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# Phase Equilibrium Measurements and Modeling of 1-propanethiol + 1-butanethiol + CH<sub>4</sub> in Methane + Water Ternary Systems at 303, 336, and 365 K and Pressure Up to 9 MPa

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## Abstract

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New vapor-liquid equilibrium (VLE) data for 1-propanethiol + 1-butanethiol + CH<sub>4</sub> ternary system is reported. Measurements were performed at three different temperatures (303, 336 and 368 K), while the pressure was ranged from 1 to 9 MPa. The total system pressure was maintained by CH<sub>4</sub>. The inlet mole fraction of 1-propanethiol ( $x = 5.43 \times 10^{-1}$ ) and 1n-butanethiol ( $x = 4.56 \times 10^{-1}$ ) in the liquid phase were same in all experiments. A static analytic method was used for performing phase equilibrium measurements. The new VLE data have been modeled successfully with Cubic-Plus-Association (CPA) EoS.

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*keywords:* static analytic method, phase equilibria, CPA EoS, thiols (mercaptan) removal

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## 1. Introduction

The knowledge of thermodynamic properties of mixtures of sulfur compounds with hydrocarbons is important in the petroleum as well as in the chemical industry. An understanding of the thermo physical properties and equilibrium data of such mixtures facilitates the rationale design of processes for the removal sulfur compounds from petroleum streams and also for the purification of sulfur compounds in order to be used as chemical intermediates<sup>1</sup>. 1-propanethiol (n-propylmercaptan) and 1-butanethiol (n-butylmercaptan) are common organic sulfur components present in natural gas, synthesis gas and various refinery process streams. Their typical presence in the host gas stream can range from several parts per million to 5 percent by volume<sup>2</sup>. The environmental protection forces the petrochemical industry to decrease the sulfur content in the various petroleum fluids. Furthermore, any thiols/mercaptans (RSH) not absorbed from the sour gas through the amine purification units, complicate the process scheme for downstream liquid treatment units<sup>3</sup>. Consequently, the equilibrium data and thermo physical properties of thiols with methane, ethane, propane and other hydrocarbons in the presence and absence of water is important to both process optimization and product specifications.

This work is the continuation of our studies<sup>4,5,6</sup> on the VLE and VLLE measurements of the systems containing CH<sub>4</sub>, water and thiols. Herein we measure new VLE data for ternary mixture 1-propanethiol (C<sub>3</sub>H<sub>7</sub>SH) + 1-butanethiol (C<sub>4</sub>H<sub>9</sub>SH) + methane (CH<sub>4</sub>) at three temperatures (303, 336, and 368 K) and pressures up to 9 MPa. The Cubic-Plus-Association (CPA) equation of state has been used to predict the new VLE ternary data with no adjustable parameters.

## 2. Experimental section

The experimental work has been carried out at Mines ParisTech, France, where a “static-analytic” technique based apparatus consisting of an equilibrium cell equipped with one moveable Rapid Online Sampler Injector (ROLSI<sup>TM</sup>) was used. The detail of the experimental setup has been discussed in our previous manuscript<sup>7</sup>. The equipment is the same used by Zehioua *et al.*<sup>8</sup> and the procedure is identical to Coquelet *et al.*<sup>9</sup>. 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). CAS numbers, purities, and suppliers of materials are provided in table 1. no further purification of chemicals has made.

