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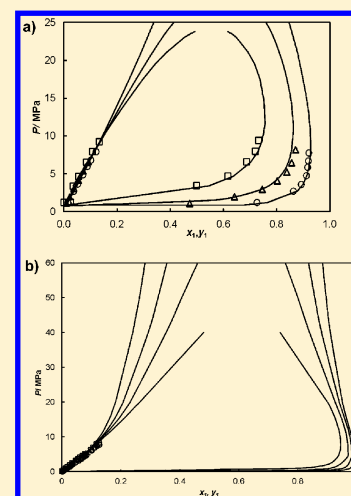
Phase Equilibria of Three Binary Mixtures: Methanethiol + Methane, Methanethiol + Nitrogen, and Methanethiol + Carbon Dioxide

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ABSTRACT: New vapor–liquid equilibrium (VLE) data for methanethiol (MM) + methane (CH₄), methanethiol (MM) + nitrogen (N₂), and methanethiol (MM) + carbon dioxide (CO₂) is reported for temperatures of (304, 334, and 364) K in the pressure range (1 to 8) MPa. A “static–analytic” method was used for performing the measurements. The objective is to provide experimental VLE data for methanethiol with other natural gas contents at its crude form, for which no data are available in the open literature. The new VLE data for the aforementioned systems have been modeled successfully with the cubic-plus-association equation of state (CPA EoS).



1. INTRODUCTION

Interest in the phase behavior of systems containing low molecular weight thiols (mercaptans) like methanethiol and ethanethiol is based upon the fact that they are present in varying concentrations in natural gas, crude oil, and petroleum products. Because thiols contain sulfur, have a distinct odor, and may freeze out in natural gas liquefaction. The knowledge of their properties and characteristics of their mixtures with hydrocarbons is important to both process design and to product specifications.¹ In the oil and gas processing industry, the necessity to model the distribution of the thiols between various streams containing light hydrocarbons, CO₂, and N₂ increases the demand of such a kind of data. Unfortunately limited or no information is available in the literature for the phase behavior of such kinds of mixtures.

Carroll and Mather² presented a literature review of available experimental data for natural gas systems containing the light hydrocarbons; methane through *n*-hexane, light thiols; and methanethiol through butanethiol and several inorganic compounds found in natural gas (nitrogen, carbon dioxide, and hydrogen sulfide). The authors conclude that there exist only a few data for methanethiol + H₂S and no data are available in literature for methanethiol + N₂ and methanethiol + CO₂ systems.

Plenty of data for the solubility of CO₂ and H₂S in water and other solvents exist, but limited information about the solubility of thiols is available in the open literature (Huttenhuis et al.).³ Our study of the literature revealed no data for systems containing thiols + N₂ and thiols + CO₂. This represents a significant

void in the available database.^{2,4,5} To serve the development of a database for such compounds and to enhance better thermodynamic modeling, new vapor–liquid equilibrium data of three binary systems containing CH₃SH + CH₄, CH₃SH + N₂, and CH₃SH + CO₂ at three different temperatures, (304, 334, and 364) K, with a pressure variation from (1 to 8) MPa are reported in this work. The capability of the cubic-plus-association equation of state (CPA EoS; Soave–Redlich–Kwong, SRK, functionality) is further tested for the representation of the phase behavior of such binary systems.

2. EXPERIMENTAL SECTION

Purities and suppliers of materials are presented in Table 1. No further purifications of the chemicals were made.

Table 1. CAS Numbers, Purities, and Suppliers of Materials

chemical name	CAS no.	mass fraction purity	supplier
methanethiol (CH ₃ SH)	74-93-1	≥ 0.98	Acros
nitrogen (N ₂)	7727-37-9	0.99	Air Liquide
carbon dioxide (CO ₂)	124-38-9	≥ 0.99	Air Liquide
methane (CH ₄)	74-82-8	≥ 0.99	Messer

The experimental work has been carried out at CEP-TEP (Centre Énergétique et Procédés), MINES ParisTech, France,

