	0.546	0.0011548
Ethane	305.32	4.872	0.099493
propane	369.82	4.248	0.152291
n-butane	425.15	3.794	0.19955
i-butane	407.84	3.639	0.18444
n-pentane	469.7	3.370	0.251506
n-hexane	507.53	3.028	0.30044

The nomenclature of Huang and Radosz [24] is adopted for water and all the alkanolamines. We consider as Kontogeorgis et al. [25] that 4C association scheme is the most suitable scheme for water. For alkanolamines, 4C association scheme is used to represent their association scheme. In previous work, Avlund et al. [12,13] mentioned that 4C association scheme is a natural choice for MEA. Also, they compared different association schemes for DEA and concluded that with 4C association scheme, pure component thermodynamic properties of DEA are correctly predicted. Moreover, as the molecule structure of MDEA is similar to the one of DEA, they have assumed that 4C association scheme is also suitable for MDEA. Consequently, the parameters of association term (ϵ^{AiBj} and β^{AiBj}) of MDEA are assumed as the same as the ones of DEA.

Five parameters (a_0 , b , c_1 , ϵ^{AiBj} and β^{AiBj}) are required to represent thermodynamic properties of water, MDEA, DEA, and MEA. The parameters were regressed by minimizing an objective function (Eq. 2):

$$f_{obj,pure} = \sum_{i=1}^{n_{vap}} \left(\left| \frac{p_{sat}^{cal} - p_{sat}^{exp}}{p_{sat}^{exp}} \right| \right)_i + \sum_{i=1}^{n_{\rho}} \left(\left| \frac{\rho_{liq}^{cal} - \rho_{liq}^{exp}}{\rho_{liq}^{exp}} \right| \right)_i \quad (2)$$

Where n_{vap} and n_{ρ} are the number of vapour pressure, and liquid density. P_{sat} is the vapour pressure. ρ_{liq} is the liquid density. P_{sat}^{exp} and ρ_{liq}^{exp} were generated by using DIPPR correlations from Thermo Data Engine [16]. Pure component parameters are presented in Table 2.

Table 2. PR CPA parameters for compounds for association compounds considered in this work.

Compound	scheme	a_0 /bar L ² mol ⁻²	b /L mol ⁻¹	c_1	ϵ^{AiBj} /bar.L.mol ⁻¹	β^{AiBj}	Tc /K	Range of Tr		ARD ^a	
								For P _{sat}	For ρ_L	P _{sat}	ρ_L
MEA	4C	1.333	5.467	0.763	168.23	0.0142	671.4	0.42-0.92	0.43-0.61	1.8	0.6
DEA	4C	3.065	9.246	1.02	201.76	0.0083	768	0.45-0.88	0.41-0.48	0.3	1.3
MDEA	4C	3.339	11.346	0.695	201.76	0.0083	741.9	0.39-0.9	0.38-0.63	0.9	2
water	4C	0.123	1.445	0.674	170.48	0.0698	647.29	0.43-0.95	0.43-0.95	1	1.6

^a ARD = $1/n_p \times \sum |1 - \chi_i^{calc}/\chi_i^{exp}| \times 100\%$.

3.2. Alkanolamine-water binary systems

Like Avlund et al. [12,13], we consider a constant value of BIP to represent alkanolamine-water binary systems. For each alkanolamine-water binary system, we have adjusted the corresponding BIP and a Flash type objective function (Eq. 3) has been chosen.

$$f_{obj,amine-water} = 100 \times \sum_{i=1}^n (|x_1^{cal} - x_1^{exp}| + |y_1^{cal} - y_1^{exp}|) \quad (3)$$

Where x_i is the composition of alkanolamine in the liquid phase, y_i is the composition of alkanolamine in the vapour phase.

Table 3 summarizes the BIPs and the references used in PR-CPA EoS for the VLE data treatment of alkanolamine-water systems. For MDEA-water and DEA-water binary systems, as usually in the vapour phase the concentration of alkanolamine is very low (order of magnitude of the amine mole fraction around 10^{-6}), only compositions of liquid phase are used to estimate BIPs. For MEA-water binary system, both compositions of liquid and vapour phases have been taken into account. From Figure 1, it can be seen that PR-CPA EoS with temperature independent BIPs is able to accurately represent phase behaviour of alkanolamine-water systems.

Table 3. Average Absolute Deviation (AAD) in liquid and vapor composition between PR-CPA adjusted data and experimental ones of water with MEA, DEA or MDEA binary system.

	T /K	No BIP		Adjusted BIP		references ^b
		AAD ^a x ₁ ×100	AAD ^a y ₁ ×100	AAD ^a x ₁ ×100	AAD ^a y ₁ ×100	
MDEA-water	313-450	12.26	1.26	1.20	0.005	-0.190 [26], [27], [28], [29]
DEA-water	311-473	6.93	-	2.14	-	-0.114 [30], [31]
MEA-water	283-373	9.30	1.73	1.74	0.23	-0.142 [26], [32], [33]

^a AAD = $1/NP \times \sum |\chi_i^{calc} - \chi_i^{exp}|$; ^b isotherm and isobar VLE data