In the absence of air, 1-propanethiol (15 ml) was added into the equilibrium cell (32 cm<sup>3</sup>) followed by equal volumetric quantity of 1-butanethiol (10 ml). Then CH<sub>4</sub> was added from the top of equilibrium to reach the desired pressure. The desired temperature was obtained by placing the cell into a thermo-regulated oil bath. The vapor and the organic (liquid) samples from equilibrium cell were directly introduced to the gas chromatograph once equilibrium was established. The samples are introduced through an isothermally heated transfer line. Two 100 Ω platinum probes (Pt100) were used for temperature measurements which are inserted inside thermo-wells drilled into the body of the equilibrium cell at two different levels and are connected to an HP data acquisition unit. They were periodically calibrated against a 25 Ω reference platinum resistance thermometer (TINSLEY precision instruments, France). The expanded standard uncertainty (0.95 level of confidence, k=2) in temperature measurements was estimated to be U(T)= 0.04 K. Pressure was measured by means of a Druck<sup>TM</sup> pressure transducer (0.1 to 10 MPa), which was maintained at 353.15 K. The pressure transducer was calibrated against a dead-weight pressure balance (Desgranges & Huot 5202S, CP 0.3-40 MPa, Aubervilliers, France). The expanded standard uncertainty (0.95 level of confidence, k=2) in pressure measurements was estimated to be U(P)= 0.003 MPa. The gas chromatograph detectors were calibrated using chromatographic syringes with the relative standard uncertainties in mole numbers of 2 % in the TCD and 1.5 % in the FID, thus the expanded uncertainty (0.95 level of confidence, k= 2) in mol fraction is  $U_{max.}(x \text{ or } y, k=2)= 0.006$

The peaks of the individual components generated by gas chromatograph in liquid phase [CH<sub>4</sub> (FID), C<sub>3</sub>H<sub>7</sub>SH (TCD), C<sub>4</sub>H<sub>9</sub>SH (TCD)] and in gas phase [CH<sub>4</sub> (TCD), C<sub>3</sub>H<sub>7</sub>SH (FID), C<sub>4</sub>H<sub>9</sub>SH (FID)] were recorded using one RS-232 interface. These peaks are generated at specific retention time. The areas under the peaks correspond to the number of moles of the individual components, which come from the corresponding calibration. All the experimental data point has been analyzed around 10 times, till we have consistent values. The standard deviation ( $\sigma^A$ ) on each experimental data point was calculated<sup>7</sup> and presented in Table 2.

### 3. Modeling section

The experimental data were modeled using the CPA EoS, which in terms of the pressure is given as<sup>10,11</sup>:

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

More details about the CPA EoS can be found in the literature<sup>10,11</sup>. The CPA EoS for thiols (mercaptan containing systems) has been described in our previous studies<sup>5,6,7</sup>. All fluids of this work (1-propanethiol (C<sub>3</sub>H<sub>7</sub>SH), 1-butanethiol (C<sub>4</sub>H<sub>9</sub>SH) and methane were modeled as non-self-associating fluids. The CPA EoS

pure component parameters ( $b/\text{L}\cdot\text{mol}^{-1}$ ,  $\Gamma = a_0/(R b)/\text{K}$  and  $c_1$ ) for  $\text{C}_3\text{H}_7\text{SH}$ <sup>5</sup>,  $\text{C}_4\text{H}_9\text{SH}$ <sup>7</sup>,  $\text{CH}_4$ <sup>12</sup> and the binary Interaction parameters for  $\text{C}_3\text{H}_7\text{SH}-\text{CH}_4$  ( $k_{ij}=0.38$ )<sup>7</sup> and  $\text{C}_4\text{H}_9\text{SH}-\text{CH}_4$  ( $k_{ij}=0.38$ )<sup>7</sup> were adopted from literature. The binary interaction parameter between  $\text{C}_3\text{H}_7\text{SH}-\text{C}_4\text{H}_9\text{SH}$  is fixed equal to zero ( $k_{ij}=0.00$ ), based on an assumption that such molecules have very similar structure. Having all pure and binary parameters from the corresponding binary systems the CPA EoS is used to predict the VLE of 1-propanethiol ( $\text{C}_3\text{H}_7\text{SH}$ ) + 1-propanethiol ( $\text{C}_3\text{H}_7\text{SH}$ ) + methane ( $\text{CH}_4$ ). No adjustable parameter is optimized to the ternary experimental data.