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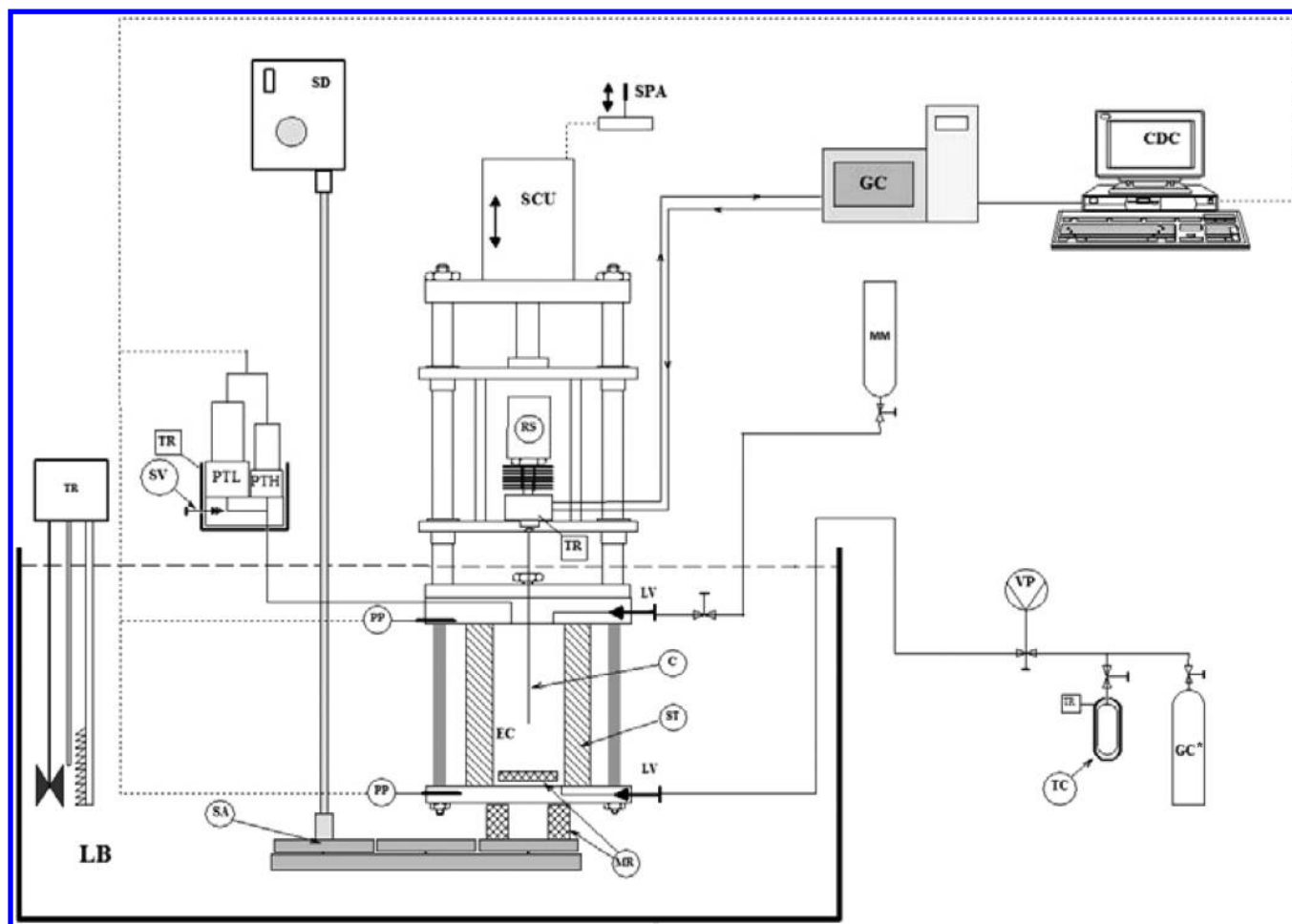