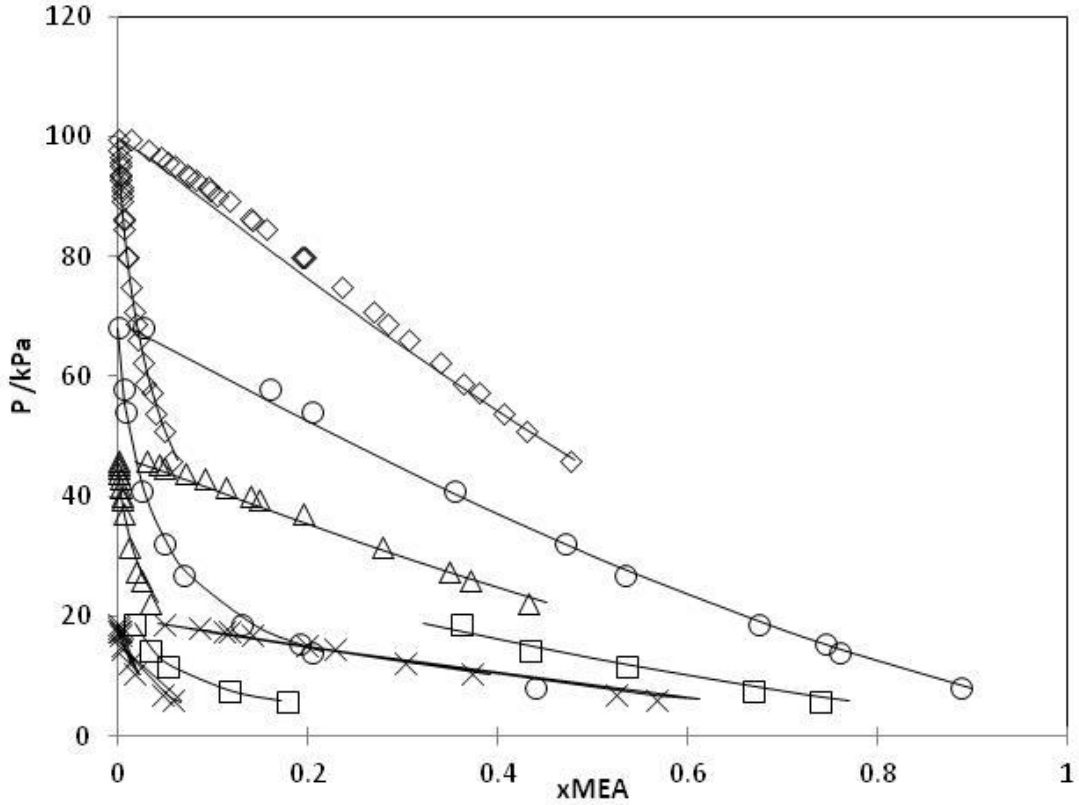


Figure 1. Comparison of experimental data (symbols) and adjusted ones using PR-CPA EoS (solid lines) for MEA-water binary system; (x)=333 K:Lenard et al. [32], (□)=343 K:Kim et al. [26], (Δ)=353 K :[26], (○)= 363 K:Tochigi et al. [33], (◇)=373 K [26].3.3. Alkane-water binary systems

As explained by Hajiw [34], we also consider a second order polynomial equation with temperature (Eq. 4) for the BIP to well describe the minimum solubility of alkane in aqueous solution. Consequently, we have considered a second order polynomial equation for the BIP (Eq. 4):

$$BIP = a + b \cdot T + c \cdot T^2 \quad (4)$$

a , b , c were estimated by fitting alkane solubility data and using a Flash type objective function (Eq. 5).

$$f_{obj, hydrocarbon - water} = 100 \times \sum_{i=1}^n \left(\frac{|x_1^{cal} - x_1^{exp}|}{x_1^{exp}} \right)_i \quad (5)$$

Table 4 summarizes the adjusted BIPs and the references used for the VLE data treatment of alkane-water binary systems. The ARD on alkane solubility in water is less than 12 %. Satisfactory results are obtained with our model compared to the ARD (less than 30%) obtained with Oliveira et al. [15]. We suspect that this higher deviation is due to their choice of using non temperature dependent BIPs.

Table 4. Comparison between alkane solubility data water with the calculated ones.

	T /K	ARD x_1	a	$b \times 10^3 / K^{-1}$	$c \times 10^6 / K^{-2}$	References
methane-water	274-423	6	-1.597	8.398	-8.29	[37,38]
ethane-water	259-444	7	-1.517	8.198	-9.236	[39,40]
propane-water	274-422	9	-1.114	6.256	-7.370	[41,42]
butane-water ^a	273-423	7	-0.751	4.074	-4.467	[43,44]
i-butane-water ^a	278-363	10	0.198	-2.152	5.205	[45]
pentane-water ^a	273-477	12	-0.704	3.932	-4.749	[35–37]
hexane-water ^a	273-425	12	-1.026	5.438	-6.565	[46,48]

^a LLE data were also considered; a, b and c are parameters in Eq. 4

3.4. Alkane-water-alkanolamine ternary systems

Previously, we have shown that using regressed BIPs for alkanolamine-water and alkane-water binary systems give satisfactory results. To the knowledge of the authors, there is no experimental VLE data concerning alkane-alkanolamine binary systems (only one set of data of methane-MDEA binary system is available in the open literature [35]). Consequently, BIPs of alkane-alkanolamine have been fitted using experimental alkane solubility in aqueous alkanolamine solutions. BIPs have the same expression as alkane-water binary systems (Eq. 4). A Flash type objective function is used and given by Equation 6.

$$f_{obj} = 100 \times \sum_{i=1}^n \left(\frac{|x_1^{cal} - x_1^{exp}|}{x_1^{exp}} \right)_i \quad (6)$$

Where x_1 is alkane solubility in aqueous alkanolamine solutions

Table 5 summarizes the obtained results. The model is generally able to describe different alkane solubilities in different aqueous alkanolamine solutions with ARD less than 10%. It is important to highlight, for each alkane-alkanolamine-water systems, thanks to a single temperature depend expression of BIPs, the model gives good accuracy (<10%) in all range of alkanolamine concentration.

Table 5. Comparison between experimental data of alkane solubility in aqueous alkanolamine solutions and the adjusted ones obtained with PR-CPA EoS.

alkanes	alkanolamines	data type	alkanolamine wt %	T /K	P /MPa	T independent BIP		T dependent BIP			ARD%	Number of point	references
						kij	ARD%	a	$b \times 10^3 / K^{-1}$	$c \times 10^5 / K^{-2}$			
Methane	DEA	VLE	5-40	310-394	0.1-20	0.441	6.0	-3.334	21.802	-3.119	4.4	53	[49]
	MDEA	VLE	35-50	298-423	1-20	0.693	10.5	-0.626	8.506	-1.383	8.4	85	[35,50,51]
	MEA	VLE	5-40	298-394	0.1-13	0.276	8.4	-6.520	41.059	-6.130	6.5	49	[49,52]
Ethane	DEA	VLE, VLLE	5-40	283-403	0.1-13	0.305	5.1	-0.544	5.269	-0.810	5.1	35	[17,53]
	MDEA	VLE	25-50	283-398	0.1-13	0.327	11.2	2.181	-9.183	1.065	6	61	[50]
	MEA	VLE	5-40	298-398	0.1-12.6	0.194	7.2	-4.193	26.400	-3.935	5.1	40	[52,53]
Propane	DEA	VLE, VLLE	0-65	298-348	0.1-1.3	0.210	6.6	3.099	-18.490	2.948	5.3	23	[17,54]
	MDEA	VLE, LLE	25-50	273-423	0.1-19.6	0.351	21.5	0.738	-1.493	0.072	5	74	[19,54]
	MEA	LLE	0-100	313	1.72	0.113	11	0.113			11	11	[54]
n-butane	DEA	VLLE	31.9-44.9	310-333	0.1-1.3	0.190	8.5	-1.982	12.957	-1.921	5.0	8	[17,55]
	MDEA	VLE, LLE	25-50	298-423	0.1-21	0.288	31	0.868	-2.349	0.161	6.2	80	[17,44,55]
i-butane	DEA	VLLE	35	310-333	0.1-1.3	0.124	4.5	-0.516	4.665	-0.837	0.3	6	[17]
	MDEA	VLLE	25-50	298-343	0.4-1.1	0.253	11.3	3.618	26.182	-4.422	8.6	12	[17]
Pentane	DEA	VLLE	35	298-333	0.5	0.132	4.0	1.926	-11.678	1.897	1.3	6	[17]
	MDEA	VLLE	25-50	298-343	0.5	0.228	7.0	3.545	23.914	-3.789	6.3	12	[17]
Hexane	DEA	VLLE	35	298-353	0.5	0.354	16.6	1.651	-8.393	1.087	7.4	10	[17]
	MDEA	VLLE	25-62	298-353	0.5	0.195	23.8	0.805	-2.476	0.155	17	32	[17,36]

For examples, Figure 2a and 2b show propane solubility in 35 wt % aqueous MDEA solution. The ARD is 5.0% for all sets of experimental data at VLE and LLE conditions. Figure 3 represents propane solubility in aqueous DEA solution in function of concentration, PR-CPA EoS is in good agreement with experimental data. Nevertheless, our model has higher ARD (17%) on n-hexane solubility in aqueous MDEA solution. In fact, this system has been treated by using two sets of experimental data (Mokraoui et al. [17] and Alheseinat et al. [36]), the ARD are 8.8% and 32.8% respectively. Since Alheseinat et al. [36] mentioned that the uncertainty of their experimental data is more than 30%, this set of data is suspicious.