#### 4. Results and discussion

Vapor-liquid equilibrium (VLE) measurements for the 1-propanethiol + 1-butanethiol +  $\text{CH}_4$  ternary system were performed at three different temperatures (303, 335 and 368 K) and pressures up to 9 MPa. To the best of author knowledge no other experimental phase equilibrium data for such ternary system exists in the open literature and, consequently, a comparison of the new experimental data, presented in Table 2, is not possible. As shown in figure 1, the solubility of methane ( $\text{CH}_4$ ) in the 1-propanethiol - 1-butanethiol rich liquid phase increases with the increase of total system pressure and temperature. The gas phase content of 1-propanethiol ( $\text{C}_3\text{H}_7\text{SH}$ ) and 1-butanethiol ( $\text{C}_4\text{H}_9\text{SH}$ ) decreases slightly with increase of pressure and increases significantly with the increase of temperature as shown in figure 2. It can be also observed that the gas phase content of 1-propanethiol ( $\text{C}_3\text{H}_7\text{SH}$ ) is always superior to 1-butanethiol ( $\text{C}_4\text{H}_9\text{SH}$ ) at the same temperature and pressure, as it is expected.

The CPA EoS predictions for the vapor-liquid equilibrium of 1-propanethiol ( $\text{C}_3\text{H}_7\text{SH}$ ) + 1-butanethiol ( $\text{C}_4\text{H}_9\text{SH}$ ) + methane ( $\text{CH}_4$ ) ternary system at 303, 335 and 368 K and up to 9 MPa are shown in figures 1, 2 and 3 respectively. It is observed that deviation between the experimental data and the CPA predictions is sometimes higher than 20 %. The CPA results are pure predictions as no parameters were adjusted to the experimental data. From this point of view, the CPA rather satisfactorily predicts the vapor-liquid regions for 1-propanethiol + 1-butanethiol +  $\text{CH}_4$  ternary system.

#### 5. Conclusion

New vapor-liquid equilibrium (VLE) data for the 1-propanethiol + 1-butanethiol +  $\text{CH}_4$  has been obtained at three temperatures (303, 335, and 368 K) and pressures up to 9 MPa. A “static-analytic” method was successfully used for performing all the measurements. The CPA EoS has been applied for the representation of ternary systems containing 1-propanethiol and 1-butanethiol. The modeling results are considered satisfactory as they are just predictions without the adjustment of any parameter to the ternary experimental data.

## Acknowledgment

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**Table 1. CAS numbers, purities, and suppliers of materials.**

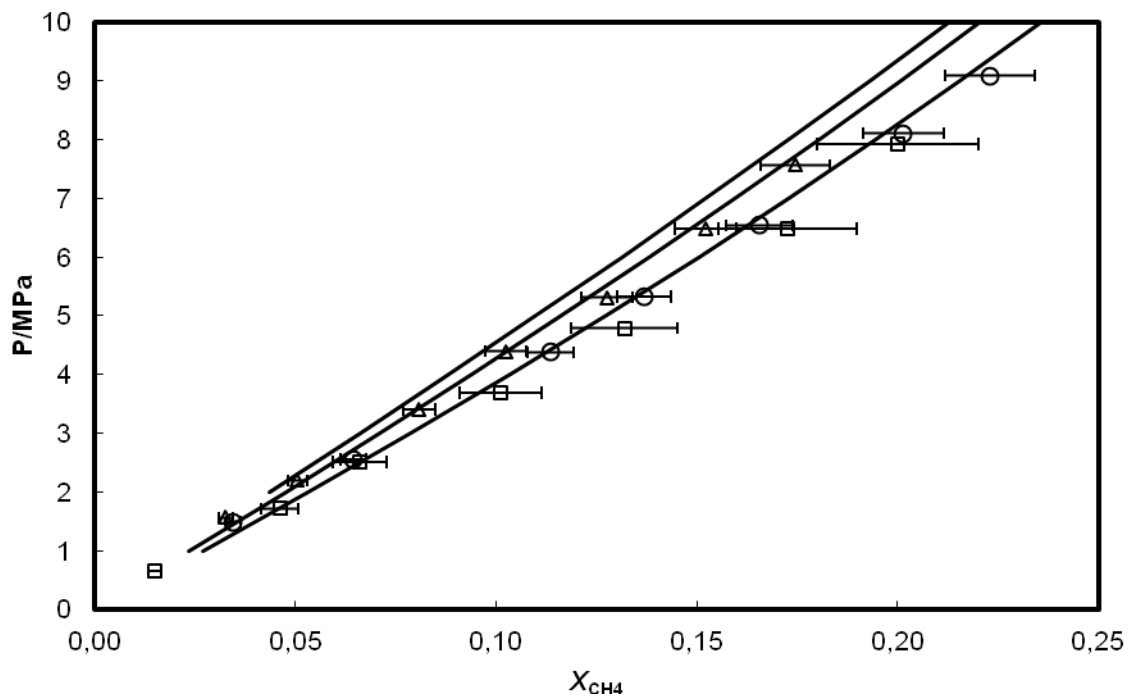
<b>Chemical Name</b>	<b>Source</b>	<b>Mole fraction purity*</b>	<b>CAS No.</b>
1-Propanethiol (C <sub>3</sub> H <sub>7</sub> SH)	ACROS	≥ 0.99	107-03-9
1-Butanethiol (C <sub>4</sub> H <sub>9</sub> SH)	ACROS	≥ 0.99	109-79-5
Methane (CH <sub>4</sub> )	Messer	0.998	74-82-8

