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Measurement and modeling of mercaptans solubility in aqueous alkanolamine solutions

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Natural gas always contains contaminants such as acid gases (CO₂ and H₂S), mercaptans and other sulfur components. With the purpose of avoiding corrosion when water is present, safety problems and environmental issues, these impurities must be removed until an acceptable specification. According to Huguet et al. [1], the treated gas contains as maximum as 2% CO₂, 2–4 ppm H₂S and 5–30 ppm total sulfur (mercaptans and COS). Absorption with alkanolamines processes are commonly used for natural gas treatment. The knowledge of the mercaptans solubility in aqueous alkanolamine solutions is important in acid gas removal process simulation and design, as it allows designers to confirm their regulatory limits. In previous works done at CTP, the activity coefficients at infinite dilution and Henry's law constant of mercaptans [2] have been determined by using gas stripping method; the solubilities of n-Propyl-mercaptan, n-Butyl-mercaptan and Dimethylsulfide in loaded, and unloaded MDEA and DEA aqueous solutions [3] were measured by using static analytic method. In this work, we report the results of Vapor Liquid Equilibrium measurements of different mercaptans (methyl- and ethyl--mercaptan) in different alkanolamine solutions of MDEA.

Thermodynamic models are crucial for acid gas removal process simulation and design. The association effects of water and alkanolamine have the most important role in these systems. Hence, Cubic-Plus-Association Equation of State [4] (CPA EoS) has been chosen. In previous work [5], CPA EoS was successfully applied to describe the phase equilibria of alkane-alkanolamine-water ternary systems. In the present work, CPA EoS was applied to represent mercaptans solubility in aqueous alkanolamine solutions. Satisfactory results are obtained for representing both liquid and vapor phase composition.

Keywords: phase equilibria, modeling, mercaptans, experimental data, CPA EoS

1. INTRODUCTION

Among fossil fuels, natural gas is the cleanest, in terms of CO₂ emission, burn efficiency and amount of air pollutant [6]. Methane is the prevailing element of natural gas; therefore, there are also a variety of impurities. In fact, it contains usually considerable amounts of acid gases (CO₂, H₂S) which can lead to corrosion in equipments and pipelines if water is present. Mercaptans are known as toxic molecules with undesirable odor, they can cause environmental issues. Acid gases and mercaptans are needed to be removed from natural gas until acceptable standard. The treated natural gas contains as maximum as 2% of CO₂, 2–4 ppm of H₂S and 5–30 ppm of total mercaptans [1]. Chemical absorption with alkanolamines [7] (such as monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA)) is the most well-established method to separate acid gas from natural gas, see Figure 1. Acid gases react with alkanolamines in the absorber, mercaptans do not react with alkanolamine molecules, and they are physically absorbed by aqueous alkanolamine solution. Then the loaded solution can be regenerated by heating in the stripper. Thermodynamic model is of high importance for the conception of the process, as it is linked directly to the accurate determination of the vapor-liquid equilibrium. Reliable thermodynamic models can allow designers not only to confirm their regulatory limits, but also to minimize the loss of valuable components (such as alkanes).

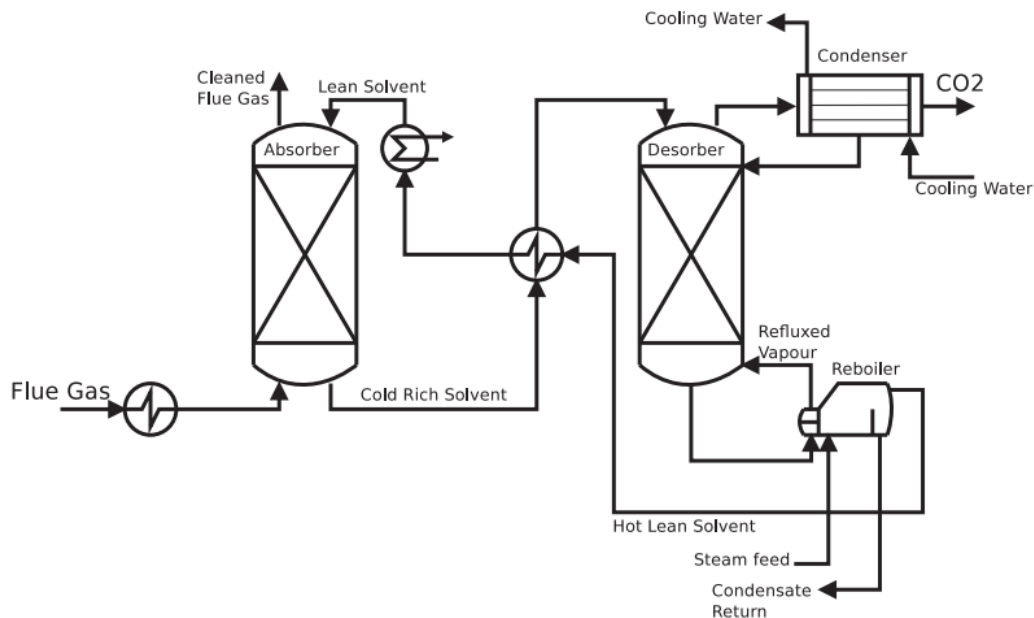


Figure 1: Schematic flow diagram of acid gas removal process [7]

Due to the presence of associating molecules like alkanolamine and water, Peng Robinson (PR)-CPA EoS is considered, because it can easily consider the presence of hydrogen bonding. In previous work [5], PR-CPA EoS was applied to describe the phase equilibria of alkanes-alkanolamines-water, parameters were fitted from experimental data, the overall performance of CPA for alkanes solubilities in alkanolamine solutions are satisfactory. In the present work, pure components parameters of water, alkanolamine and alkanes were taken from previous work [5]. As mercaptans are not association molecules, their parameters will be calculated from critical pressure, critical temperature and acentric factor by using the same method as the previous study [5]. 6 Binary Interaction Parameters (BIPs) are required to represent phase equilibrium properties of each mercaptan-water-alkanolamine-methane quaternary systems. BIP of mercaptans with other components (water, methane, and alkanolamine) will be fitted from experimental data measured in our laboratory. The main objective of this presentation is to describe Methyl-Mercaptan (MM) and Ethyl- Mercaptan (EM) solubilities in MDEA solutions by using PR-CPA EoS. This model should be able not only to predict mercaptans solubilities in the liquid phase, but also to predict the composition of the vapor phase, as well as the solubility of methane in the liquid phase.