Figure 1. Static-analytic vapor-liquid-liquid equilibrium (VLE) setup with a mobile capillary sampler. Descriptions: C, capillary; CDC, central desktop computer; EC, equilibrium cell; GC, gas chromatograph; LB, liquid bath; LV, loading valve; MM, methanethiol cylinder; PP, platinum temperature sensor; PTH, high pressure transducer; PTL, low pressure transducer; RS, phase sampler ROLSI; SCU, damper control unit; SM, stirring device (motor); SPA, sampler position adjustment joystick; ST, sapphire tube; SV, separating valve; TC, temperature controller; TR, thermal regulator; VP, vacuum pump; GC*, gas cylinder.

where a “static-analytic” technique based apparatus consisting of an equilibrium cell equipped with one moveable rapid online sampler injector (ROLSI) was used. The equipment is identical to the one used by Zehioua et al.,⁶ and the procedure is identical to Coquelet et al.⁷ The ROLSI sampler is capable of making vapor-liquid samples without disturbing the equilibrium concentration and pressure, since the size of the samples (less than 1 μL) is negligible compared to the volume of the cell, that is, 20 cm^3 . The liquid and vapor samples are analyzed using a gas chromatograph (Varian model CP-3800), equipped with a thermal conductivity detector (TCD), and a flame ionization detector (FID). The schematic diagram is shown in Figure 1.

The sampling chamber of the online sampler is connected to a GC (Varian model CP-3800) through its injector and column in such a way that the carrier gas (helium) is circulated through the analytical circuit. The sample is transferred from equilibrium cell to the sampling chamber because of positive pressure difference between them. The pressure is kept constant inside the analytical circuit around 300 kPa. ROLSI sampler is heated in order to vaporize the sample. The transfer line between the ROLSI sampler and the gas chromatograph is heated to avoid condensation of the sample. Herein a thermal

conductivity detector (TCD) and a flame ionization detector (FID) are used for analyses.

The operation of the online sampler is quite easy. The electromagnet moves the plunger for a back-and-forth stroke for an adjustable period of time. The carrier gas is continuously circulated through the ROLSI. The sample transfer lines have special arrangements to ensure that the mixture of the sample and carrier gas does not absorb, get trapped, or have partial condensation inside the analytical line: the transfer line is internally coated by inert silica. The sampler has the possibility of controlling the sample size (few μL) by adjusting the aperture opening time. The sampling position inside the equilibrium cell can be adjusted by using a suitable assembly to move the capillary of the sampler up and down inside the equilibrium cell.

Two 100 Ω platinum probes (Pt100) were used for temperature measurements, as shown in Figure 1. They were periodically calibrated against a 25 Ω reference platinum resistance thermometer (TINSLEY precision instruments, France). The resulting accuracy in temperature measurements was estimated to be within ± 0.04 K. Pressures were measured by means of a Druck pressure transducer (0.1 to 10) MPa, which was maintained at 353.15 K. Pressure and temperature were

continuously recorded through a HP34970A data acquisition unit. This online data acquisition unit was connected to a personal computer through one RS-232 interface, which allowed real time readings and storage of data throughout the experimental procedure.

The pressure transducers were calibrated against a dead-weight pressure balance (Desgranges & Huot 5202S, CP (0.3 to 40) MPa, Aubervilliers, France). Accuracies in pressure measurements have been estimated to be within ± 0.003 MPa. The gas chromatograph detectors were calibrated using chromatographic syringes with maximum mole numbers uncertainties of 2 % in the TCD and 1.5 % in the FID.

In all of the experiments at first, methanethiol was loaded to the equilibrium cell in the absence of air. CH₄, CO₂, or N₂ were added to reach the desired pressure. The required temperature was obtained by putting the cell into a thermoregulated oil bath. Once the temperature and pressure were constant for a specific inlet concentration, the vapor and liquid samples from equilibrium cell were directly introduced to gas chromatograph through the isothermal transfer line. The gas chromatograph generates peaks of the individual components of CH₄ (FID), CH₃SH (FID), CO₂ (TCD), and N₂ (TCD) at specific retention times. The area under such peaks corresponds to the number of moles of the individual components, which come from the corresponding calibration.