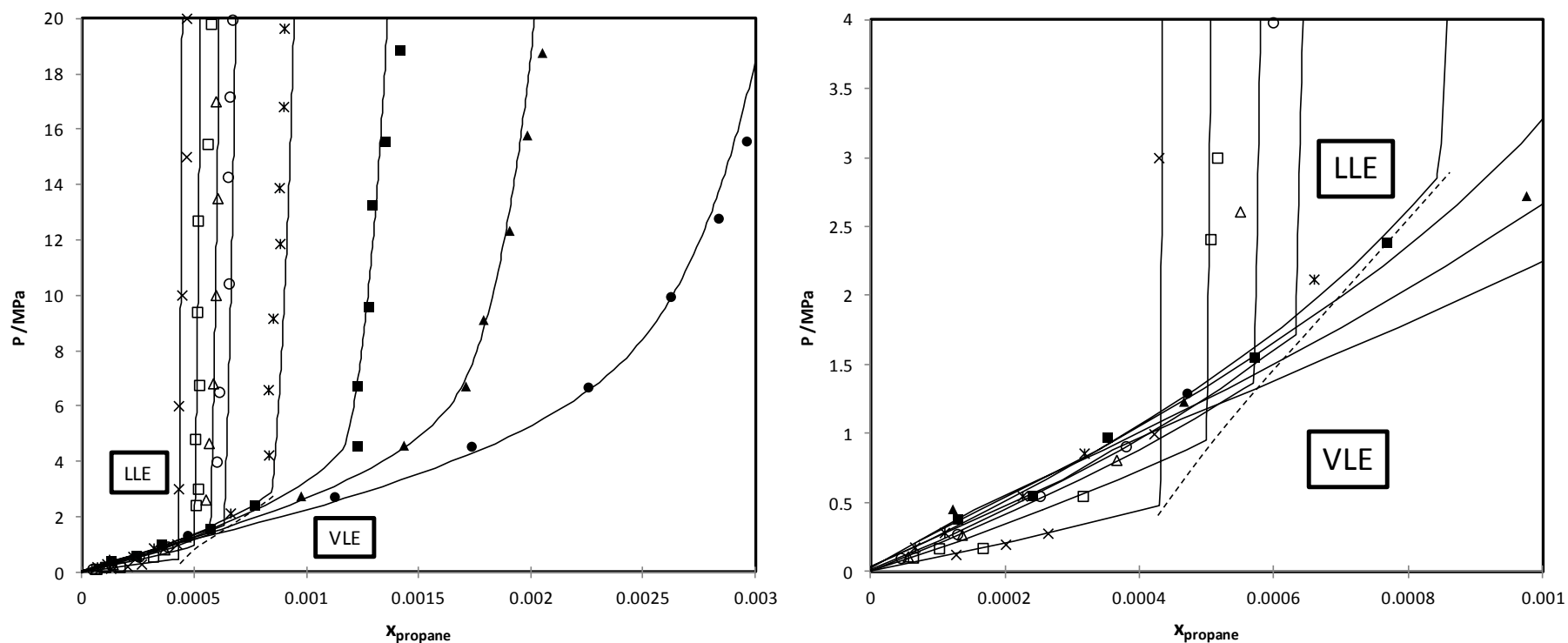


Figure 2. (b. is the zoom of a.) Comparison between experimental data from Jou et al.[21] for propane solubility in 35 wt % aqueous MDEA solution and adjusted data using PR-CPA EoS (solid lines). (x)=273 K, (□)=298 K, (Δ)=313 K (○)=323 K, (*)=348 K, (■)=398 K, (▲)=398 K, (●)=423 K, dashed line: VLLE interface.

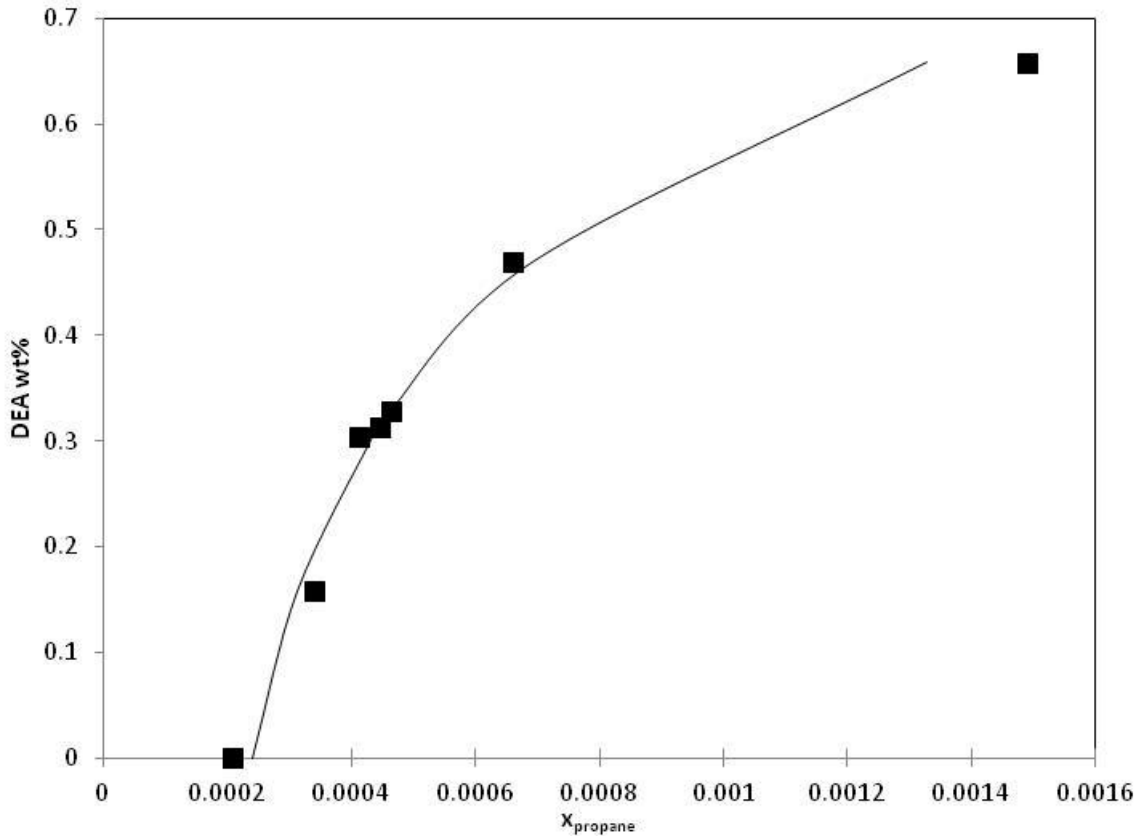


Figure 3. Propane solubility as function of DEA concentration up to 65 wt % at 313K and 17.24bar, symbol: experimental data from Jou et al. [54], solid line: data calculated by PR-CPA EoS.

