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Vapour-liquid equilibria of n-butane and ethyl mercaptan: experiments and modelling

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Abstract

Design of debutaniser in fractionation train in gas processing requires accurate knowledge of phase equilibrium properties of n-butane with sulphur compounds like mercaptan. In this paper, we report high-quality isothermal vapor–liquid equilibrium data for n-butane + ethyl mercaptan (or ethanethiol) between 298.14 K to 388.18 K and pressures up to 2.0029 MPa. An equipment whose experimental technique is based on static-analytic method was considered. The equipment is composed by an agitated equilibrium cell with two online micro samplers connected to a Gas Chromatograph. The data was correlated with the Peng Robinson equation of state with classical alpha function. A comparison was also performed with two predictive models, PPR78 and PSRK UNIFAC.

Key words:
Equation of state, Static analytic method, data treatment, gas processing

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1. Introduction

Worldwide total energy requirements are increasing and natural gas appears to be the best temporary solution in the context of the energy transition. In order to have a safe and environmentally-friendly production, challenges related to processing and environmental protection arise. The presence of significant quantities of sulphur compounds in the exploited gas resources is one of these challenges. Mercaptans are sulphur compounds are present in natural gas. One major operation in Gas processing is to remove the acid gases (in an acid gas removal unit) [1]. During this operation some mercaptans are also removed. Hydrogen sulfide (H_2S) and carbon dioxide (CO_2) are removed by amine treating but the majority of amine solvents remove few to no mercaptans [2]. Mercaptans may then be removed in dehydration units. Any remaining mercaptan in the natural gas tends to accumulate in hydrocarbon condensates After dehydration, fractionation is performed. A fractionation train is composed of a series of distillation columns; a deethaniser, a depropaniser and debutaniser. Several products can be obtained: GNL, gaseous methane, Ethane/Propane mixtures (EP), Commercial Propane, Propane/Butane mixture (LPG), Butane and isobutene, Natural Gasoline and Mixtures with a vapour pressure specification. Mercaptans are not the only contaminants: Hydrogen sulphide, Carbon dioxide, Carbonyl sulphide, Carbon disulphide, Organic sulphides, Nitrogen, Water, methanol (prevention of hydrate formation) can also be present.

Determining thermodynamic properties of systems composed of mercaptans and hydrocarbons is required to better understand how organic sulfur compounds in raw feed gas are distributed in the products of NGL fractionation systems. The main properties of interest are vapour-liquid equilibria in the range of pressure and temperature of the operating conditions in the train of fractionation. In the last 6 years, our research group has published VLE data of binary and ternary systems involving mercaptans (without water) in several articles: Awan et al. [3] (Phase Equilibria of Three Binary Mixtures: Methanethiol + Methane, Methanethiol + Nitrogen, and Methanethiol + Carbon Dioxide), Awan et al. [4] (1-Propanethiol+ 1-Butanethiol+ CH_4), Afzal et al. [5] (Ethane + Ethyl mercaptan). Mercaptans have similar molecular structure to alcohols with the oxygen (O) atom replaced by a sulfur (S) atom. This change gives mercaptans a more acidic behaviour compared to their alcohol counterparts. Mercaptans are only slightly acidic, and this acidity decreases with their molecular weight.

Moreover, the knowledge of thermodynamic properties of mixtures of sulfur compounds with hydrocarbons is not only important in gas processing but also in the petroleum and chemical industries. The thermophysical properties and equilibrium data are important for the rational design of processes for the removal of sulfur compounds from petroleum streams but also for the purification of sulfur compounds for use in chemical processes. Because all of these sulphur compounds are highly toxic and volatile, obtaining reliable thermodynamic data like vapour-liquid equilibrium (VLE) data is not straight-forward. The Centre of Thermodynamics of Processes (CTP) at MINES ParisTech is one of the few places where toxic fluids can be studied to produce reliable data.

About the binary system ethylmercaptan n-butane, the authors have found one set of data in the open literature from Giles and Wilson [6]. It concerns PTx data obtained using a synthetic method.

The classical Peng Robinson Equation of state [7] with its classical mixing rule was used to correlate the data. A comparison was performed with two predictive models: PPR78 [8] and PSRK UNIFAC [9].

