

Phase Equilibrium Measurements and Modeling of 1-propanethiol + 1-butanethiol + CH4 in Methane + Water Ternary Systems at 303, 336, and 365 K and Pressure Up to 9 MPa

Javeed A. Awan, Christophe Coquelet, Ioannis Tsivintzelis, Georgios M.

Kontogeorgis

▶ To cite this version:

Javeed A. Awan, Christophe Coquelet, Ioannis Tsivintzelis, Georgios M. Kontogeorgis. Phase Equilibrium Measurements and Modeling of 1-propanethiol + 1-butanethiol + CH4 in Methane + Water Ternary Systems at 303, 336, and 365 K and Pressure Up to 9 MPa. Journal of Chemical and Engineering Data, 2016, 61, pp.41-44. 10.1021/acs.jced.5b00134 . hal-01258498

HAL Id: hal-01258498 https://minesparis-psl.hal.science/hal-01258498

Submitted on 19 Jan 2016 $\,$

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Phase Equilibrium Measurements and Modeling of 1-propanethiol + 1-butanethiol + CH₄ in Methane + Water Ternary Systems at 303, 336, and 365 K and Pressure Up to 9 MPa

Javeed A. Awan^{a,c}, Christophe Coquelet^b, Ioannis Tsivintzelis^d, Georgios Kontogeorgis^a*

^a_Center for Energy Resources Engineering, Department of Chemical and Biochemical Engineering, Technical university of Denmark, Building 229, DK-2800 Kgs. Lyngby, Denmark. ^b CTP–Center for the Thermodynamics of Processes, MINES Paris Tech, PSL Research University, Rue Saint Honore, 77305 Fontainebleau, France, ^cInstitute of Chemical Engineering and Technology, Faculty of Engineering and Technology University of the Punjab, Lahore, Pakistan. ^dDepartment of Chemical Engineering, Aristotle University of Thessaloniki, GR-54124, Thessaloniki, Greece.

Abstract

New vapor-liquid equilibrium (VLE) data for 1-propanethiol + 1-butanethiol + CH₄ ternary system is reported. Measurements were performed at three different temperatures (303, 336 and 368 K), while the pressure was ranged from1 to 9 MPa. The total system pressure was maintained by CH₄. 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.

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

*: Corresponding author, Email: <u>gk@kt.dtu.dk</u>. (Professor Georgios Kontogeorgis), Phone: +45 45252859, Fax: +45 45882258

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 intermediates¹. 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 volume². 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 units³. 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^{4.5,6} on the VLE and VLLE measurements of the systems containing CH_4 , water and thiols . Herein we measure new VLE data for ternary mixture 1-propanethiol $(C_3H_7SH) + 1$ -butanethiol $(C_4H_9SH) + methane (CH_4)$ 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 (ROLSITM) was used. The detail of the experimental setup has been discussed in our previous manuscript⁷. The equipment is the same used by Zehioua *et al.*⁸ and the procedure is identical to Coquelet *et al.*⁹. 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 cm³) followed by equal volumetric quantity of 1-butanethiol (10 ml). Then CH₄ 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 expended 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 DruckTM 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 expended 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 expended uncertainty (0.95 level of confidence, k= 2) in mol fraction is U_{max} (x or y, k=2)= 0.006

The peaks of the individual components generated by gas chromatograph in liquid phase [CH₄ (FID), C₃H₇SH (TCD), C₄H₉SH (TCD)] and in gas phase [CH₄ (TCD), C₃H₇SH (FID), C₄H₉SH (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 (σ^A) on each experimental data point was calculated⁷ and presented in Table 2.

3. Modeling section

The experimental data were modeled using the CPA EoS, whichin terms of the pressure is given as ^{10,11}:

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

More details about the CPA EoS can be found in the literature^{10,11}. The CPA EoS for thiols (mercaptan containing systems) has been described in our previous studies^{5,6,7}. All fluids of this work (1-propanethiol (C_3H_7SH), 1-butanethiol (C_4H_9SH) and methane were modeled as non-self-associating fluids. The CPA EoS

pure component parameters (b/ L.mol⁻¹, $\Gamma = a_0/(R b)/$ K and c₁) for C₃H₇SH⁵, C₄H₉SH⁷, CH₄¹² and the binary Interaction parameters for C₃H₇SH-CH₄ (k_{ij} =0.38)⁷ and C₄H₉SH-CH₄ (k_{ij} =0.38)⁷ were adopted from literature. The binary interaction parameter between C₃H₇SH-C₄H₉SH 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 (C₃H₇SH) +1-propanethiol (C₃H₇SH) + methane (CH₄). 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 + CH₄ 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 (CH₄) 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 (C₃H₇SH) and 1-butanethiol (C₄H₉SH) 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 (C₃H₇SH) is always superior to 1-butanethiol (C₄H₉SH) at the same temperature and pressure, as it is expected.

The CPA EoS predictions for the vapor-liquid equilibrium of 1-propanehiol (C_3H_7SH) + 1-butanethiol (C_4H_9SH) + methane (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 + CH₄ ternary system.

5. Conclusion

New vapor-liquid equilibrium (VLE) data for the 1-propanethiol + 1-butanethiol + 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

we acknowledge DET FRIE FORSKNINGSRAD Danmark for the independent research grant no.09-066450 to Dr. Javeed A. Awan at Center for Energy Resources Engineering, DTU Chemical Engineering. We appreciate discussions with Prof. Jean-Noel Jaubert (ENSIC, France) and Prof. Dominique Richon (Mines ParisTech, France). The authors wish also to thank CHIGP consortium companies *i.e* Statoil * (Norway), Gassco (Norway), BP (UK, USA), TOTAL (France), DONG Energy and Mærsk Oil & Gas (Denmark) for supporting the CPA-*EoS* part of this work as part of the project.