\* Information provided by suppliers.

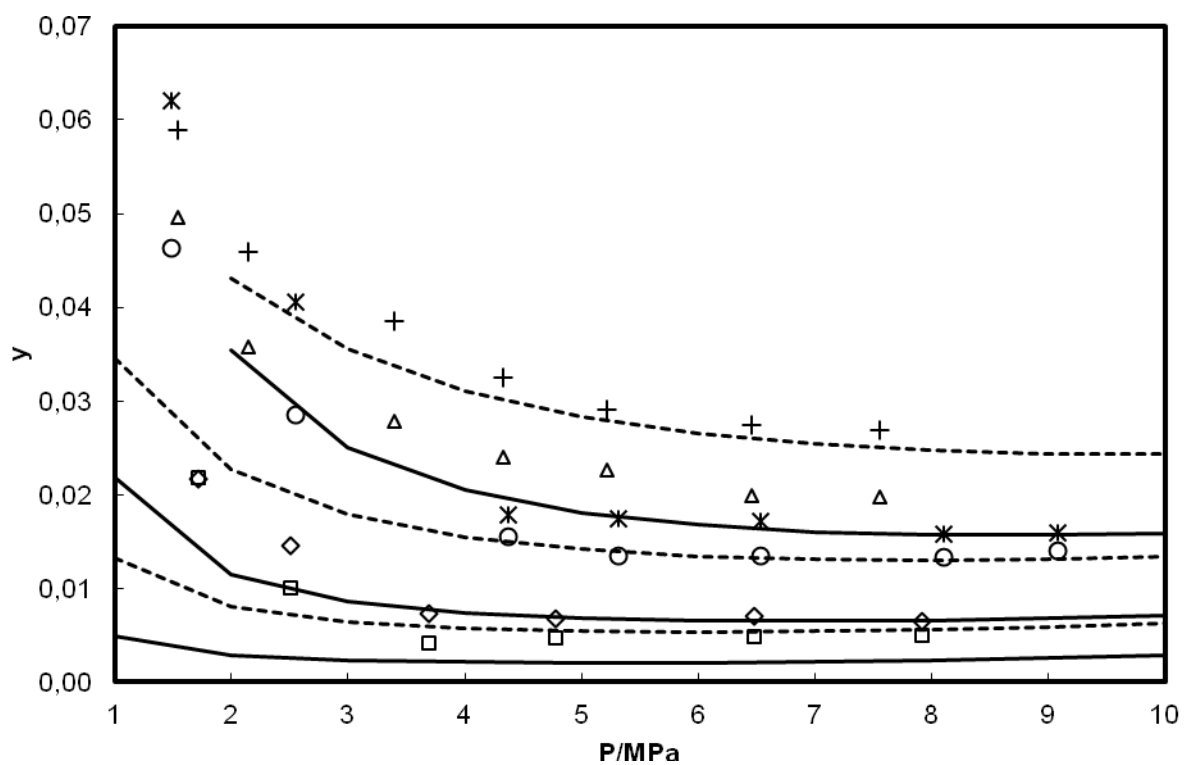
**Table 2. Experimental Vapor-liquid Equilibrium Data for the 1-propanethiol (C<sub>3</sub>H<sub>7</sub>SH) + 1-butanethiol (C<sub>4</sub>H<sub>9</sub>SH) + methane (CH<sub>4</sub>) ternary mixture**