4 Discussion

4.1. Temperature of minimum solubility of methane

Hajiw [34] (2014) and Hajiw et al. [11] (2015) have tested the capacity of PR-CPA EoS to predict the temperature of minimum of solubility for alkane-water binary systems. In this paper, the authors have also demonstrated that the prediction of this temperature is strongly dependant on the use of a temperature dependent BIP and recommended a second order polynomial expression. Using our model for methane-water binary system and at 5 MPa, we have predicted a temperature of 407 K. As shown in Figure 4, we have predicted the methane solubility as function of temperature (273-405 K) for 3 different aqueous MDEA solutions (25, 35 and 50 wt %) at 7.5 MPa (Since the solubility of methane do not have the same order of magnitude, their values are normalized). We observed that for each aqueous MDEA solution, it exists a temperature of minimum methane solubility. After, we also predict the temperature of minimum of solubility of methane in 3 MDEA aqueous solutions (25, 35 and 50 wt %) and pure water at 3 different pressures 5, 7.5 and 10 MPa, the result is summarized in Table 6. In fact, the temperature of methane minimum solubility is influenced by two factors: the concentration of alkanolamine and the pressure.

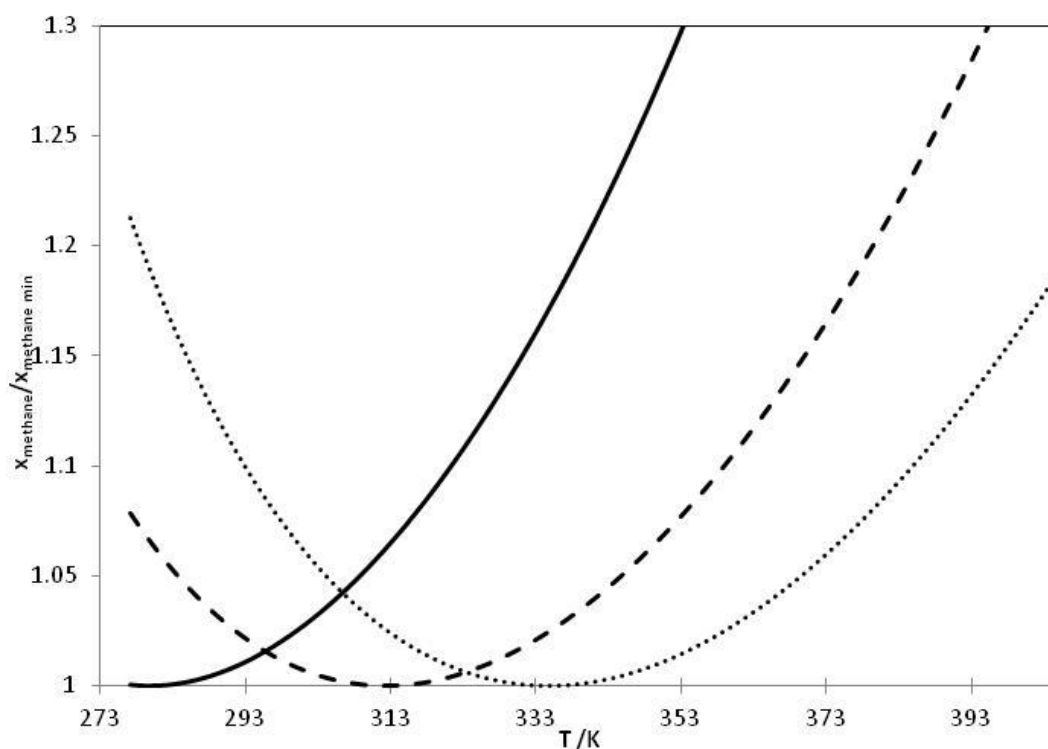


Figure 4. PR-CPA EoS prediction of the ratio of methane solubility and the minimum solubility as function of temperature at 75 bar. solide line=25 wt % MDEA, dashed line=35 wt % MDEA, dotted line=50 wt % MDEA.

As shown in Figure 5, the temperature of the minimum solubility decreases as the MDEA weight percent increases. It could be explained by the fact that the hydrogen bond between water is destroyed by introducing MDEA molecules. Less energy is needed to absorb the same quantity of methane in a higher MDEA concentration solution. Seen in Figure 6, the temperature of methane minimum solubility decreases while the pressure increases. In fact, higher pressure makes methane more soluble. Consequently, lower temperature is required. The same approach can be applied to all alkanes.

Table 6. Methane minimum solubility temperature in aqueous MDEA solution and in pure water predicted by PR-CPA EoS.

P /MPa		T /K		
5	407	340	317	286
7.5	402	335	312	280
10	395	330	306	277
wt % MDEA	0	25	35	50

