Vapor−Liquid Equilibrium Measurements and Modeling of the Propyl Mercaptan + Methane + Water System

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In this work, vapor−liquid equilibrium (VLE) measurements of propyl mercaptan (PM) in pure water were performed at three different temperatures, (303, 323, and 365) K, with a pressure variation from (1 to 8) MPa. The total system pressure was maintained by CH_4. The inlet mole fraction of propyl mercaptan in all experiments was the same, around $4.5 \cdot 10^{-4}$ in the liquid phase. The objective was to provide experimental VLE data points of the propyl mercaptan + methane + water system for modeling since there is a lack of available data. These data will allow the industrial modeling of sulfur emission. The thermodynamic model used for the description of VLE is the extended UNIQUAC model. The model parameters are valid in the temperature range similar to the measured data and a pressure range up to 8 MPa.

Introduction

Natural gas and petroleum industries deal with raw materials containing variable concentrations of acid gases (CO_2, H_2S) and traces $x = (1 \text{ to } 4) \cdot 10^{-4}$ of organic sulfur species like mercaptans and dimethylsulfide. Treatment processes have to remove not only H_2S and CO_2 but also sulfur species because worldwide regulations for environmental protection are forcing the petroleum industry to decrease the sulfur content in petroleum fluids.

Mercaptans belong to the thiol group of compounds which contain an −SH group bound to a radical R. Mercaptan properties are governed to a large extent by the length of this radical. Like H_2S, mercaptans have acidic properties, but they are much weaker acids than H_2S. This is due to the lipophilic properties of the hydrocarbon radical which makes them behave less like acids and more like hydrocarbons. This phenomenon becomes more pronounced as a function of the hydrocarbon chain length.[1] Mercaptans can react with alkaline solutions to form mercaptide salts where typically the H in the −SH group is substituted by a metal. Mercaptans exist as free mercaptans and mercaptide ions in alkaline solutions. As a result, the solubility of mercaptans in alkaline amine solutions tends to be higher than in simple physical solvents like water. The solubility increases with higher alkalinity of the solvent and decreases with increased temperature.

The solubility of mercaptans is of great interest to the petroleum industry. Unfortunately, it has only been reported by a limited number of authors. Iliuta and Larachi[2] presented a detailed review on solubility of sulfur species in different solvents and emphasized the need for new experimental data for the mercaptan + water system at higher temperatures. There are limited solubility data available for the propylmercaptan (PM) + water system at different temperatures and pressures.

Experimental VLE data of PM in pure water at three different temperatures, (303, 323, and 365) K, with a pressure variation from (1 to 8) MPa are reported in this work. A thermodynamic model is used for the description of VLE data of the ternary PM + H_2O + CH_4 system measured in this study. This model is the extended UNIQUAC model for electrolytes which combines the UNIQUAC local composition model with the Debye−Hückel law and the Soave−Redlich−Kwong equation of state.[3] LLE data for the PM + H_2O + CH_4 system are unfortunately not available in the literature; therefore, only the presented VLE data are used for the parameter estimation.

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

chemical name	CAS no.	purity/%	supplier
propyl mercaptan (PM)	107-03-9	99 + GC	Aldrich
methane (CH_4)	74-82-8	99.995/vol.	Messer

Experimental Section

Materials. Purities and suppliers of materials are provided in Table 1. No further purifications of chemicals were made. Ultra pure water was produced in the laboratory using commercial equipment (Millipore, model Direct-Q5).

Apparatus and Experimental Procedure. An apparatus based on the “static-analytic” method and consisting of an equilibrium cell coupled with two rapid online samplers (ROLSI, Armines' patent) was used in this work. The details of the experimental setup have been given in a previous communication.[4] The ROLSI samplers used in this investigation are capable of making small vapor/liquid extractions from the equilibrium cell. This is done with minor disturbances on the equilibrium concentration and pressure since the size of the samples [(1 to 2) μL] is negligible compared to the volume of the cell, 30 cm^3. The samplers are fixed on top of the equilibrium cell. The liquid and vapor samples are analyzed using a gas chromatograph (PERICHROM model PR2100, France) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). A Porapack R type column (1.2 m length and 1/8” wide, 80/100 mesh) has been used to separate the components.