We will also present some experimental data of these systems in terms of apparent Henry's law constant. The equipment used to obtain these data is based on a "static-analytic" method with liquid and vapor phase samplings [3].

2. EXPERIMENTAL MEASUREMENTS

Experimental setup used in this paper is described in detail in the GPA research report 207 [8]. However, a brief description is given below. The apparatus, shown in Figure 2, is based on the “static-analytic” method with liquid and vapor phase samplings [3]. The equilibrium cell is made of a sapphire tube and its volume is about 31.1 mL. It can operate up to 10 MPa and 473 K. The system is stirred through a variable speed stirrer to achieve a fast thermodynamic equilibrium. The equilibrium cell is totally immersed in a liquid bath regulated by a temperature controller maintaining the desired temperature in the bath within 0.1 K. Separation of components is realized by a Porapak column R (80/100 Mesh 1.20 m) and a temperature program with an oven temperature range from 333 to 518 K. The samples are analyzed by FID and TCD detectors

Regarding the working condition of ROLSI® Capillary Sampler-Injector (minimum 3-4 bar in the equilibrium cell is requested), the measurement of mercaptan solubility in aqueous alkanolamine solutions was carried out with pressurization by methane. Thus, in the modeling part, it is necessary to take consideration of methane. i.e., we need to investigate on mercaptan-alkanolamine-water-methane quaternary systems.

Concerning the experimental procedure, we have prepared a solution of MDEA 25wt % and dissolved a known quantity of mercaptan (MM or EM) inside in order to obtain a solution with a known concentration of mercaptan and then this solution is loaded in the equilibrium cell. Methane is added after in order to reach the pressure desired.

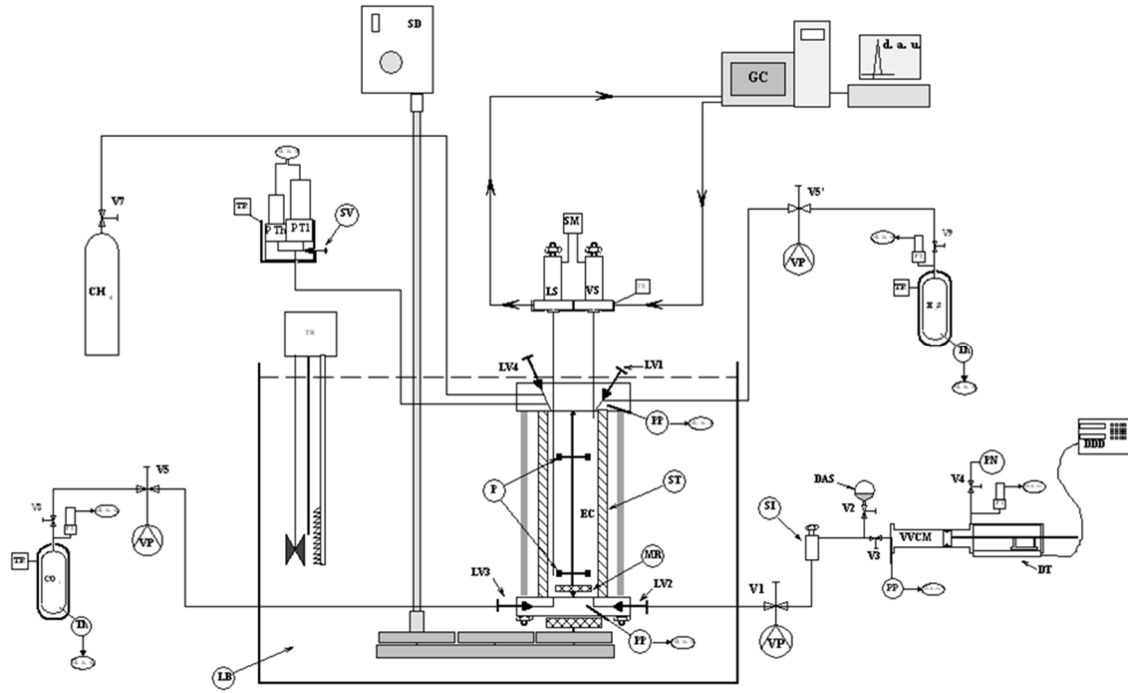


Figure 2: Schematic diagram of apparatus: CI: Cylindrical tube Injector; DAS: Degassed Aqueous Solution; d. a. u. : Data Acquisition Unit; DDD : Digital Displacement Display; DM : Degassed Mixture; DT : Displacement Transducer; EC : Equilibrium Cell; GC : Gas Chromatograph; LB: Liquid Bath; LS : Liquid Sampler; LVi : Loading Valve; MR; Magnetic Rod; P: Propeller; PN: Pressurized nitrogen; PP : Platinum Probe; PTh: Pressure transducer for high pressure values; PTI: Pressure transducer for low pressure values; PT: pressure transducer. SD: Stirring Device; SM: Sample Monitoring; ST: Sapphire tube; SV: Selection Valve; Th: Thermocouple; TR: Thermal Regulator; Vi: Valve; VP: Vacuum Pump; VS: Vapor Sampler; VVCVM: Variable Volume Cell for Mixture.