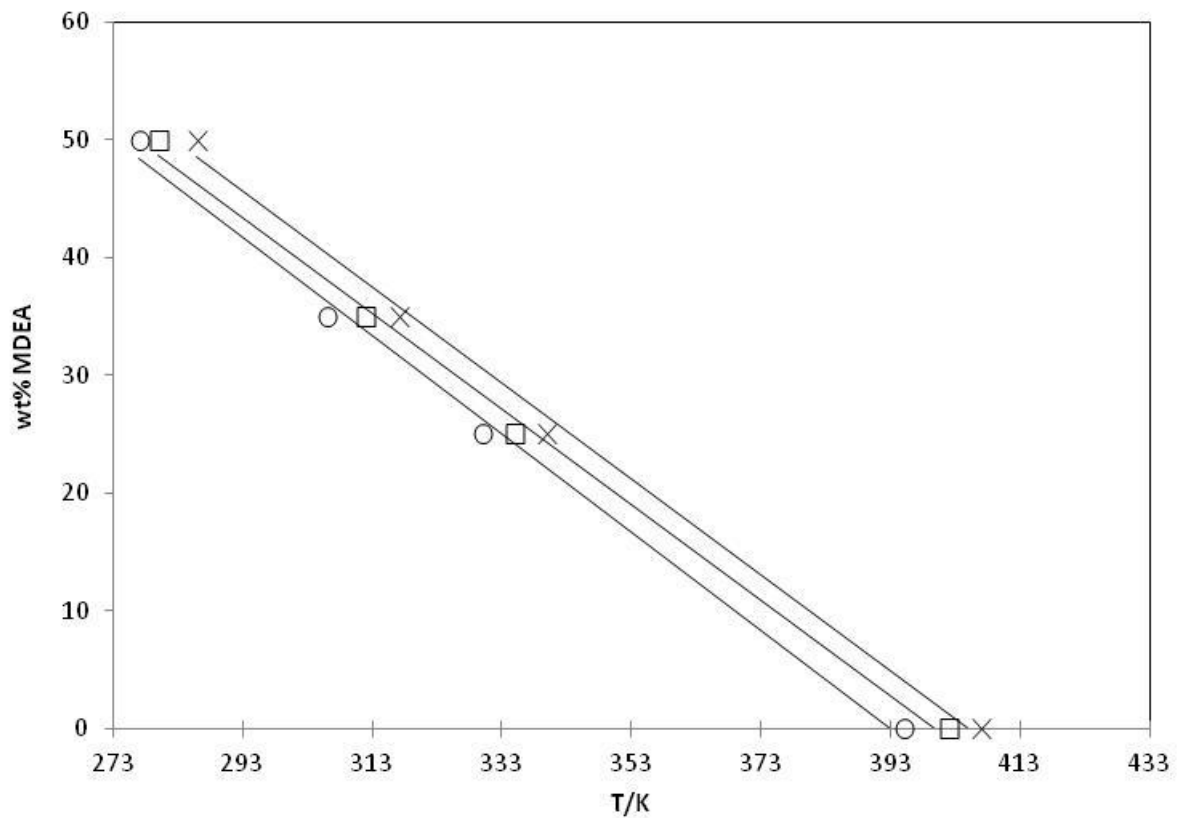


Figure 5. PR-CPA EoS prediction of the temperature of minimum solubility of methane as function of MDEA concentration at different pressure. (x)=5 MPa, (□)=7.5 MPa, (○)=10 MPa.

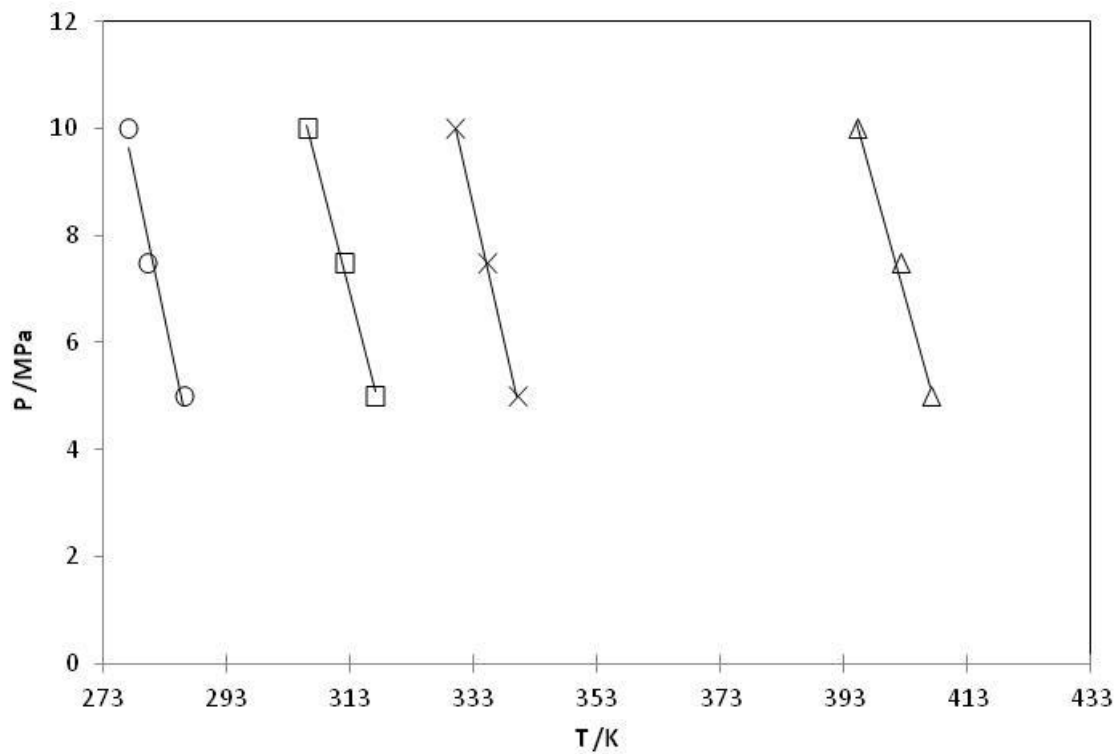


Figure 6. PR-CPA EoS prediction of the temperature of minimum solubility of methane as function of pressure in different aqueous MDEA solutions (□)=25 wt % MDEA, (x)=35 wt % MDEA, (○)=50 wt % MDEA and (Δ)=pure water.

4.2 Propane-MDEA-water alkane rich phase prediction

The ability of the model to predict water content was also evaluated. As seen in Figure 7, at VLE condition, predicted water contents are in good agreement with the only experimental data found in the literature and measured by Carroll et al. [19] in 1992. The ARDs are less than 20%. However, the model fails to predict water content in LLE conditions. After comparison with experimental data of Carroll et al. [19]. The ARDs are less than 124%. The biggest deviations are observed at low temperatures. It is not surprising that EoS fails to predict both VLE and LLE without mixing rules. We suggest as an alternative solution, to modify the expression of the co-volume b , by introducing a binary interaction parameter l_{ij} .

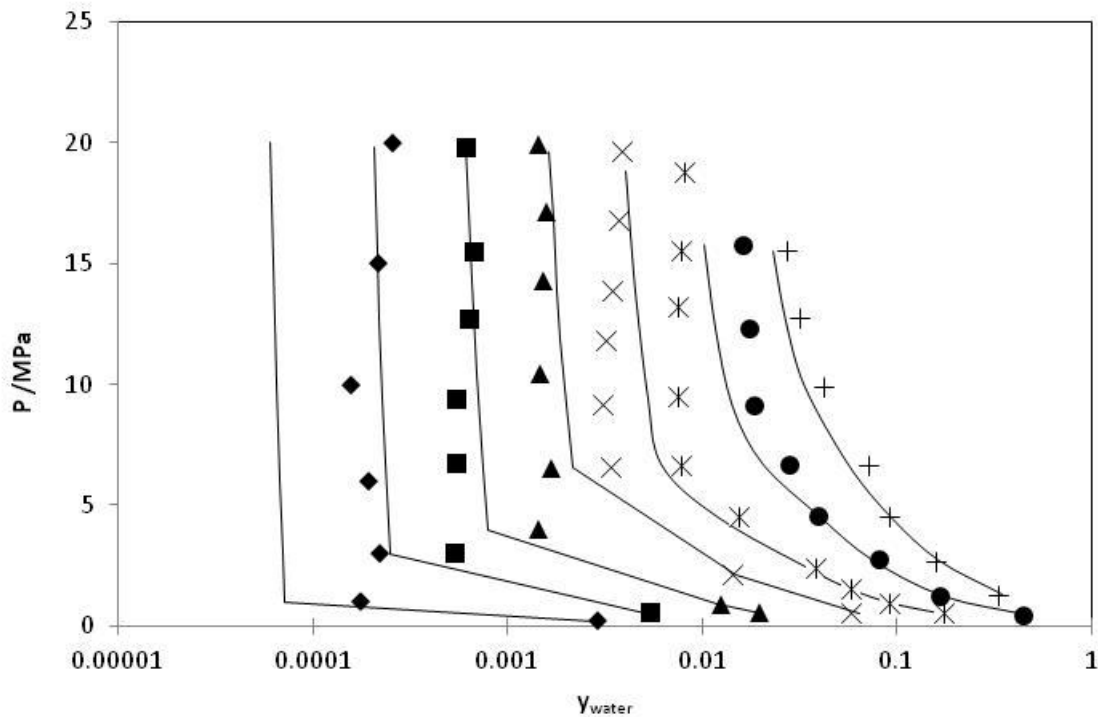


Figure 7. Comparison between experimental data from Carroll et al. [19] for water content in propane rich phase of propane-MDEA(35 wt %)-water ternary system and predicted data using PR-CPA EoS (solid lines). (◆)=273K, (■)=298K, (▲)=323K, (×)=348K, (*)=373K, (●)=398K, (+)=423K.