2. Materials and methods

2.1. Materials

In Table 1 are listed the chemicals used for the VLE measurements. Research grade n-butane with minimum purity of 99.95 % (obtained from Air Products) and ethyl mercaptan with minimum purity 99 % (obtained from Acros) were used. No further purification of the chemical products was needed, only degassing when loading the chemicals into the equilibrium cell.

Table 1. Purities and suppliers of the chemicals used in this work

Chemicals	Purity (GC)	Supplier
n-butane	99.95 vol%	Air Products
Ethylmercaptan	≥ 99 vol%	Acros

2.2. Methods

In order to measurements in the whole range of pressure, we have used two different equipments with an experimental technique based on the analytic-static method.

At low pressure, we have used an equipment previously presented and described by Zhang et al. [10] and Théveneau et al. [11]. The equilibrium cell is immersed in a thermo-regulated liquid bath (LAUDA Proline RP 3530 C). Two (Pt-100) platinum probes are used to measure the temperature at the bottom and top of the cell. The two probes were calibrated by comparison with a 25 Ω reference platinum probe (Tinsley, France). The accuracy of the two probes was estimated to ± 0.02 K. Also, the pressure was measured by one pressure transducer (General Electric, model UNIK 5000) with a maximum absolute pressure of 10 bar. The pressure transducer is maintained at a constant temperature (353 K) by means of a PID regulator (FUJI, model PXE-4). The accuracy of the pressure transducer was estimated to ± 3 mbar after calibration. Both temperature and pressure signals were transmitted to a data acquisition unit (Agilent 34972A). Two samplers are connected to the equilibrium cell in order to take samples of vapor and liquid phases. Liquid and vapor samples were analyzed by means of a gas chromatograph (Perichrom, model PR-2100). A thermal conductivity detector (TCD) was calibrated and used to determine the molar composition of the two phases.

At high pressure (P>0.5 MPa), we have used an equipment similar to the equipment used by Afzal et al. [5]. Briefly, the equilibrium cell consists of one sapphire tube, held between two flanges in Hastelloy with suitable o-rings. On each flange are located valves for loading, vaccum and cleaning of the cell. An agitation assembly is installed in the sapphire tube for the stirring of the two phases with two propellers. The agitation assembly is magnetically coupled to an external agitation motor capable of producing the desired level of agitation inside the cell.

Like the low-pressure equipment, two calibrated 100 Ω platinum resistance thermometer sensors (Pt-100) are used to measure equilibrium temperatures at the lower and upper parts of the cell. The accuracy of the two probes was estimated to ± 0.03 K. The pressures are measured using one calibrated Druck pressure transducer (Druck, model PTX 611) maintained at constant temperature (higher than the maximum temperature of study). The temperature is controlled by a PID regulator (WEST instrument, model 6100). The accuracy of the pressure transducer was estimated to ± 9 mbar after calibration. Two capillary samplers (ROLSI®, Armines's patent) were vertically mounted on the equilibrium cell, one for liquid phase and the other for vapour phase. The samplers are connected to the Gas chromatograph. A thermal conductivity detector (TCD) is used for analysis.

The two GC of the two equipments were equipped with a 4-meter long packed Porapack Q column. The WINILAB III (Perichrom, France) data acquisition software was used for peak integration. The relative accuracies of mole numbers are ±1.1% for n-butane and ±2.4 for ethylmercaptan. Consequently the maximum calibration uncertainty of mole fractions, calculated at $x_{butane} = 0.5$ is $u_{max}(x,y) = 0.007$.

At equilibrium conditions, each composition was determined 6-8 times for each phase and average values are reported along with relative standard deviation (σ). Equation 1 reminds the expression of the composition of component *i* (ncomp is the number of component in the mixture).

$$x_i = \frac{n_i}{\sum_i^{ncomp} n_i} \tag{1}$$

Equation 2 is used for the calculation of the uncertainty of mixture composition of component *i*.

$$u_{cal}(x_i) = \sqrt{\sum_j^{ncomp} \left(\frac{\partial x_i}{\partial n_j} \right)_{j \neq i}^2 u^2(n_j)} \tag{2}$$

Consequently, for a binary system, one can calculate uncertainty on mole fraction x_1 by using equation 3.

$$u_{cal}(x_1) = x_1(1 - x_1)\sqrt{\left(\frac{u(n_1)}{n_1} \right)^2 + \left(\frac{u(n_2)}{n_2} \right)^2} \tag{3}$$

Equation 4 reminds the combined standard temperature uncertainty on molar composition.

$$u(x_i) = \pm\sqrt{u_{calib}(x_i)^2 + u_{rep}(x_i)^2} \tag{4}$$

u_{rep} is obtained by considering the standard deviation (σ) accounting for the repeatability of the measurements. The experimental results are presented in Table 2 with the calculated uncertainties.