3. THERMODYNAMIC MODELING: THE PR-CPA EoS

The CPA EoS has an explicit part to account for hydrogen bonding, making it well suited for describing water- alkanolamines-hydrocarbons systems, where water and alkanolamines molecules form hydrogen bonds between them and themselves. CPA EoS takes a cubic EoS as the basis and adds a correction for hydrogen bonding [4]. In this work, we used Peng-Robinson EoS [9] for the cubic part and the association part is from Wertheim [10]. PR-CPA EoS is given as (Eq1):

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

The model is detailed in the previous work [5]. For LLE and VLE measurements, liquid and vapor compositions were calculated by two phases flash using algorithm of Michelsen et al. [11].

4. Results and discussion

4.1 pure component

Pure components parameters for water, alkanolamine and methane are taken from the previous study [5] and shown in Table 1. Mercaptans are considered as non-association molecules in this study, their parameters are calculated from critical pressure, critical temperature and acentric factor by using the same method in previous study [5] and presented also in Table 1.

Table 1: PR-CPA parameters of pure component.

Compound	scheme	a ₀ /bar L ² mol ⁻²	b /L mol ⁻¹	c ₁	ϵ^{AiBj} /bar.L.mol ⁻¹	β^{AiBj}	T _c /K	ARD ^a	
								P _{sat}	ρ_L
MM	-	0.966	4.209	0.6			469.87		
EM	-	1.427	5.856	0.66			498.8		
methane	-	0.249	2.68	0.392			190.6		
DEA	4C	3.065	9.246	1.02	201.76	0.0083	768	0.3	1.3
MDEA	4C	3.339	11.346	0.695	201.76	0.0083	741.9	0.9	2
water	4C	0.123	1.445	0.674	170.48	0.0698	647.29	1	1.6

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

4.2 Binary systems without mercaptans

6 BIPs listed in Table 2 are required to represent each mercaptan-water-alkanolamine-methane quaternary systems. BIPs for alkanes-water, alkanolamine-water and alkanes-alkanolamines are taken from the previous study [5], these parameters as well as the Average Absolute Deviation (AAD) or the Average Relative Deviation (ARD) are shown in Table 3 and Table 4.

Table 2 List of BIPs required representing mercaptan-water-alkanolamine-methane quaternary systems.

	Mercaptan	Alkanolamine	Water	Methane
Mercaptan	NA	this work	this work	this work
Alkanolamine		NA	previous work [5]	previous work [5]
Water			NA	previous work [5]
Methane				NA

Table 3: BIPs values and AAD of liquid (x) and vapor (y) compositions between PR-CPA EoS adjusted data and experimental ones obtained for water (1) with DEA or MDEA binary system according to Wang et al. [1].

	T /K	No BIP		Adjusted BIP		k_{ij}
		AAD ^a $x_1 \times 100$	AAD ^a $y_1 \times 100$	AAD ^a $x_1 \times 100$	AAD ^a $y_1 \times 100$	
MDEA-water	313-450	12.26	1.26	1.20	0.005	-0.190
DEA-water	311-473	6.93	-	2.14	-	-0.114

^a AAD = $1/NP \times \sum |\chi_i^{calc} - \chi_i^{exp}|$

Table 4 : BIPs values and ARD of liquid (x) composition between PR-CPA EoS adjusted data and experimental ones obtained for methane (1)-water and methane (1)-alkanolamines binary systems according to Wang et al. [1]

	T /K	ARD x_1	a^a	$b \times 10^3 /K^{-1}$	$c \times 10^6 /K^{-2}$
methane-water	274-423	4	-1.597	8.398	-8.29
Methane-DEA	310-394	4	-3.334	21.802	-30.119
Methane-MDEA	298-423	8	-0.626	8.506	-1.383

^a a, b and c are parameters of BIP: $BIP = a + b \cdot T + c \cdot T^2$

4.3 Binary systems with mercaptans

All the BIPs concerning mercaptans with other components are adjusted from experimental data. The objective function used in this study is given by equation 2:

$$f_{obj} = 100 \times \sum_{i=1}^n \left(\frac{|x_1^{cal} - x_1^{exp}|}{x_1^{exp}} \right) i \quad (2)$$

Where x_i is the composition of mercaptans in the aqueous phase.

4.3.1 Mercaptan-methane binary systems

There is no solvation effect between methane and mercaptans, because both of them are not association molecules. BIPs for methane-MM and methane-EM are adjusted from experimental data of Awan et al. [12]. Temperature independent BIPs are considered for these two systems, the value of BIPs and ARD are reported in Table 5.

Table 5: BIPs values and ARD of liquid (x) composition between PR-CPA EoS adjusted data and experimental ones obtained for methane (1) with MM or EM binary system.

	T /K	ARD x_1	BIP	reference
methane-EM	272-313	3.2	0.0933	[12]
methane-MM	243-363	1.2	0.0898	[12]

The phase diagram of methane-EM binary system at 272 K is shown in Figure 3, it can be seen that the composition of EM calculated by the model is in good agreement with experimental data. Figure 4 demonstrates the phase diagram of methane-MM binary system at 304 K, we can observe that MM liquid and vapor compositions are well described by PR-CPA EoS.