T/K	P/MPa	yCH <sub>4</sub>	yC <sub>3</sub> H <sub>7</sub> SH	yC <sub>4</sub> H <sub>9</sub> SH	T/K	P/MPa	xCH <sub>4</sub>	xC <sub>3</sub> H <sub>7</sub> SH	xC <sub>4</sub> H <sub>9</sub> SH
302.92	0.652	0.891	0.059	0.050	302.98	0.653	0.015	0.432	0.553
303.00	1.715	0.968	0.019	0.013	303.06	1.716	0.046	0.429	0.525
303.06	2.505	0.975	0.014	0.010	303.08	2.507	0.066	0.430	0.504
303.18	3.687	0.989	0.007	0.004	303.18	3.689	0.101	0.429	0.470
303.19	4.784	0.989	0.007	0.005	303.19	4.785	0.132	0.419	0.449
303.09	6.478	0.988	0.007	0.005	303.09	6.481	0.173	0.398	0.429
303.02	7.916	0.989	0.007	0.005	303.08	7.928	0.200	0.384	0.416
336.14	1.486	0.892	0.062	0.046	336.11	1.491	0.035	0.435	0.531
336.16	2.550	0.931	0.041	0.028	336.05	2.554	0.064	0.422	0.514
336.15	4.371	0.967	0.018	0.015	336.15	4.377	0.114	0.413	0.474
336.11	5.320	0.969	0.017	0.013	336.11	5.325	0.137	0.396	0.467
335.99	6.533	0.969	0.017	0.013	335.97	6.538	0.165	0.389	0.445
335.98	8.100	0.971	0.016	0.013	335.97	8.108	0.201	0.369	0.430
335.76	9.078	0.970	0.016	0.014	336.02	9.088	0.223	0.361	0.415
367.59	1.541	0.902	0.051	0.046	367.84	1.562	0.033	0.393	0.574
368.78	2.145	0.918	0.046	0.036	368.91	2.195	0.050	0.389	0.561
367.89	3.398	0.934	0.038	0.028	367.94	3.405	0.081	0.379	0.540
366.45	4.325	0.944	0.032	0.024	366.78	4.396	0.102	0.371	0.527
368.16	5.216	0.948	0.029	0.023	368.36	5.309	0.128	0.367	0.505
368.10	6.454	0.953	0.027	0.020	368.54	6.480	0.152	0.361	0.487
368.53	7.560	0.953	0.027	0.020	368.56	7.565	0.175	0.347	0.478