Table 2: Experimental isothermal VLE data for the n-Butane (1) + Ethylmercaptan (2) mixture system and their standard uncertainties. Maximum calibration uncertainty on composition u(x,y, k=2)=0.008.

T: 298.14 K u(T, k=2)= 0.02 K u(P, k=2) = 0.0004 MPa								
P/ MPa	**n**	**x_1**	**σx_1**	**$u(x_1)$**	**n**	**y_1**	**σy_1**	**$u(y_1)$**
0.0942	7	0.0644	0.0007	0.0009	5	0.2932	0.0007	0.003
0.1261	7	0.161	0.003	0.002	5	0.5174	0.0002	0.004
0.1439	7	0.236	0.003	0.003	5	0.6041	0.0005	0.004
0.1691	7	0.387	0.002	0.004	5	0.7158	0.0008	0.003
0.183	8	0.484	0.004	0.004	5	0.7558	0.0007	0.003
0.2044	11	0.666	0.007	0.004	6	0.8308	0.0002	0.002
0.2126	13	0.733	0.006	0.003	8	0.8598	0.0002	0.002
0.2226	3	0.8358	0.0002	0.002	5	0.904	0.002	0.001
0.2394	5	0.9606	0.0002	0.0006	4	0.9794	0.0001	0.0003
T: 328.04 K u(T, k=2)= 0.02 K u(P, k=2) = 0.0004 MPa								
0.2300	6	0.0411	0.0002	0.0006	5	0.1845	0.0002	0.002
0.2395	6	0.0513	0.0006	0.0008	6	0.2122	0.0006	0.003
0.2752	6	0.0965	0.002	0.001	5	0.3525	0.0004	0.004
0.3030	6	0.149	0.001	0.002	6	0.437	0.001	0.004
0.3181	5	0.176	0.003	0.002	5	0.4835	0.0003	0.004
0.3409	6	0.226	0.001	0.003	6	0.539	0.001	0.004
0.3632	8	0.282	0.005	0.003	6	0.5892	0.0004	0.004
0.3947	5	0.360	0.002	0.004	5	0.6466	0.0002	0.004
0.4180	5	0.428	0.004	0.004	4	0.692	0.002	0.003
0.4212	4	0.4353	0.0003	0.003	4	0.6964	0.0007	0.002
0.4423	7	0.505	0.003	0.004	7	0.7374	0.0006	0.003
0.4596	4	0.5569	0.0004	0.003	6	0.760	0.002	0.002
0.5188	5	0.775	0.002	0.002	6	0.862	0.005	0.001
0.5333	4	0.8298	0.0003	0.002	5	0.892	0.004	0.001
0.5475	5	0.8893	0.0008	0.001	5	0.9284	0.0009	0.0008
0.5573	5	0.9477	0.0003	0.0006	6	0.9632	0.0003	0.0004
T: 358.11 K u(T, k=2)= 0.02 K u(P, k=2) = 0.0009 MPa								