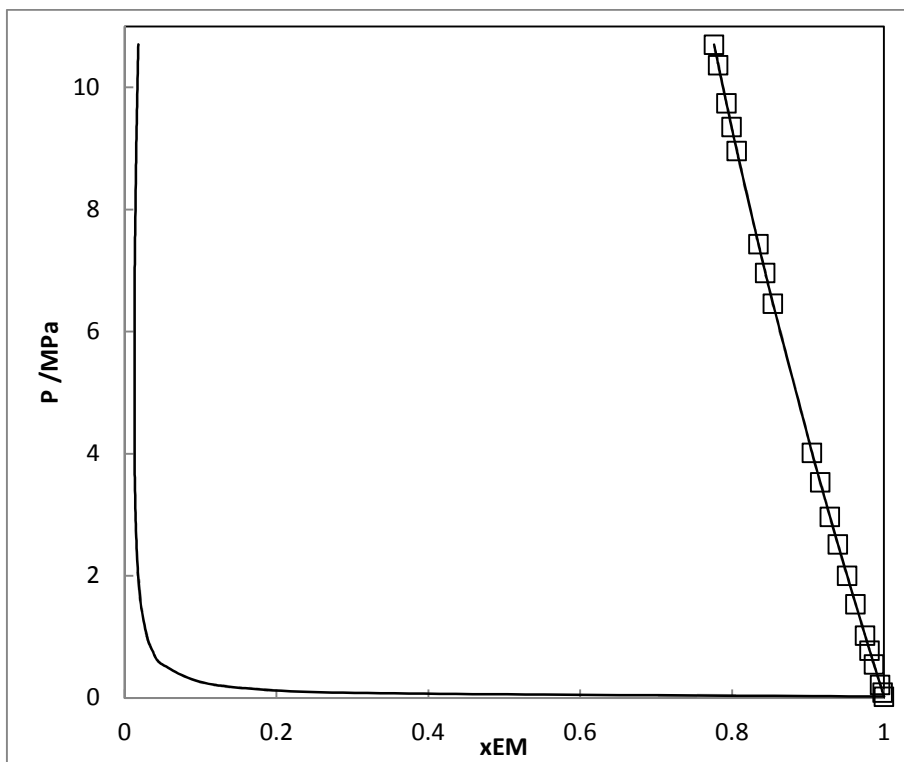


Figure 3 Phase diagram (P - x - y) of methane-EM binary system at 272K, symbol: experimental data [12], Lines: adjusted data obtained with PR-CPA EoS.

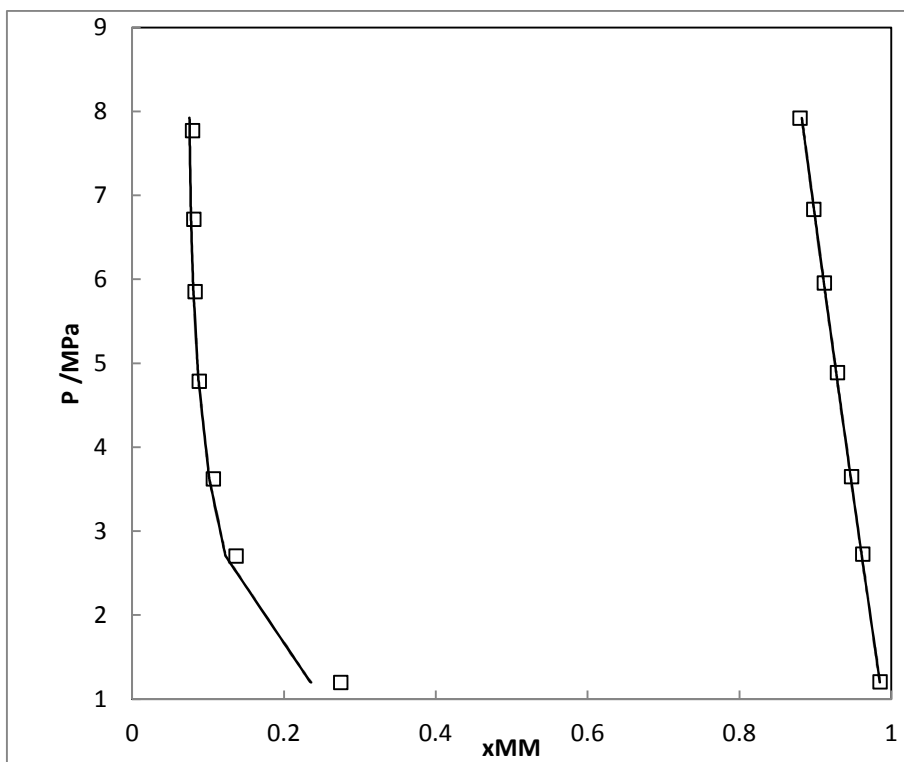


Figure 4 Phase diagram (P , x , y) of methane-MM binary system at 304K, symbol: experimental data [12], Lines: adjusted data obtained with PR-CPA EoS.

4.3.2 Mercaptan-water binary systems

In previous study, Awan et al. [13] showed that it is better to consider the solvation effect between mercaptan and water. In this study, we fixed the cross association energy between mercaptan and water by using the same values as Awan et al. [13], then we adjusted the cross association volume and BIPs from experimental data. The results are shown in Table 6. Figure 5 shows the phase diagram of water-MM binary system at 470 K, the solubility of MM in water is well described by PR-CPA EoS, however, the composition of MM in the vapor phase at high pressure seems to be overestimated. Regarding the shape of the phase diagram, we may suspect a Liquid Liquid Equilibrium at higher pressure. That may explain the overestimation of our model as parameters are adjusted from VLE data.

Table 6 : BIPs values and ARD of liquid (x) composition between PR-CPA EoS adjusted data and experimental ones obtained for water (1) with MM or EM binary system.