MDEA composition has been also measured by Carroll et al. [19] in propane rich phase, the composition of MDEA corresponds to few ppm at low temperature. MDEA composition is poorly predicted by our model. In fact, predicted MDEA composition is 10-100 times lower than experimental data at LLE conditions. The only agreement between model and experimental data is at temperature above 373 K and pressure under 5 MPa. Mokraoui et al. [17] did not manage to measure the same system as Carroll et al. [19]. Meanwhile, for pentane solubility in aqueous MDEA solutions, Mokraoui et al. [17] showed that the concentration of MDEA is less than 10 ppm in the liquid alkane rich phase. We conclude that more studies concerning the measurement of MDEA composition in different alkanes rich phase data are needed for the model validation.

We have also evaluated the model performance to predict the water content of this ternary system without BIPs for propane-water and propane-MDEA systems, the ARD on water content is 21% in VLE region. The water content value concerning propane-water-MDEA ternary system at given T and P should be lower but very close to the one of propane-water binary system in the same condition of T and P because the molar composition of water is 64.4 % in the aqueous solution. Therefore, we have predicted the water content without BIP for propane-water binary system, the ARD is 8% compared to the experimental data published by Kobayashi et al. [41] and Blanco et al. [56]. We conclude that the vapour phase data published by Carroll et al. [19] are probably suspicious.

4.3. Alkane-alkanamine-water ternary systems prediction at VLLE conditions

The experimental VLLE data of ethane-MDEA-water, propane-MDEA-water, and n-butane-MDEA-water ternary systems were not used for data adjustment, since for these systems we have already enough VLE or LLE data. Therefore, VLLE data is used for model validation; they are compared with those predicted with PR-CPA EoS, see Figures 8, 9 and 10. For ethane-MDEA-water ternary system, the overall ARD for ethane solubility is less than 6% in MDEA with three concentrations (0% wt%, 25 wt % and 50 wt %). The largest ARDs, 14 % are observed for ethane solubility in pure water. For propane-MDEA-water ternary system, the ARD for all concentrations of MDEA are less than 2 %. For n-butane-MDEA-water ternary system, PR-CPA EoS can accurately predict n-butane solubility in pure water, 25 wt % MDEA, 35 wt % MDEA and 50 wt % MDEA. The ARDs are less than 8 %.

Moreover, the slope of each curve represents the enthalpy of absorption of solute i (Δh_i^{abs}) given by Equation 7.

$$\left(\frac{\partial \ln x_i}{\partial 1/T}\right)_P = -\frac{\Delta h_i^{abs}}{R} \quad (7)$$

The absorption is endothermic, if the sign is negative, otherwise exothermic. For propane and n-butane, the absorption is always endothermic because once need energy to destroy the hydrogen bound between water–water, water-MDEA and MDEA-MDEA once alkanes molecules are introduced. However, for ethane, it seems that we have a particular behaviour since there is no tendency of the enthalpy of absorption (exothermic, athermic and endothermic for 0, 25 and 50 wt % MDEA respectively).

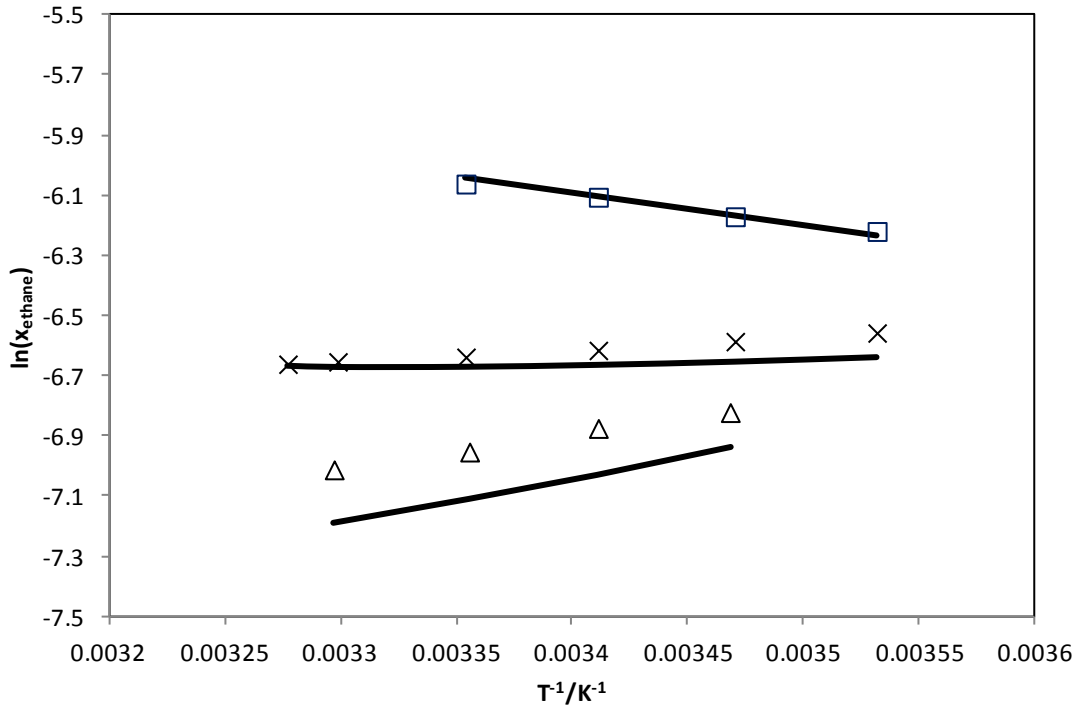


Figure 8. Comparison between experimental data from Mokraoui et al. [17] for solubility of ethane in aqueous MDEA solution and predicted data using PR-CPA EoS (solid lines). (Δ)=Pure water, (\times)=25 wt % MDEA, (\square)=50 wt % MDEA.