The standard deviation on each experimental datum (σ^A) is calculated and presented along with data. The method for the calculation of standard deviation on experimental data (σ^A) is reported in our previous article.⁸

The standard deviation which comes from the experimental value can be written as

$$\sigma^A = \frac{1}{x^*} \sqrt{\frac{\sum (x - x^*)^2}{n - 1}} \quad (1)$$

where x is the measured value, x^* is the average of the measured values, and n is the number of sample analyses.

3. THERMODYNAMIC MODELING

The CPA EoS is given in terms of the pressure, as a sum of the SRK EoS and an associating contribution, in eq 2. The association term in this equation is a simpler form, but mathematically identical to the term used in SAFT. This form was proposed by Michelsen and Hendriks.⁹ The CPA EoS, proposed by Kontogeorgis et al.,^{10,11} can be expressed for mixtures in terms of pressure, P , as:

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

where V_m is the molar volume, while $\alpha(T)$ and b are the energy and covolume parameters respectively. The key element of the association term is X_{A_i} , which represents the fraction of A-sites on molecule i not bonded with other active sites, while x_i is the mole fraction of component i . X_{A_i} is related to the association

strength Δ^{A,B_i} between two sites belonging to two different molecules, for example, site A on molecule i and site B on molecule j , with the following expression:

$$X_{A_i} = \frac{1}{1 + \rho \sum_j x_j \sum_{B_j} X_{B_j} \Delta^{A,B_j}} \quad (3)$$

where the association strength Δ^{A,B_i} in CPA is expressed as:

$$\Delta^{A,B_j} = g(\rho) \left[\exp\left(\frac{\epsilon^{A,B_j}}{RT}\right) - 1 \right] b_{ij} \beta^{A,B_j} \quad (4)$$

where $b_{ij} = (b_i + b_j)/2$. The radial distribution function is defined as

$$g(\rho) = \frac{1}{1 - 1.9n'} \quad n' = \frac{1}{4} b \rho \quad (5)$$

where n' is the reduced fluid density. Finally, the energy parameter of the EoS is given by a Soave-type temperature dependency, while b is temperature-independent:

$$\alpha(T) = a_0(1 + c_1(1 - \sqrt{T_r}))^2 \quad (6)$$

where

$$T_r = T/T_c$$

where T_c is the experimental critical temperature.

In the expression for the association strength Δ^{A,B_i} (eq 5) the parameters ϵ^{A,B_j} and β^{A,B_j} are called the association energy and the association volume, respectively. These two parameters and the three parameters, that is, $(\Gamma = a_0/(bR), b, c_1)$, are the five parameters of the CPA EoS. Usually, the three parameters of the CPA EoS (SRK-functionality) term $(\Gamma = a_0/(bR), b, c_1)$ are obtained by fitting vapor pressure and liquid density data and using the average absolute deviation (AAD) as an objective function.

$$\% \text{AAD} = \frac{1}{n} \sum_i \left| \frac{X_i^{\text{cal}} - X_i^{\text{exp}}}{X_i^{\text{exp}}} \right| \cdot 100 \quad (7)$$

where X is the property and n is the number of experimental data points. These parameters can also be calculated in the conventional manner from critical data and acentric factor values.

When the CPA EoS is used for mixtures, the conventional mixing rules are employed in the physical term (SRK) for the energy and covolume parameters. The geometric mean rule is used for the energy parameter a_{ij} . The interaction parameter k_{ij} is, in the applications reported so far, the only adjustable binary parameter of CPA, unless cross association or solvation is present.

$$\alpha(T) = \sum_i \sum_j x_i x_j a_{ij} \quad \text{where} \quad \alpha_{ij} = \sqrt{\alpha_i \alpha_j} (1 - k_{ij}) \quad (8)$$

$$b = \sum_i x_i b_i \quad (9)$$

In this work, methanethiol is considered as a nonself-associating fluid. Previously¹² the phase equilibrium in terms of Henry's law constant of MM (methanethiol), EM (ethanethiol), n-PM (propane-1-thiol), n-BM (butane-1-thiol), and DMS (dimethyl sulfoxide) with water was modeled with the CPA EoS. In that work the calculations for methanethiol and ethanethiol were made using two approaches: considering thiols as inert compounds and the cross association interactions between thiols and water. The temperature dependency of the binary