	T /K	ARD x_1	BIP	$\beta^{A_i B_j}$	$\epsilon^{A_i B_j}$ /bar.L.mol-1	reference
water-EM	310-588	2.3	0.02726	0.0627	83.275	[14]
water-MM	310-588	9	0.000365	0.0124	83.275	[14]

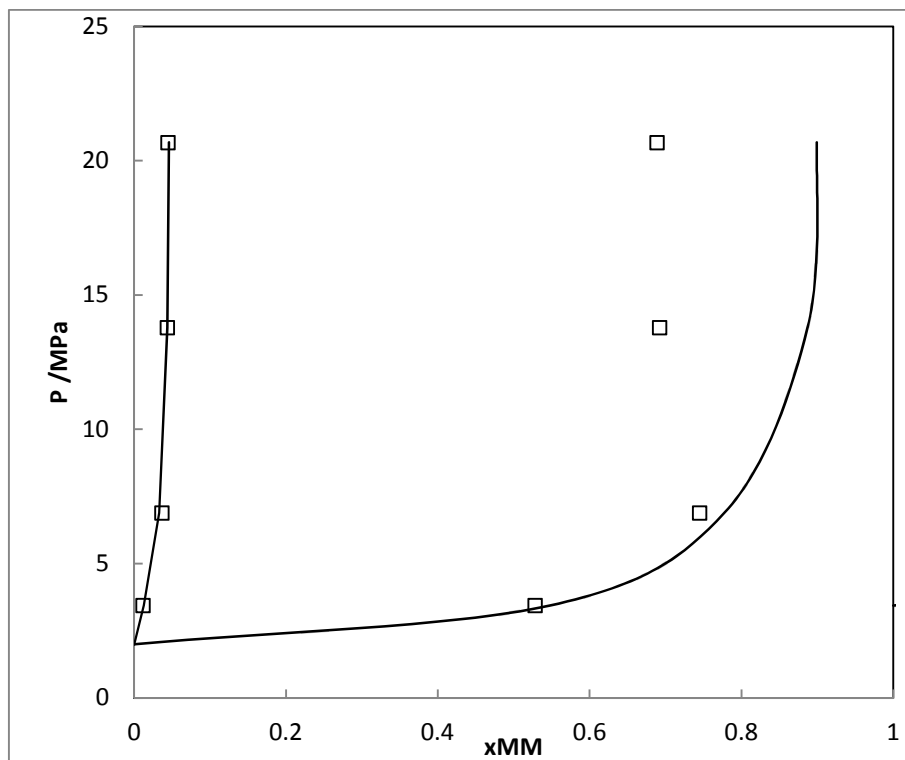


Figure 5 Phase diagram (P,x,y) of water-MM binary system at 470K, symbol: experimental data [12], Lines: adjusted data obtained with PR-CPA EoS.

4.4 Mercaptan-water-alkanolamine-methane quaternary systems

To the best of our knowledge, there are no available experimental data for mercaptan-alkanolamine binary systems, meaning that BIPs are not available also. Nevertheless, we fitted these parameters from experimental data of mercaptan –water-alkanolamine systems. It may have solvation between mercaptans and alkanolamines, however, compared with the quantity of water, the quantity of alkanolamine is minority, for example, for 25 wt% MDEA aqueous solution, the molar composition of MDEA is 0.048 against 0.952 on water. Therefore, we neglected the solvation effect between alkanolamines and mercaptans. The BIPs and ARD are shown in Table 7.

Table 7 : BIPs values and ARD of liquid (x) composition between PR-CPA EoS adjusted data and experimental ones obtained for MM or EM with water-alkanolamine systems.

	T /K	ARD x_1	Amine concentration	BIP	reference
Water-MDEA-EM	313 and 343	9	50 wt%	-0.0553	[15]
Water-MDEA-MM	314 and 343	18	50 wt%	-0.047	[15]
Water-DEA-EM	313 and 343	15	35 wt%	-0.075	[15]
Water-DEA-MM	314 and 343	14	35 wt%	-0.098	[15]

From Figure 6 and 7, we can see that EM or MM solubilities calculated by PR-CPA EoS are in good agreement with experimental data. It is interesting to notice that methane solubilities and EM or MM vapor composition are also well described, the ARD are 5% and 15% respectively.