0.5335	7	0.0685	0.0003	0.0007	6	0.2092	0.0006	0.002
0.6446	8	0.1775	0.0003	0.002	5	0.4011	0.0004	0.003
0.7447	7	0.2974	0.0003	0.002	4	0.5312	0.0006	0.003
0.8420	9	0.4336	0.0005	0.003	5	0.6371	0.0003	0.003
0.9231	8	0.5691	0.0003	0.003	5	0.725	0.002	0.002
1.0118	7	0.7159	0.0001	0.002	5	0.813	0.002	0.002
1.0513	5	0.7881	0.0002	0.002	5	0.8574	0.0006	0.001
1.0877	5	0.8838	0.0001	0.001	5	0.9187	0.0002	0.0009
1.1101	6	0.9330	0.0003	0.0007	5	0.9514	0.0002	0.0005
T: 388.18 K			u(T, k=2)= 0.02 K		u(P, k=2) = 0.0009 MPa			
1.0182	6	0.0681	0.0002	0.0007	6	0.168	0.001	0.002
1.1923	6	0.1760	0.0003	0.002	6	0.3443	0.0006	0.003
1.3764	5	0.3100	0.0008	0.002	5	0.4882	0.0007	0.003
1.6589	5	0.5596	0.0001	0.003	6	0.6827	0.0002	0.002
1.7145	5	0.6152	0.0001	0.003	5	0.7229	0.0002	0.002
1.8182	7	0.7243	0.0001	0.002	6	0.7961	0.0002	0.002
1.8734	5	0.7856	0.0002	0.002	4	0.8397	0.0006	0.002
1.9402	4	0.8688	0.0002	0.001	4	0.8989	0.0002	0.001
2.0029	6	0.9435	0.0002	0.0006	6	0.9552	0.0003	0.0005

3. Results and discussion

3.1. Data treatment

The critical temperatures (Tc), pressures (Pc) and acentric factors (ω) for pure n-butane and Ethylmercaptan are provided in Table 3.

Table 3. Thermal properties for ethane and Ethylmercaptan pure components (Source Simulis Thermodynamics™)

Component	T_c /K	P_c /MPa	Acentric factor ω
n-butane	425.12	3.796	0.200164
EthylMercaptan	499.15	5.490	0.187751

The experimental VLE data of (ethane + Ethylmercaptan) system were correlated using the Peng Robinson equation of state (Peng and Robinson, 1978) with the classical van der Waals mixing rules (model 1). PPR78 and PSRK Original alpha function is considered. Simulis Thermodynamics™ software by PROSIM (France) was used. k_{ji} is adjusted directly to the VLE data using the objective function given in Eq. (5). Calculations are based on a bubble point algorithm. The parameters are presented in Table 4 and experimental and modelling results are presented on Fig. 1. Relative volatility is presented on Fig. 2. We can see on figure 2 that the evolution of relative volatility follows the good trend.

$$F = \frac{100}{N}\left[\sum_1^N \left(P_{\text{exp}} - P_{\text{cal}}\right)^2 + \sum_1^N \left(y_{\text{exp}} - y_{\text{cal}}\right)^2\right] \quad (5)$$

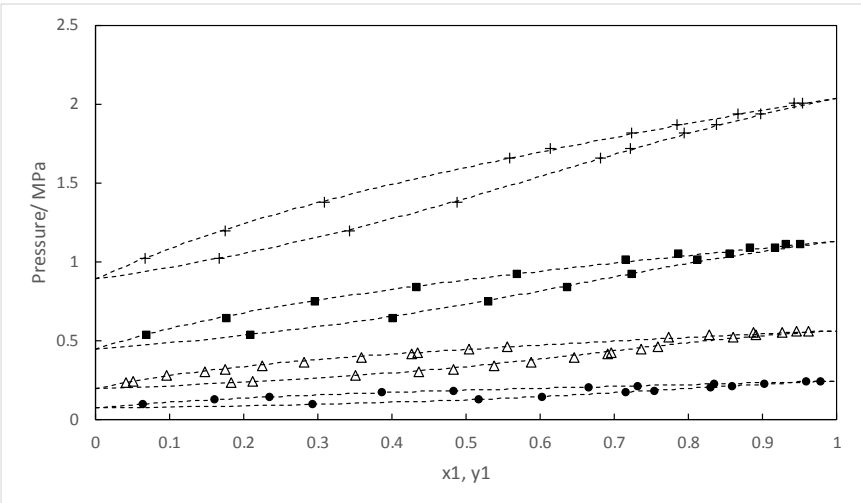

Fig. 1: Pressure as a function of n-butane mole fraction in the n-butane (1) + Ethylmercaptan (2) mixture at different temperatures. ●: 298.14 K, Δ : 328.04 K, ■: 358.11 K, +: 388.18 K. Dashed lines: calculated with PR EoS with binary intercation parameters from Table 4.