Table 2. Experimental VLE Data for the CH₄ (1) + CH₃SH (2) Binary Mixture

T/K	P/MPa	y _{CH₄}	10 ³ ·σ ₁	y _{CH₃SH}	10 ³ ·σ ₂	P/MPa	x _{CH₄}	10 ³ ·σ _{x1}	x _{CH₃SH}	10 ³ ·σ _{x2}
304.74	1.201	0.7250	3.6	0.2750	2.0	1.209	0.0147	0.1	0.9853	0.1
304.74	2.706	0.8632	2.1	0.1368	1.2	2.731	0.0376	0.4	0.9624	0.4
304.75	3.625	0.8929	1.7	0.1071	1.0	3.654	0.0523	0.5	0.9477	0.5
304.75	4.789	0.9116	1.5	0.0884	0.8	4.893	0.0710	0.7	0.9290	0.7
304.75	5.858	0.9169	1.4	0.0831	0.8	5.960	0.0882	0.8	0.9118	0.8
304.75	6.720	0.9186	1.2	0.0814	0.8	6.838	0.1020	0.8	0.8980	0.8
304.75	7.776	0.9204	1.1	0.0796	0.8	7.924	0.1202	0.9	0.8798	0.8
333.70	1.106	0.4720	2.1	0.5280	2.1	1.116	0.0091	0.2	0.9898	0.2
333.70	1.990	0.6409	2.8	0.3591	1.5	2.013	0.0214	0.5	0.9786	0.5
333.70	3.014	0.7447	2.2	0.2553	1.2	3.048	0.0371	0.6	0.9629	0.6
333.70	4.086	0.8018	1.9	0.1982	1.0	4.136	0.0550	0.9	0.9450	0.9
333.70	5.278	0.8371	1.8	0.1629	1.0	5.347	0.0738	1.0	0.9251	1.0
333.70	6.473	0.8545	1.6	0.1455	1.1	6.588	0.0930	1.1	0.9070	1.1
333.70	8.180	0.8705	1.5	0.1295	1.1	8.295	0.1198	1.2	0.8802	1.1
334.28	8.853	0.8716	1.6	0.1284	1.1	8.987	0.1311	1.2	0.8689	1.1
363.82	9.267	0.7319	5.4	0.2681	3.0	9.402	0.1331	0.2	0.8645	0.2
363.82	7.906	0.7196	3.2	0.2804	1.8	7.975	0.1080	0.5	0.8900	0.5
363.82	6.535	0.6867	2.6	0.3133	1.4	6.589	0.0852	0.7	0.9148	0.7
363.82	4.669	0.6172	2.2	0.3828	1.2	4.717	0.0552	1.0	0.9445	1.0
363.82	3.396	0.4995	2.1	0.5005	1.1	3.416	0.0338	1.2	0.9652	1.2
363.82	1.213	0.0250	1.8	0.9750	1.2	1.213	0.0007	1.3	0.9994	1.2