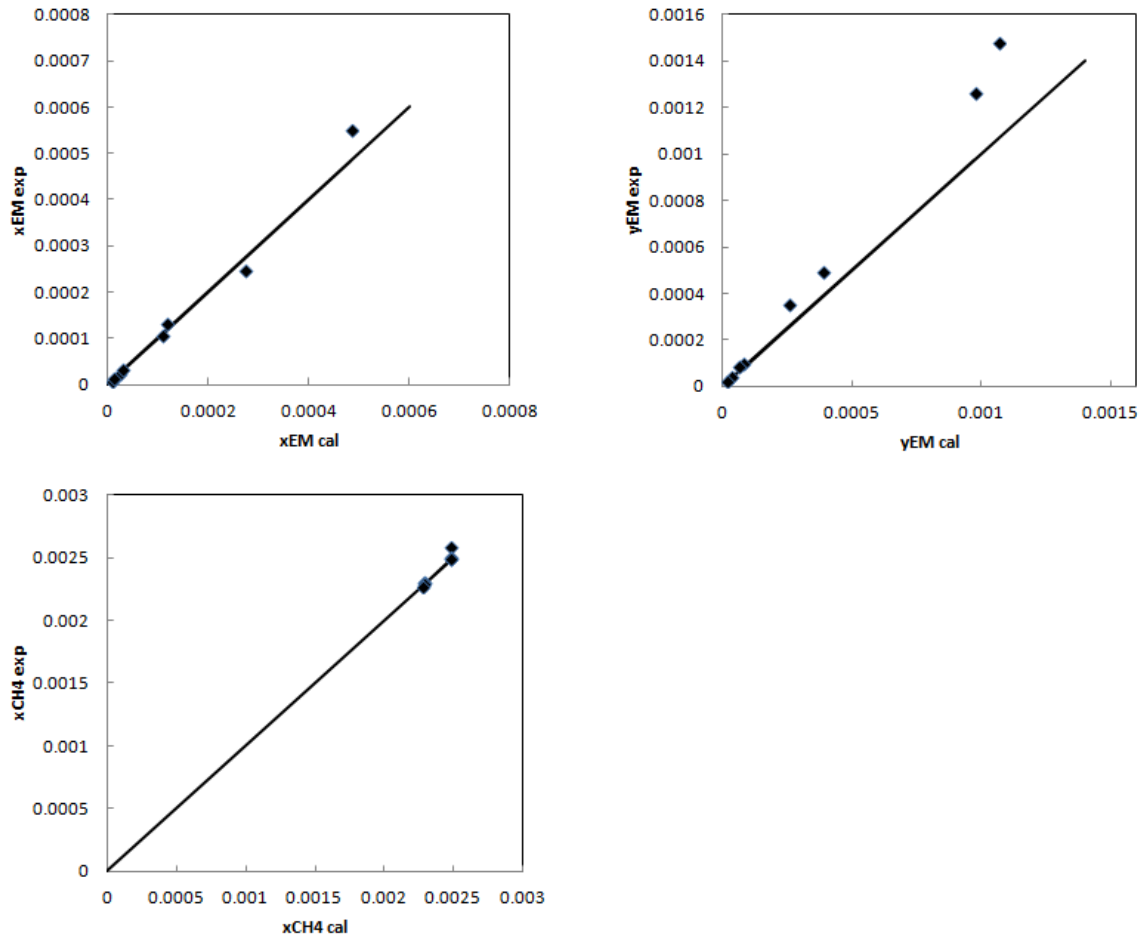


Figure 6 Comparison between experimental data [15] and ones obtained with PR-CPA EoS for EM-water –MDEA system (50 wt% MDEA): a. EM solubility, b. Methane solubility and c. EM composition in vapor phase.

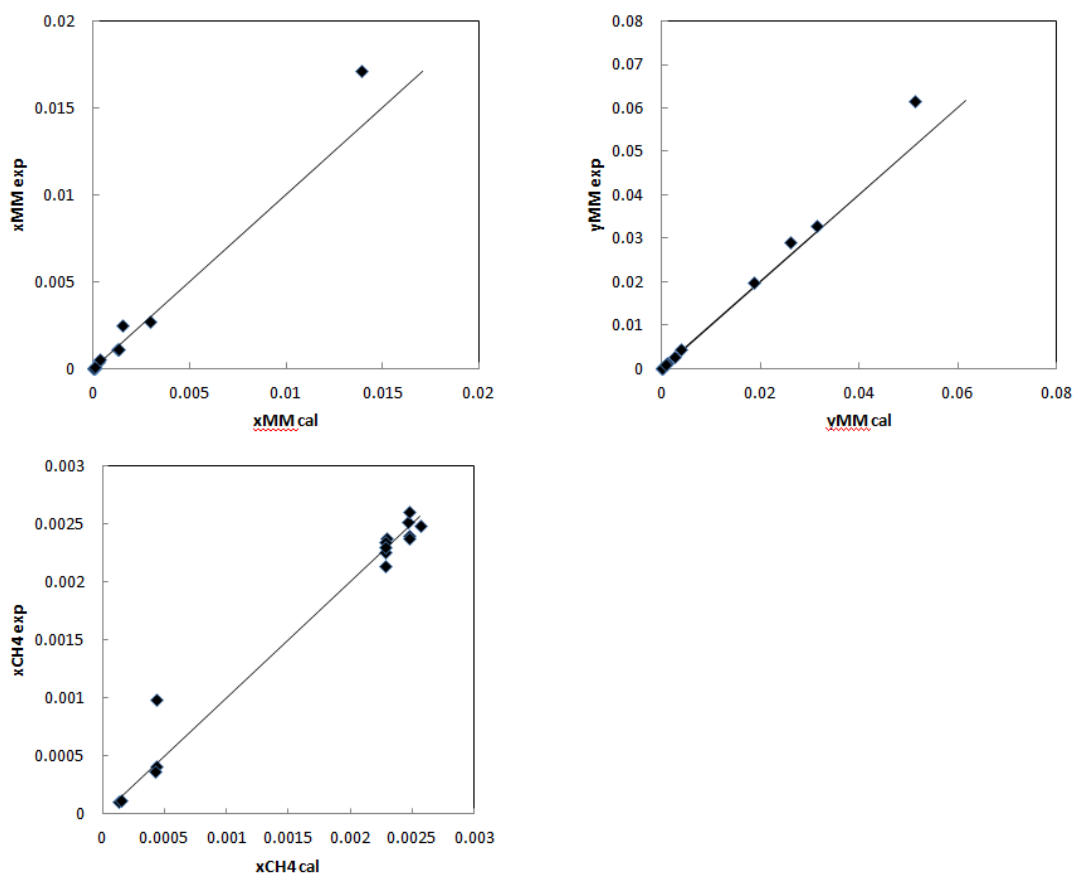


Figure 7 Comparison between experimental data [15] and ones obtained with PR-CPA EoS for MM-water –MDEA system (50 wt% MDEA): a. MM solubility, b. Methane solubility and c. MM composition in vapor phase.

4.5 Model validation: comparison with measurements results

In previous work [5], we demonstrated that the model is accurate to predict alkanes solubilities in aqueous solution with a wide range of alkanolamine concentration. In this paper, we will only present alkanes solubility in aqueous MDEA solutions. As shown in Table 8, once can notice that the model has good predictability since the ARD are less than 10%.