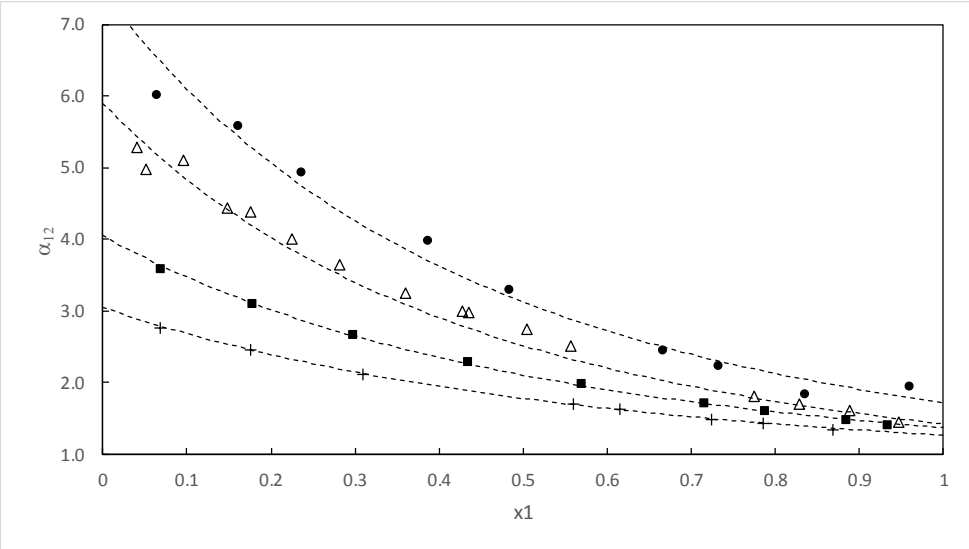

Fig. 2: Relative volatility of the n-butane (1) + Ethylmercaptan (2) binary system at different temperatures. ●: 298.14 K, Δ : 328.04 K, ■: 358.11 K, +: 388.18 K. Dashed: calculated with PR EoS with binary interaction parameters from Table 4.

Table 4: Values of the binary interaction parameters and objective function at each temperature.

T/ K	k_{12}	*F*
298.14	0.035	0.001
328.04	0.044	0.002
358.11	0.037	0.001
388.18	0.033	0.001

The variance of the binary interaction parameter was calculated using experimental data. Considering the objective function f given in Eq. (6), the variance is calculated using Eq. (7).

$$f(k_{ij}) = \left[\sum_1^N (P_{\text{exp}} - P_{\text{cal}})^2 + \sum_1^N (y_{\text{exp}} - y_{\text{cal}})^2\right] \quad (7)$$

The variance of k_{ij} is given by Eq. 8.

$$var(k_{ij}) = \frac{1}{V_r}\left(\frac{\partial^2 f(k_{ij})}{\partial k_{ij}^2}\right)^{-1} \quad (8)$$

With $V_r = \frac{2*f(k_{ij})}{N_{data} - N_{parameter}}$ the residual variance. We have done the calculation at each temperature. The standard deviation for the binary interaction is the square root of the variance. Its value is almost constant and equal to 0.004 (k=2). The binary interaction parameters are plotted on Fig. 3.

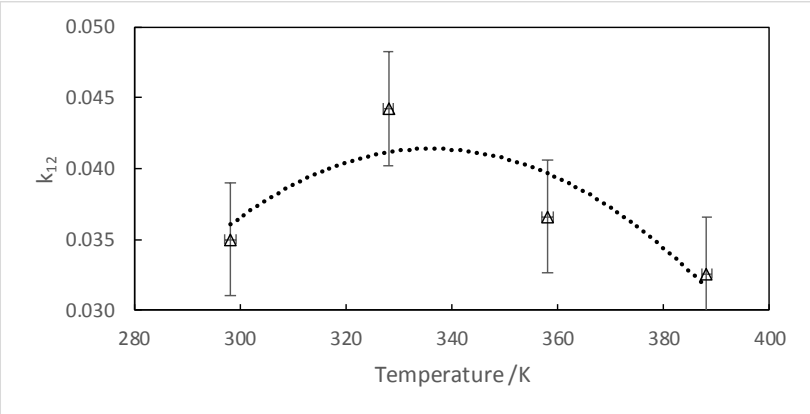

Fig. 3: Evolution of the Binary interaction parameter k_{ij} as a function of temperature. Error bar: 0.004.