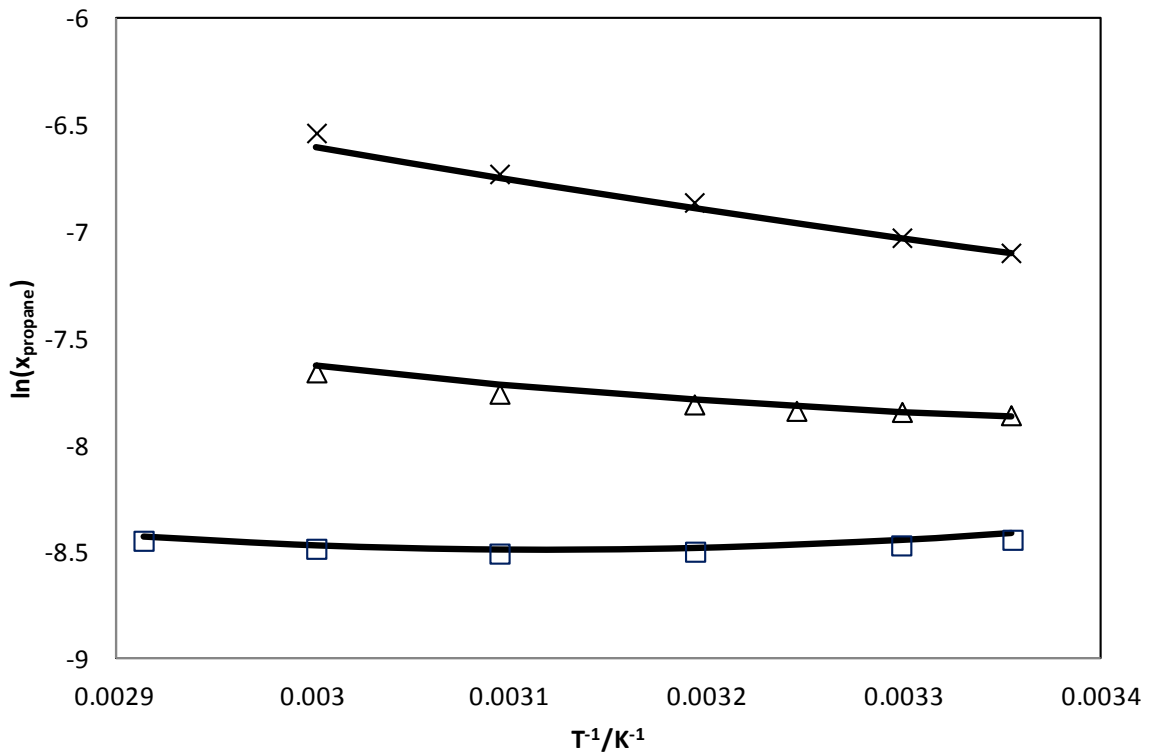


Figure 9. Comparison between experimental data from Mokraoui et al. [17] for solubility of propane in aqueous MDEA solution and predicted data using PR-CPA EoS (solid lines). (Δ)=Pure water, (\times)=25 wt % MDEA, (\square)=50 wt % MDEA.

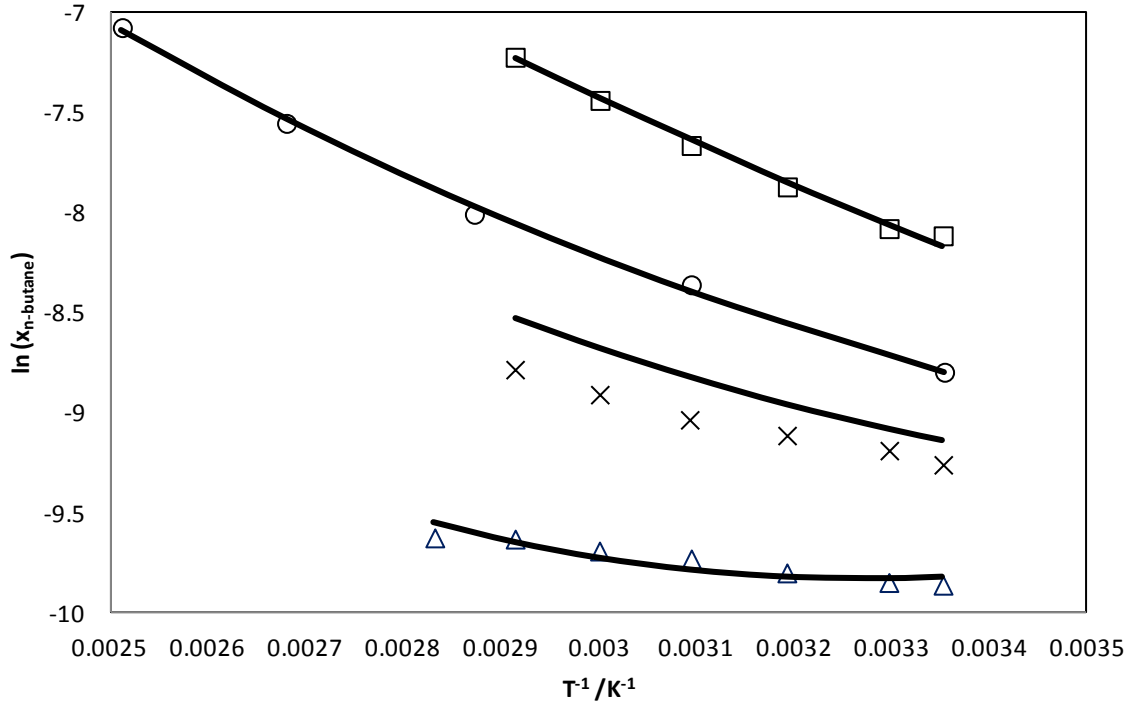


Figure 10. Comparison between experimental data from Mokraoui et al. [17], Jou et al. [44] for solubility of butane in aqueous MDEA solution and predicted data using PR-CPA EoS (solid lines). (Δ) =Pure water [17], (\times)=25 wt % MDEA [17], (\circ)=35 wt % MDEA [44], (\square)=50 wt % MDEA [17].

4.4. Multi-component alkanes solubilities prediction in aqueous amine solutions

As a final test, we have used our model to predict multi-component alkanes solubilities in alkanolamine solutions. Few experimental data for alkane mixtures solubility in aqueous alkanolamine solutions are available. Mokraoui et al. [17] measured the solubility of two mixtures (MIX1 and MIX2, Table 7) in 35 wt % DEA, 25 wt % and 50 wt % MDEA, within temperature range from 298 to 333 K and pressure range from 0.6 to 4 MPa. The reported data concern VLE and VLLE conditions.

Table 7. Alkane mixture composition from Mokraoui et al. [17].

Alkanes	Mole Composition	
	MIX1	MIX2
ethane	0.5	0.02
propane	0.3	0.5
n-butane	0.1	0.23
i-butane	0.02	0.1
n-pentane	0.05	0.1
n-hexane	0.03	0.05

As for non-associative molecules, the PR-CPA EoS is reduced to PR EoS, the BIP between alkanes one taken from the work of Gao et al. [57].

From Table 8 one can notice that the model has good predictability for the majority compounds, i.e. ethane and propane for MIX1; propane and n-butane for MIX 2. The ARDs are less than 30% for ethane and propane. Meanwhile, for C4 to C6, ARDs are more important.