Table 8 ARD of alkane solubility in aqueous MDEA solutions between experimental and the predicted ones obtained with PR-CPA EoS

alkanes	ARD%
Methane	8.4
Ethane	6
Propane	5
n-butane	6.2
i-butane	8.6
Pentane	6.3

Apparent Henry's law constant of mercaptans in aqueous amine solutions is crucial for the choice of absorption solution, since it is directly linked to the solubility of mercaptan. The relation between apparent Henry's law constant (H_i), solubility (liquid composition x_i), pressure (P) and vapor phase composition (y_i) is given by equation 3:

$$Py_i = x_i H_i \quad (3)$$

The experimental results obtained for EM-MDEA-water-methane and MM-MDEA-water-methane are shown in Table 9 (a, b and c). We have also predicted apparent Henry's law constant and compared to that calculated from equation 3. For EM-MDEA-water-methane systems, as shown in Figure 8, the variation of apparent Henry's constant in function of pressure, temperature and EM initial composition has been successfully predicted. When the temperature increase, EM is less soluble in the aqueous MDEA solution, because desorption is more appreciated at higher temperature. It is interesting to notice that, for every condition, EM becomes less soluble while pressure increases. Similar results have been found for MM-MDEA-water-methane, shown in Figure 9. We have also compared bubble point of EM and MM in 25 wt% MDEA, the ARD are 22% and 18% respectively.

Table 9. Vapor Liquid equilibrium data of MM and EM in aqueous MDEA solution (25 wt% MDEA) Table 9a. Vapor Liquid equilibrium data of MM in aqueous MDEA solution (25 wt% MDEA) (global concentration of MM: 2438 ppm). δx corresponds to the standard deviation due to repeatability measurements.

T K	P MPa	n	MM		CH ₄		MDEA		H ₂ O		n	MM		CH ₄	
			x	δx	x	δx	x	δx	x	δx		y	δy	y	δy
332.68	2.0033	6	2.22E-03	2E-05	3.60E-04	1E-06	4.78E-02	8E-07	9.50E-01	2E-05	4	4.12E-02	1E-04	9.59E-01	1E-04
332.71	4.0292	6	1.87E-03	2E-05	7.45E-04	1E-05	4.78E-02	1E-06	9.50E-01	3E-05	5	1.99E-02	1E-05	9.80E-01	1E-05
332.69	7.0543	7	1.44E-03	2E-05	1.25E-03	1E-05	4.78E-02	1E-06	9.50E-01	2E-05	6	1.01E-02	3E-05	9.90E-01	3E-05
364.54	1.9405	7	1.78E-03	2E-05	3.38E-04	3E-06	4.78E-02	1E-06	9.50E-01	2E-05	10	5.92E-02	9E-05	9.41E-01	9E-05
364.58	4.0580	7	1.56E-03	2E-05	7.59E-04	9E-06	4.78E-02	1E-06	9.50E-01	2E-05	4	2.74E-02	1E-05	9.73E-01	1E-05
364.00	7.0408	7	1.35E-03	1E-05	1.31E-03	2E-05	4.78E-02	1E-06	9.50E-01	2E-05	5	1.50E-02	2E-05	9.85E-01	2E-05

Table 9b. Vapor Liquid equilibrium data of EM in aqueous MDEA solution (25 wt% MDEA) (global concentration of EM: 1112 ppm). δx corresponds to the standard deviation due to repeatability measurements.

T K	P MPa	n	EM		CH ₄		MDEA		H ₂ O		n	EM		CH ₄	
			x	δx	x	δx	x	δx	x	δx		y	δy	y	δy
333.97	2.0067	5	0.000426	8E-6	0.000456	9E-6	0.04794	4E-7	0.95118	8E-6	20	0.0079	2E-4	0.9921	2E-4
333.98	4.3155	7	0.000475	4E-6	0.001041	2E-5	0.04791	9E-7	0.95057	2E-5	6	0.0045	1E-4	0.9955	1E-4
333.97	6.8929	6	0.00042	2E-5	0.001683	3E-5	0.04788	2E-6	0.95002	3E-5	5	0.00299	9E-5	0.9970	2E-4

T	P		EM		CH₄		MDEA		H₂O			EM		CH₄	
K	MPa	n	x	δx	x	δx	x	δx	x	δx	n	y	δy	y	δy
364.68	1.1996	5	0.000371	4E-6	0.000450	2E-6	0.04794	2E-7	0.95123	4E-6	9	0.0124	1E-4	0.9876	1E-4
365.71	4.0190	6	0.000367	3E-6	0.001006	9E-6	0.04792	4E-7	0.95071	7E-6	20	0.00719	5E-5	0.99281	5E-5
365.58	7.0163	8	0.000337	1E-5	0.001697	7E-6	0.04788	4E-7	0.95008	9E-6	8	0.00429	5E-5	0.99573	8E-5

Table 9c. Vapor Liquid equilibrium data of EM in aqueous MDEA solution (25 wt% MDEA) (global concentration of EM: 2281 ppm). δx corresponds to the standard deviation due to repeatability measurements.

T	P		EM		CH₄		MDEA		H₂O			EM		CH₄	
K	MPa	n	x	δx	x	δx	x	δx	x	δx	n	y	δy	y	δy
330.30	2.1754	9	5.39E-04	3E-06	3.78E-04	2E-06	4.8E-02	2E-07	9.51E-01	4E-06	6	7.89E-03	2E-05	9.92E-01	2E-05
333.32	4.0419	7	4.96E-04	6E-06	6.92E-04	4E-06	4.8E-02	4E-07	9.51E-01	8E-06	6	4.66E-03	5E-06	9.95E-01	5E-06
333.28	6.9601	14	4.10E-04	3E-06	1.13E-03	7E-06	4.8E-02	4E-07	9.51E-01	7E-06	8	2.97E-03	3E-05	9.97E-01	3E-05
365.12	2.0088	9	5.09E-04	3E-06	3.74E-04	1E-05	4.8E-02	6E-07	9.51E-01	1E-05	5	1.36E-02	3E-05	9.86E-01	3E-05
365.12	4.0410	6	4.51E-04	5E-06	7.81E-04	2E-05	4.8E-02	9E-07	9.51E-01	2E-05	8	7.04E-03	6E-06	9.93E-01	6E-06
365.12	7.1768	7	3.50E-04	4E-06	12.7E-03	8E-06	4.8E-02	3E-07	9.51E-01	6E-06	6	4.10E-03	2E-05	9.96E-01	2E-05