In order to evaluate the quality of the data treatment, the Mean Relative Deviation (MRDU), and the BiasU were calculated based on pressures and vapour phase mole fractions, as defined in Eqs. (9) and (10).

$$\mathrm{MRDU} = \frac{100}{N}\sum\left|\frac{U_{\mathrm{cal}}-U_{\mathrm{exp}}}{U_{\mathrm{exp}}}\right| \tag{9}$$

$$\mathrm{BiasU} = \frac{100}{N}\sum\frac{U_{\mathrm{exp}}-U_{\mathrm{cal}}}{U_{\mathrm{exp}}} \tag{10}$$

where N is the number of data points, and $U = P$ or y_1. The MRDU and BiasU indicators, which give information on the agreement between model and experimental results, are presented in Table 5.

Table 5: Mean Relative deviation MRDU and BiasU obtained in fitting experimental VLE data with PR EoS and Van Ness test.

T/K	BiasP %	MRD*P* %	Bias*Y* %	MRD*Y* %	Van Ness test	
					Δy	**ΔP**
298.14	-0.19	0.62	-0.18	1.50	0.8	0.6
328.04	-0.42	1.10	0.77	1.74	0.9	1.1
358.11	0.10	0.99	0.02	0.32	0.2	1.0
388.18	-0.03	0.53	-0.17	0.20	0.1	0.5

The Gibbs-Duhem equation (Eq. (11)) is considered to examine the consistency of the data.

$$\sum_i x_i d\ln\gamma_i - \frac{v^E}{RT}dP + \frac{h^E}{RT}dT = 0 \tag{11}$$

Where v^E and h^E are the excess volume and excess enthalpy respectively and γ_i the activity coeffcient of component i. At constant temperature and after integration, Eq. (12) is obtained.

$$A = 100\left(\int_0^1 ln\left(\frac{\gamma_1}{\gamma_2}\right)dx + \int_0^1 \frac{v^E}{RT}\left(\frac{\partial P}{\partial x}\right)_T dx\right) \quad (12)$$

By neglecting the excess volume v^E, we obtained Eq. (13) wich can be used to test the consistency of our data: consistent data means A=0.

$$A = 100\left(\int_0^1 ln\left(\frac{\gamma_1}{\gamma_2}\right)dx\right) \quad (13)$$

The activity coefficient is estimated from Eq. (14). This equation can only be considered for low pressure data. Consequently, it is difficult to use the test with our data.

$$\gamma_i = \frac{Py_i}{x_i P_i^0} \quad (14)$$

Where P_i^0 is the pure component vapor pressure of component i. Therefore, the van Ness test (van Ness et al. [12]) was preferred, using our model and our data treatment. This test, also called modelling capability test consists of applying a thermodynamic model and calculating pressure and vapour deviations as defined by Eqs. (15) and (16).

$$\Delta P = \frac{100}{N}\sum\left|\frac{P_i^{exp} - P_i^{cal}}{P_i^{exp}}\right| \quad (15)$$

$$\Delta y = \frac{100}{N}\sum\left|y_i^{exp} - y_i^{cal}\right| \quad (16)$$

where *N* is the number of data points. If ΔP and Δy are less than 1, the test is validated. The results of the van Ness test are presented in Table 5. As we can see, our data passes the test and so consistency of our data is validated.

3.2. Comparison with literature data

We have compared our results with literature data (Giles and Wilson [6]) and two predictive models, PPR78 and PSRK UNIFAC. Using literature data, obtained by a synthetic method (PTx data) as explained in the paper, we have applied the Eq. (17) to estimate the value of the binary interaction parameter as a function of temperature. The parameters of the Eq. (17) are determined by using parameters presented in Table 3.

$$k_{ij} = -3.66405 \times 10^{-6}T^2 + 0.002465T - 0.373188 \quad (17)$$

Figure 4 presents the comparison and Table 6 the Mean Relative Deviation (MRDU), and the BiasU, applied on equilibrium pressure. The deviations are less than 1% and so the two sets of data, from literature and this work are in very good agreement.