Table 8. PR-CPA EoS prediction of alkane mixture solubility in aqueous alkanolamine solutions.

		ARD ^a %			
		T /K	P /MPa	Ethane	Propane
MIX1	50 wt% MDEA	298-333	0.6-4.2	22	13
	25 wt% MDEA	298-333	0.7-4.0	16	11
	35 wt% DEA	298-333	0.6-4.3	29	17
MIX2 ^b	50 wt% MDEA	298-333	0.5-1.3	-	30
	25 wt% MDEA	298-333	0.5-1.3	-	19
	35 wt% DEA	298-333	0.5-1.4	-	9

a: ARD is average relative deviation determined on solubility of main components

b: propane is the main component of MIX 2

5 Conclusion

In this work, the PR-CPA EoS was applied to describe the solubility of alkanes in aqueous MDEA, DEA and MEA solutions. Pure compounds parameters of associating compounds were determined by regression from experimental data. The model describes both pure component liquid density and vapour pressure within ARD lower than 3%. Then, PR-CPA EoS was applied to model phase equilibria of alkanolamine-water and alkane-water binary systems. It showed good agreement for these binaries studied in this work.

Experimental data of alkanes in aqueous alkanolamine solutions (solubility) were used to correlate BIPs of corresponding alkane-alkanolamine binary systems. With optimized parameters, alkane solubilities in aqueous alkanolamine solutions were successfully described by the model; the ARDs are under 10%. Furthermore, the temperature of minimum solubility of methane was well described.

Water content was also accurately predicted in VLE conditions (ARDs are less than 12%) but not in LLE conditions, PR-CPA EoS must be improved. Solubility of two alkanes mixtures in aqueous alkanolamine solutions were studied in this work. The model was able to predict main components solubility (The ARDs are less than 30%).

This study showed that PR-CPA EoS is accurate for predicting alkane solubility in aqueous alkanolamine solutions. Our future objective is to improve our model by taking into account the impact of acid gases. The introduction of H₂S and CO₂ leads to chemical reaction taking place with alkanolamine and water and different electrolyte species will be formed.

6 Nomenclature

List of abbreviations

AAD=average absolute deviation
ARD=average relative deviation
cal=calculated by the model
CPA=cubic-plus-association
DEA=diethanolamine
EoS=equation of state
Exp=experimental
LLE=liquid-liquid equilibria
MEA=monoethanolamine
MDEA=methyldiethanolamine
PR=Peng Robinson
SAFT=statistical associating fluid theory
VLE=vapour-liquid equilibria
VLLE=vapour-liquid-liquid equilibria

Roman symbols

a_0 =parameter in the energy term (a) (bar L mol^{-2})
 A_i =site A in molecule i
 b =covolume parameter (L mol)
 B_j =site B in molecule j
 c_j =parameter in the energy term (a)
 g =radial distribution function
BIP=binary interaction parameter
P=pressure
T=temperature
 Tr =reduced temperature by critical temperature
 V_m =molar volume
 x_i =liquid mole fraction of component i
 X_{A_i} =fraction of i molecules, not bonded at site A
 y_i =vapour mole fraction of component i

Greek letters

$\beta^{A_i B_j}$ =association volume parameter between site A in molecule I and site B in molecule j
 Δ =association strength (L/mol)
 $\varepsilon^{A_i B_j}$ =association energy parameter between site A in molecule I and site B in molecule j (bar L mol^{-1})
 η =reduced density
 ρ =density (mol/L)

7 References

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APPENDIX A: PR-CPA description

Where V_m is the molar volume, b is the molar co volume parameter, $a(T)$ the temperature dependent energy parameter of the equation of state, ρ the molar density ($\rho=1/ V_m$), g_r the radial distribution function, and X_{A_i} the fraction of sites A on molecule i (hence the subscript A_i) that do not form bonds with other hydrogen bonding sights. X_{A_i} is dependent on the association strength $\Delta^{A_iB_j}$ between it and sights belonging to other molecules of the same or different substance, like for example sight B on molecule j named B_j (hence the superscript A_iB_j on Δ). X_{A_i} is given as

$$X_{A_i} = \frac{1}{1 + \rho \sum_j x_j \sum_{B_j} X_{B_j} \Delta^{A_iB_j}} \quad \text{Eq (A. 1)}$$

X_{B_j} is the fraction of sites B on molecule j that don't form hydrogen bonds. The association strength $\Delta^{A_iB_j}$ is dependent on the radial distribution function g_r , the association energy $\varepsilon^{A_iB_j}$, and the association volume $\beta^{A_iB_j}$ between sights A_i and B_j . The relation is given by equation:

$$\Delta^{A_iB_j} = g_r \left[\exp\left(\frac{\varepsilon^{A_iB_j}}{RT}\right) - 1 \right] b_{ij} \beta^{A_iB_j} \quad \text{Eq (A. 2)}$$

The cross-association between two associating molecules is modelled by using the CR1 combining rule (Eq. A 3) and (Eq. A 4) for the cross-association energy and volume.

$$\varepsilon^{A_iB_j} = \frac{\varepsilon^{A_iB_i} + \varepsilon^{A_jB_j}}{2} \quad \text{Eq (A. 3)}$$

$$\beta^{A_iB_j} = \sqrt{\beta^{A_iB_i} \beta^{A_jB_j}} \quad \text{Eq (A. 4)}$$

Therefore, the values of ε and β were found by fitting to pure compound vapour pressure and liquid density experimental data. The equation used to find the radial distribution function is:

$$g_r = \frac{1}{1 - 1.9\eta} \quad \text{Eq (A. 5)}$$

$$\eta = \frac{1}{4} b \rho \quad \text{Eq (A. 6)}$$

The values of $a(T)$ and b for the mixture are founded using classical van der Waals mixing rules:

$$a(T) = \sum_i \sum_j x_i x_j a_{ij} \quad \text{Eq (A. 7)}$$

$$b = \sum_i x_i b_i \quad \text{Eq (A. 8)}$$

Where b_i is the molar co volume parameter of the equation of state for pure substance i . For associative molecules, it is determined by fitting to pure compound vapour pressure and liquid density experimental data. For alkanes b_i was calculated from critical properties acentric factor:

$$b_i = 0.07780 \frac{RT_c}{P_c} \quad \text{Eq (A. 9)}$$

Where k_{ij} is the binary interaction parameter. While a_i and a_j are the energy parameters of the equation of state for pure substances i and j respectively. For substance i , a_i is defined as:

$$a_i = a_{0,i} \left(1 + c_{1,i} \left(1 - \sqrt{\frac{T}{T_{c,i}}} \right) \right)^2 \quad \text{Eq (A. 10)}$$

Where $a_{0,i}$ and $c_{1,i}$ are parameters of the equation of state for substance i . For water and alkanolamines they were fit to vapour pressure and liquid density experimental data. For alkanes they were calculated from critical properties and the acentric factor:

$$a_i = 0.45724 \frac{R^2 T_c^2}{P_c} \quad \text{Eq (A. 11)}$$

$$c_{1,i} = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad \text{Eq (A. 12)}$$