Table 3. Experimental VLE Data for the N₂ (1) + CH₃SH (2) Binary Mixture

T/K	P/MPa	y _{N₂}	10 ³ ·σ ₁	y _{CH₃SH}	10 ³ ·σ ₂	P/MPa	x _{N₂}	10 ³ ·σ _{x1}	x _{CH₃SH}	10 ³ ·σ _{x2}
304.07	1.091	0.7139	3.7	0.2861	6.1	1.111	0.0025	0.1	0.9975	0.1
304.07	2.267	0.8535	2.3	0.1465	3.8	2.317	0.0063	0.2	0.9937	0.2
304.07	3.661	0.9015	1.6	0.0985	2.7	3.734	0.0104	0.3	0.9896	0.3
304.07	6.394	0.9343	1.7	0.0657	2.4	6.490	0.0186	0.3	0.9814	0.3
333.78	1.285	0.4313	4.4	0.5687	7.4	1.307	0.0031	0.1	0.9969	0.1
333.78	2.434	0.6611	2.7	0.3389	4.5	2.468	0.0071	0.2	0.9929	0.2
333.78	3.957	0.7693	1.9	0.2307	3.2	4.035	0.0127	0.4	0.9873	0.4
333.78	5.511	0.8244	2.1	0.1756	2.9	5.597	0.0188	0.4	0.9812	0.4
333.78	6.637	0.8500	2.2	0.15	3.0	6.736	0.0231	0.4	0.9769	0.4
363.64	2.622	0.3981	4.4	0.6019	7.4	2.665	0.0075	0.1	0.9925	0.1
363.64	4.219	0.5976	2.7	0.4024	4.5	4.197	0.0144	0.2	0.9856	0.2
363.64	4.392	0.6012	1.9	0.3988	3.2	4.328	0.0148	0.4	0.9852	0.4
363.64	6.518	0.7027	2.1	0.2973	2.9	6.667	0.0273	0.4	0.9727	0.4
363.64	8.138	0.7415	2.2	0.2585	3.0	8.308	0.0373	0.4	0.9627	0.4

interaction parameter (k_{ij}) and the solvation effect involved in the association volume (β_{cross}) was accentuated in MM (methanethiol) + water, EM (ethanethiol) + water, and DMS (dimethyl sulfoxide) + water systems. As no hydrogen bonding is present in methanethiol + CH₄, methanethiol + N₂ or methanethiol + CO₂, no association and no solvation effect have been considered in this work.

4. RESULTS AND DISCUSSION

The obtained new vapor–liquid equilibrium (VLE) data for the CH₃SH + CH₄, CH₃SH + N₂, and CH₃SH + CO₂ binary systems at three different temperatures, (304, 334, and 364) K, and at pressures varying from (1 to 8) MPa are shown in Tables 2, 3, and 4, respectively. The accuracy of the measuring procedure has been previously discussed in literature.^{4,8} The objective was to provide experimental VLE data of the methanethiol with CH₄, N₂, and CO₂ because the solubility data of methanethiol are in general quite scarce over a large temperature and pressure range. Privat et al.⁵ have been

working for the extension of PPR-78 model to the mercaptan containing systems. They could not extend the PPR-78 model for thiols due to the unavailability of the experimental data for (mercaptan + CO₂) and (mercaptan + N₂). The authors also report the modeling of limited solubility data (PTx) of CH₃SH + CH₄ available in the open literature.¹³ To the best of our knowledge, prior to this study there were no experimental data for the solubility of methanethiol with N₂ and CO₂ at high pressures and different temperatures.

The CPA parameters, that is, b , $\Gamma = a_0/(Rb)$, and c_1 , have been fitted to experimental vapor pressure and liquid density data as shown in Table 5. The VLE data of binary systems, which consist of methanethiol (MM) + methane (CH₄), methanethiol (MM) + nitrogen (N₂), and methanethiol (MM) + carbon dioxide (CO₂) at different temperatures and pressures, were successfully modeled with CPA using small binary interaction parameters (k_{ij}) as shown in Figures 2a, 3, and 4. The (PTx) data of methanethiol (MM) + methane (CH₄) between (258 and 293) K¹³ have also been successfully modeled with CPA and plotted in Figure 2b.

Table 4. Experimental VLE Data for the CO₂ (1) + CH₃SH (2) Binary Mixture

T/K	P/MPa	y _{CO₂}	10 ³ ·σ ₁	y _{CH₃SH}	10 ³ ·σ ₂	P/MPa	x _{CO₂}	10 ³ ·σ _{x1}	x _{CH₃SH}	10 ³ ·σ _{x2}
303.80	1.011	0.6322	4.2	0.3678	9.3	1.015	0.0712	2.6	0.9286	2.1
303.80	1.918	0.8030	4.2	0.1970	9.4	1.929	0.1722	2.7	0.8279	2.4
303.80	3.290	0.8610	4.3	0.1390	9.5	3.300	0.3725	2.7	0.6284	2.6
333.40	1.472	0.3887	3.8	0.6113	8.4	1.451	0.0410	2.8	0.9590	2.7
333.40	2.512	0.6076	3.9	0.3924	8.5	2.523	0.1259	2.5	0.8739	2.1
333.40	4.448	0.6134	4.1	0.3866	8.7	4.508	0.2921	2.6	0.7078	2.0
363.48	7.525	0.6655	4.0	0.3345	8.9	7.513	0.3661	9.3	0.6347	9.3
363.48	4.915	0.5874	4.2	0.4126	9.3	4.959	0.2183	9.7	0.8065	9.7
363.48	2.444	0.3667	4.4	0.6333	9.8	2.472	0.0629	10.2	0.9369	10.2