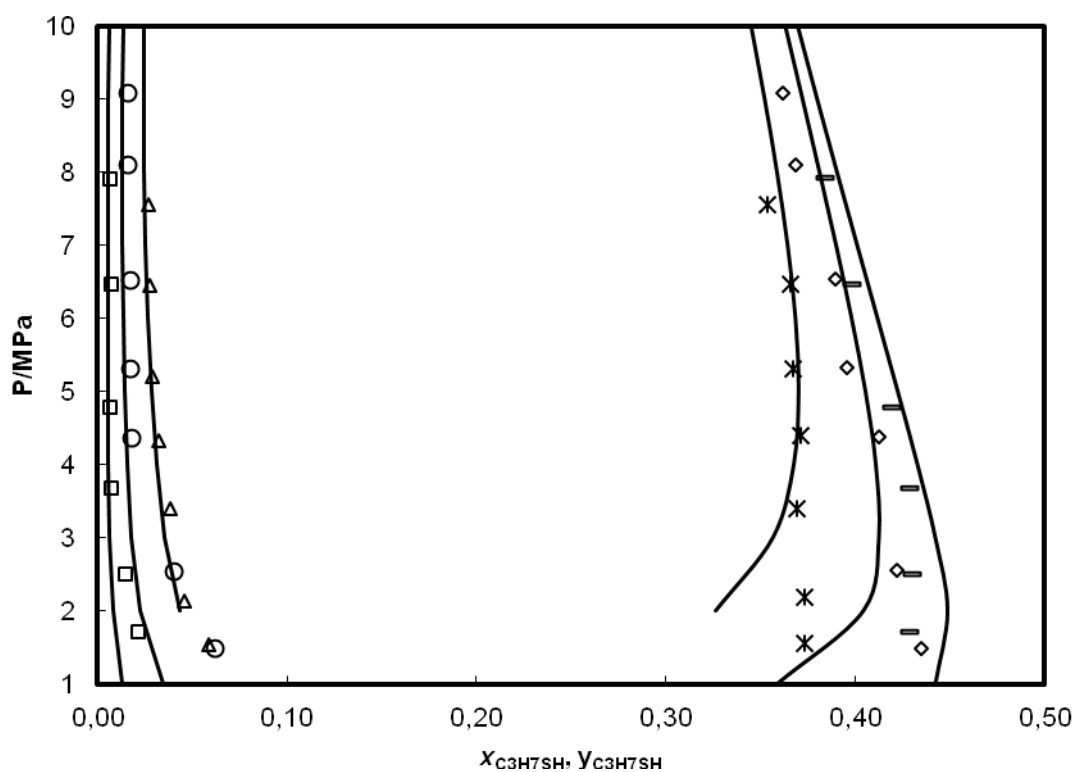
The expanded standard uncertainties with 0.95 level of confidence (k=2) are U(T)= 0.04, U(P)=0.003, U( x or y)=0.009; where y stands for mole fraction in vapor phase and x stands for mole fractions in organic phase.



**Figure 1.** The solubility of  $CH_4$  in the liquid 1-propanethiol ( $C_3H_7SH$ ) + 1-butanethiol ( $C_4H_9SH$ ) rich phase at 303 K ; (□) , 335 K ; (○) , 365 K ; (△), Solid lines: CPA EoS Predictions, error band  $\pm 5\%$ .



**Figure 2.** Mole fraction of 1-propanethiol ( $\text{C}_3\text{H}_7\text{SH}$ ) and 1-butanethiol ( $\text{C}_4\text{H}_9\text{SH}$ ) in the vapor phase Vapor phase mole fraction of 1-propanethiol at 303 K ; ( $\square$ ), 335 K ; ( $\circ$ ), 368 K ; ( $\Delta$ ), Vapor phase mole fraction 1-butanethiol at 303 K ; ( $-$ ), 335 K ; ( $\diamond$ ), 368 K ; (\*), dotted lines: CPA EoS predictions for 1-propanethiol vapor phase content, solid lines: CPA EoS predictions of 1-butanethiol vapor phase content.



**Figure 3.** Vapor-liquid equilibria of 1-propanethiol ( $C_3H_7SH$ ) + 1-butanethiol ( $C_4H_9SH$ ) + methane ( $CH_4$ ). 1-propanethiol liquid phase mole fraction at 303 K ; ( $\square$ ), 335 K ; ( $\circ$ ), 368 K ; ( $\Delta$ ), 1-propanethiol vapor phase mole fraction at 303 K ; ( $-$ ), 335 K ; ( $\diamond$ ), 368 K ; (\*), Solid lines: CPA EoS predictions.