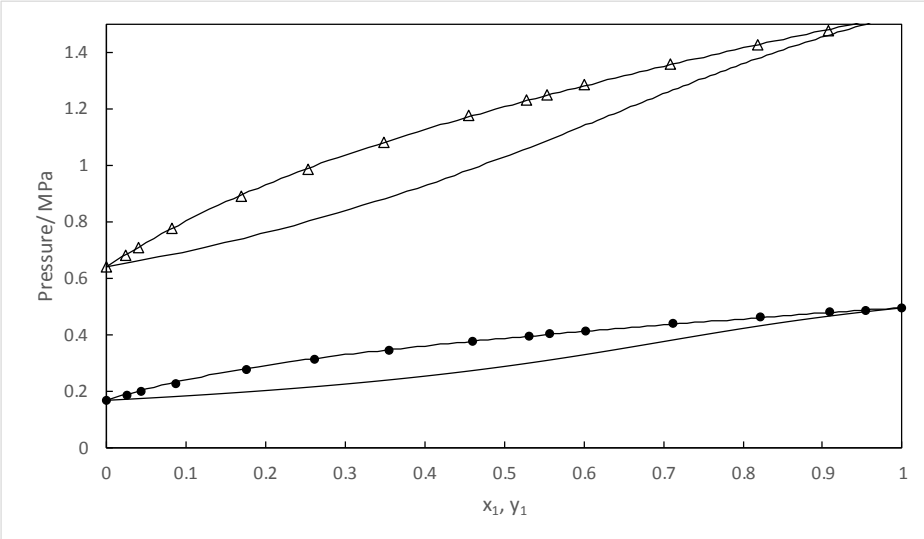

Fig. 4: Pressure as a function of n-butane mole fraction in the n-butane (1) + Ethylmercaptan (2) mixture at 323.15 (•) and 373.15 K (Δ) and comparison with the data from Giles and Wilson [6].

Table 6: Mean Relative deviation MRDU and BiasU obtained in application of our model to the data from Giles and Wilson [6].

T/K	Bias P %	MRD P %
323.15	-0.16	0.56
373.15	-0.01	0.21

Table 7 presents the Mean Relative Deviation (MRDU), and the BiasU, applied on pressures and vapour phase mole fractions for the two predictive models. The performance of the two models is very similar with a slightly lower deviation for PSRK UNIFAC model.

Table 7: Mean Relative deviation MRDU and BiasU obtained in fitting experimental VLE data with PPR78 and PSRK UNIFAC.

T/K	BiasP %	MRD*P* %	Bias*Y* %	MRD*Y* %
	PPR78			
298.14	-5.24	5.24	-1.98	3.38
328.04	-1.40	1.91	0.22	1.94
358.11	-1.29	1.72	-0.90	1.47
388.18	-1.35	1.36	-1.15	1.50
	PSRK UNIFAC			
298.14	2.08	2.28	1.35	2.49
328.04	3.39	3.39	4.20	4.52
358.11	0.82	0.82	0.52	1.14
388.18	-0.44	0.44	-0.25	0.53

4. Conclusion

Isothermal (*P*-*x*-*y*) VLE data for n-butane + Ethylmercaptan binary system were measured at four temperatures ranging from 298.14 K to 388.18 K using a static-analytic method. Two equipments for low and high pressure measurements were used to generate the data. The measured data are in good agreement with literature data from Gils and Wilson [6] and are very well predicted using PPR78 and PSRK models. This work is in the continuity of experimental and modelling work realised in the Centre of Thermodynamics from Mines ParisTech on the study of binary system phase diagrams involving sulphur components for gas processing industries.

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Fig. 1: Pressure as a function of n-butane mole fraction in the n-butane (1) + Ethylmercaptan (2) mixture at different temperatures. ●: 298.14 K, Δ : 328.04 K, ■: 358.11 K, +: 388.18 K. Solid lines: calculated with PR EoS with parameters from Table 3.

Fig. 2: Relative volatility for the binary n-butane (1) + Ethylmercaptan (2) mixture at different temperatures. ●: 298.14 K, Δ : 328.04 K, ■: 358.11 K, +: 388.18 K. Solid lines: calculated with PR EoS with parameters from Table 4.

Fig. 3: Evolution of the Binary interaction parameter k_{ij} as a function of the temperature. Error bar: 0.004.

Fig. 4: Pressure as a function of n-butane mole fraction in the n-butane (1) + Ethylmercaptan (2) mixture at 323.15 and 373.15 K and comparison with the data from Giles and Wilson [6].