Table 5. CPA Pure Component Parameters Used and Estimated in This Work^a

component	T _c ¹⁴	b	Γ = a ₀ /bR	c ₁	% AAD in P ^{Sat}	% AAD in ρ ^{liq}
	K	L·mol ⁻¹	K			
methanethiol (MM)	469.95	0.0437	2266.27	0.8007	0.69	0.47
methane (CH ₄) ¹⁵	190.6	0.0291	959.1	0.4471	0.35	1.97
carbon dioxide (CO ₂) ¹⁵	304.21	0.0272	1551.2	0.7602	0.20	0.80
nitrogen (N ₂)	615.02	0.02605	633.44	0.4985	0.50	2.1

^aAverage absolute deviation (AAD) is defined as % AAD = 1/n ∑ |X_i^{cal} - X_i^{exp}/X_i^{exp}| · 100 where X stands for P^{Sat} or ρ^{liq} and n is the number of experimental data points.

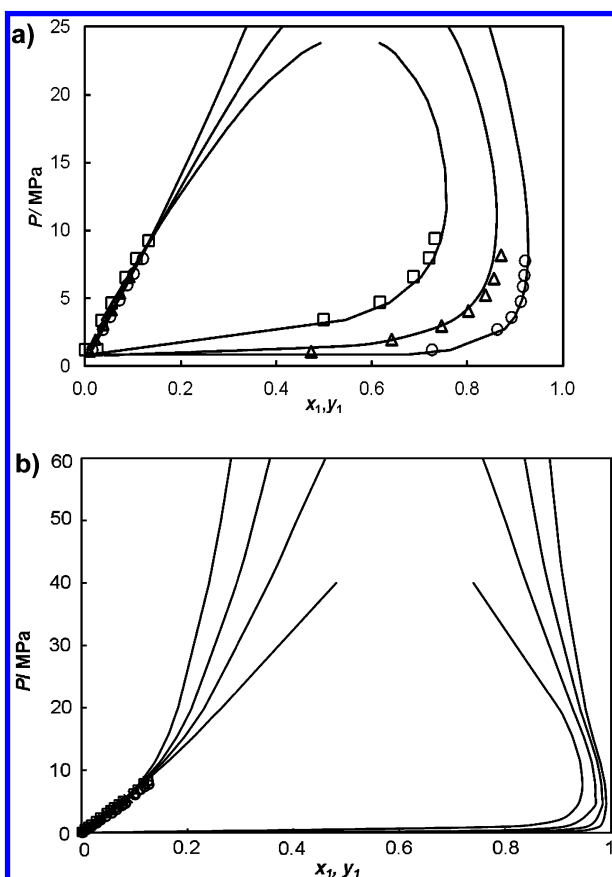


Figure 2. Pxy diagram of the methane (1) (CH₄) + methanethiol (2) (MM) binary system at (a) ○, 304 K; △, 334 K, and □, 364 K; (b) ○, 293 K; △, 273 K; ◇, 243 K, and □, 258 K; solid lines: CPA EoS with $k_{ij} = 0.079$.