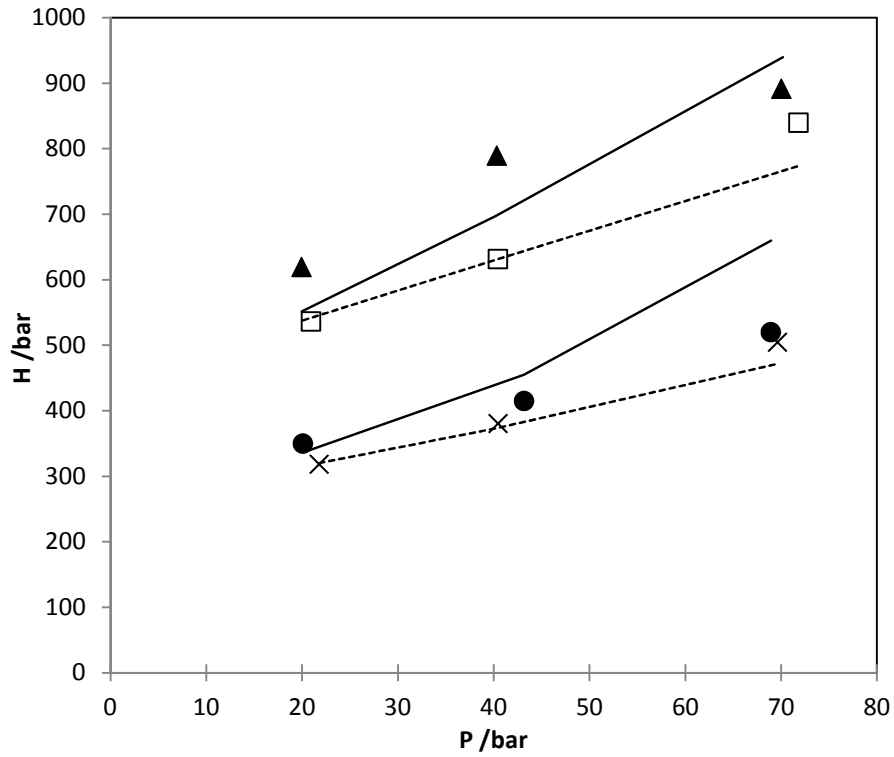


Figure 8 Henry's law constant in function of pressure for EM in aqueous MDEA solution. Symbols: experimental data [2] (×) = 333 K and 2000 ppm EM, (□) = 365 K and 2000 ppm EM, (●) = 333K and 1000 ppm EM, (▲) = 365K and 1000 ppm EM. Solid lines: model prediction for systems with 1000 ppm EM, dotted lines model prediction for systems with 2000 ppm EM.

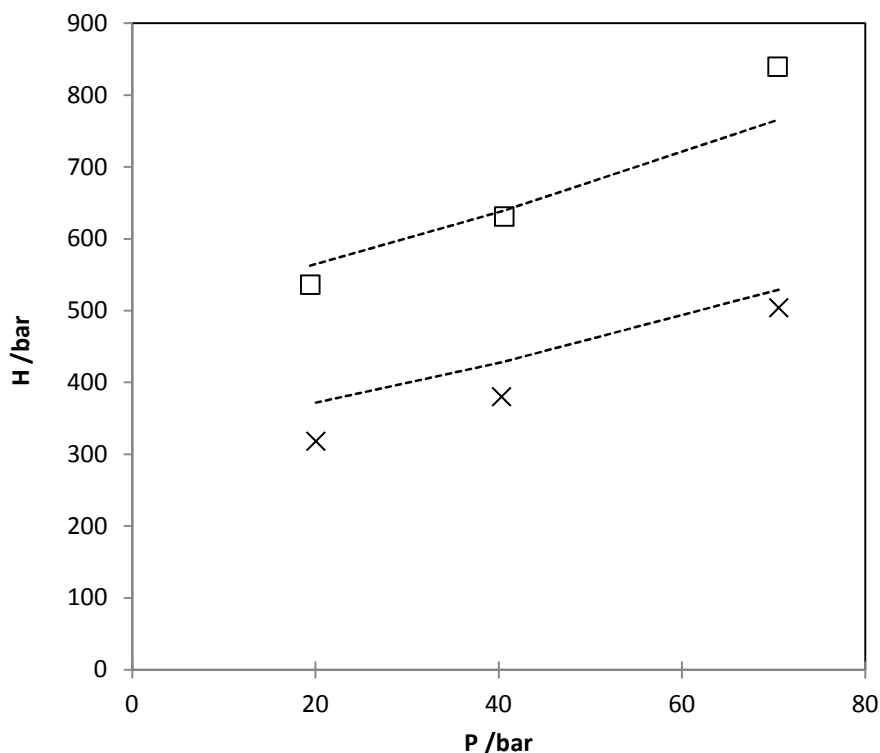


Figure 9 Henry's law constant in function of pressure for MM in aqueous MDEA solution. Symbols: experimental data [2] (×) = 333 K and 1000 ppm MM, (□) = 365 K and 1000 ppm MM. Dotted lines model prediction

5. CONCLUSION

Systems containing mercaptans, alkanolamine, water and methane have been studied experimentally and modeled with PR-CPA EoS. In this work, mercaptans pure component parameters, BIP for mercaptans-water, mercaptans-methane and mercaptans-alkanolamine have been determined. Other parameters were taken from previous work [5]. Satisfactory results have been found for pure components, binary systems, ternary systems and quaternary systems. However, more experimental data for mercaptan-alkanolamine binary systems are required in order to evaluate model precision. The model has been validated by comparing prediction with experimental data which are not used while adjusting the BIPs. Thermodynamic properties such as mercaptan solubility and Henry's law constant have been successfully predicted. 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

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