Literature Cited

- Allred, G. C.; Beets, J. W.; Parrish, W. R. Excess properties for 1-butanethiol + N-heptane, cyclohexane, benzene, and toluene. Excess molar volumes at 283.15 and 298.15 K, *J. Chem. Eng. Data*, **1990**, 35 (3), 328-331
- (2) Bymaster, A. Molecular Modeling the Microstructure and Phase Behavior of Bulk and Inhomogeneous Complex Fluids. PhD Thesis, Rice University, Houstan-Texas, USA, 2009.
- (3) Awan, J. A.; Tsivintzelis, I.; Valtz, A.; Coquelet, C.; Kontogeorgis, G. M. Vapor–Liquid–Liquid Equilibrium Measurements and Modeling of the Methanethiol + Methane + Water Ternary System at 304, 334, and 364 K, *Ind. Eng. Chem. Res.*, 2012, 51 (35), 11561–11564.
- (4) Awan, A. J.; Thomsen, K.; Coquelet, C.; Fosbøl L. Philip.; Richon, D. Vapor-Liquid Equilibrium Measurements and Modeling of the Propyl Mercaptan + Methane + Water System. J. Chem. Eng. Data, 2010 55, 842-846.
- (5) Awan, J. A.; Tsivintzelis, I.; Breil, M.; Coquelet, C.; Richon, D.; Kontogeorgis, G. M. Phase Equilibria of Mixtures Containing Organic Sulfur Species (OSS) and Water/Hydrocarbons: VLE Measurements and Modeling Using the Cubic-Plus-Association Equation of State, *Ind. Eng. Chem. Res.* 2010, 49, 210, 12718-12725.
- (6) Awan, J. A.; Tsivintzelis, I.; Coquelet, C.; Kontogeorgis, G. M. Phase Equilibria on Three Binary Mixtures; Methyl mercaptan + Methane, Methyl mercaptan + Nitrogen and Methyl mercaptan + Carbon dioxide., *J. Chem. Eng. Data*, **2012**, 57, 896-901.
- (7) Awan, J. A.; Kontogeorgis, G. M.; Tsivintzelis, I.; Coquelet, C. Vapor-Liquid-Liquid Equilibrium Measurements and Modeling of Ethanethiol + Methane + Water,

1-Propanethiol + Methane + Water and 1-Butanethiol + Methane + Water Ternary Systems at 303, 335,and 365 K and Pressure Up to 9 MPa. *Ind. Eng. Chem. Res.* **2013**, 52, 14698–14705

- (8) Zehioua, R.; Coquelet, C.; Meniai, A. H.; Richon, D. Isothermal vapour liquid equilibrium data of 1,1,1,2-tetrafluoroethane (R134a) + dimethylformamide (DMF) working fluids for absorption heat transformer. J. Chem Eng. Data 2009, 55, 985–988.
- (9) Coquelet, C.; Chareton, A.; Richon, D. Vapour-Liquid Equilibrium Measurements and Correlation of the Difluoromethane (R32) + Propane (R290) + 1,1,1,2,3,3,3-Heptafluoropropane (R227ea) Ternary Mixture at Temperatures from 269.85 to 328.35 K. *Fluid Phase Equilibr* 2004, 218, 209–214.
- (10) Kontogeorgis, G. M.; Michelsen, M. L.; Folas, G. K.; Derawi, S.; Solms, N. V.; Stenby, E. H. Ten Years with the CPA (Cubic-Plus-Association) Equation of State. Part-I. Pure Compounds and Self-Associating Systems, *Ind. Eng. Chem. Res.* 2006, *45*, 4855-4868.
- (11) Kontogeorgis, G. M.; Voutsas, E. C.; Yakoumis, I. V.; Tassios, D. P. An Equation of State for Associating *Fluids. Ind. Eng. Chem. Res.* **1996**, *35*, 4310–4318.
- (12) Tsivintzelis, I.; Kontogeorgis, G. M.; Michelsen, M. L.; Stenby, E, H. Modeling Phase Equilibria for Acid Gas Mixtures Using the CPA Equation of State. I. Mixtures with H2S. *AIChE J.* 2010, *Volume 56, Issue 11, 2965-2982.*

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

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

* Information provided by suppliers.

T/K	P/MPa	yCH4	yC ₃ H ₇ SH	yC4H9SH	T/K	P/MPa	xCH4	xC ₃ H ₇ SH	xC ₄ H ₉ 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

Table 2. Experimental Vapor-liquid Equilibrium Data for the 1-propanethiol (C3H7SH) + 1-butanethiol (C4H9SH) + methane (CH4) ternary mixture

The expended 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-propanehiol (C_3H_7SH) + 1-butanethiol (C_4H_9SH) rich phase at 303 K ; (\Box) , 335 K ; (o), 365 K ; (Δ), Solid lines: CPA EoS Predictions, error band \pm 5%.



Figure 2. Mole fraction of 1-propanehiol (C_3H_7SH) and 1-butanethiol (C_4H_9SH) in the vapor phase Vapor phase mole fraction of 1-propanehiol at 303 K ; (\Box) , 335 K ; (o), 368 K ; (Δ), 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-propanehiol (C_3H_7SH) + 1-butanethiol (C_4H_9SH) + methane (CH_4).1-propanethiol liquid phase mole fraction at 303 K ; (\Box) , 335 K ; (o), 368 K ; (Δ),1-propanethiol vapor phase mole fraction at 303 K ; (-) , 335 K ; (\diamond), 368 K ; (*), Solid lines: CPA EoS predictions.