The proposed binary interaction parameters for methanethiol (MM) + methane (CH₄), methanethiol (MM) + nitrogen (N₂), and methanethiol (MM) + carbon dioxide (CO₂) systems are

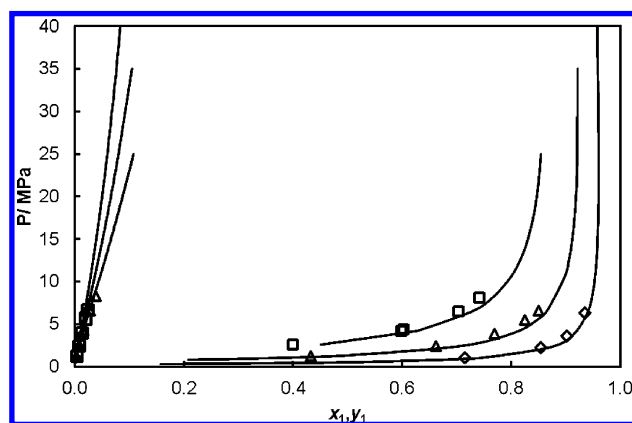


Figure 3. Pxy diagram of the nitrogen (1) (N₂) + methanethiol (2) (MM) binary system at ◇, 304 K; △, 334 K, and □, 364 K; solid lines: CPA EoS with $k_{ij} = 0.159$.

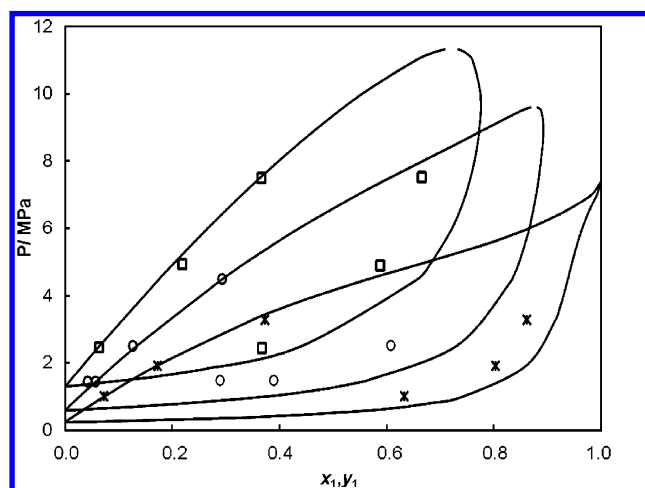


Figure 4. Pxy diagram of the carbon dioxide (1) (CO₂) + methanethiol (2) (MM) binary system at *, 304 K; ○, 334 K, and □, 364 K; solid lines: CPA EoS with $k_{ij} = 0.091$.

Table 6. Binary Interaction Parameters Estimated in This Work

binary systems	k_{ij}	MAE ^a of $x/\%$	MAE of $y/\%$	T/K (range)
methane + methanethiol	0.079	2.06	1.89	253–323
nitrogen + methanethiol	0.159	4.01	3.53	304–373
carbon dioxide + methanethiol	0.091	4.24	9.32	304–383

^aMAE = mean average error; $MAE = 1/n \sum_{i=1}^n |X_i^{CPA} - X_i^{exp}|$ where X stands for mole fraction, x or y , and n is the number of experimental data points.

reported in Table 6. As stated previously, the thiols are not considered to self-associate.¹² Even with this assumption the CPA results for the binary mixtures of CH₄ + CH₃SH and N₂ + CH₃SH without association consideration are considered to be very satisfactory.

5. CONCLUSIONS

New VLE data have been reported for CH₄ + CH₃SH, N₂ + CH₃SH, and CO₂ + CH₃SH with a pressure variation from (1 to 8) MPa. A static–analytic method was used for performing all of the measurements. The CPA EoS (SRK functionality) has been successfully applied for the representation of binary systems containing methanethiol. These modeling results for the binary mixtures of CH₄ + CH₃SH, N₂ + CH₃SH, and CO₂ + CH₃SH without association consideration are satisfactory. For the system CO₂ + CH₃SH, the deviations between the experimental data and CPA modeling are significant, which may be attributed to the temperature dependency or specific interaction as CO₂ is a particular molecule.

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Notes

The authors declare no competing financial interest.

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NOTE ADDED AFTER ASAP PUBLICATION

This paper was published on February 3, 2012, with errors in Figure 1, the reference section, and throughout the text. These were corrected in the version published on February 17, 2012.