Two 100 Ω platinum resistance thermometer devices (Pt100) were used for temperature measurements inside the equilibrium

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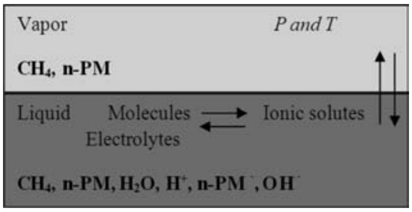

Figure 1. Physical and chemical equilibrium in a system of ionic species OH^-, PM^-, and H^+ and molecular species CH_4, H_2O, and PM. (There are only traces of water in the vapor phase.)

cell. They were periodically calibrated against a 25 Ω reference platinum resistance thermometer (TINSLEY precision instruments). The resulting uncertainty in temperature measurements is estimated to be within ± 0.04 K. Pressures were measured by means of a Druck pressure transducer, (0 to 10) MPa, which was maintained at a constant temperature, i.e., 353.15 K. Pressures and temperatures were continuously registered through a data acquisition unit HP34970A. 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). Uncertainties in pressure measurements are estimated to be within ± 0.003 MPa. The relative uncertainty in the PM mole fractions is 0.06 mol %. The gas chromatograph detectors were calibrated using chromatographic syringes with maximum uncertainties of 2 % in the TCD and 1.5 % in the FID. Water content is negligible in the vapor phase.

At first water is loaded into a variable-volume cell (VVCM) by a gravimetric method under vacuum. A known mass of water is loaded into the equilibrium cell from the VVCM. It carries the PM into the equilibrium cell which is injected along the path of the solution through a special septum arrangement on a cylindrical tube injector. Finally, methane is added to the system to reach the desired pressure. The required temperature is obtained thanks to a thermoregulated oil bath.

The standard deviation on experimental data (σ^A) is calculated with eq 1, and the uncertainty for individual components (σ_i) is calculated with eq 2.

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

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

where x is the measured value; $\bar{x}$ is the average of the measured value; and n is the number of samples analysis.

$$\sigma_i = x_i(1 - x_i)\sum_{i=1} \frac{\Delta n_i}{n_i} \tag{2}$$

Thermodynamic Consideration of the PM (1) + CH₄ (2) + H₂O (3) System. The equilibrium representation of a system containing CH_4, H_2O, and PM, at a specified temperature and pressure, is shown in Figure 1. It can be divided into physical and chemical equilibrium. Water is considered as the solvent, thus formation of RS^- ions due to acid dissociation of RSH makes it a weak electrolyte system. The molecular species, i.e., CH_4, H_2O, and PM, in the liquid phase are in equilibrium with the ionic species, RS^-, H^+, and OH^-, in the liquid phase and the molecular species in the vapor phase.

Chemical Equilibria. The PM + H_2O + CH_4 system is considered to be a weak electrolyte system which may contain one cation H^+ with anions like RS^- and OH^- as shown in Figure 1. It can be presented by the following equation

$$RSH_{(aq)} \overset{K_a}{\rightleftharpoons} RS^-_{(aq)} + H^+_{(aq)} \tag{3}$$

K_a is the acid dissociation constant of mercaptan in the aqueous phase, which is described in the literature.[5]

Vapor−Liquid Equilibria. The extended UNIQUAC model for electrolytes is used for representation of the VLE in the PM + CH_4 + H_2O system. Only a volume (r) and a surface area (q) parameter for each component (see Table 2) and binary interaction parameters for each component pair (see Table 3) are used in the model. The interaction parameters are temperature dependent. The determination of parameters is based upon the ternary VLE data measured in this study.

A Henry's law approach is useful for the determination of aqueous phase composition, and it is often helpful to describe the overall solubility due to both physical and chemical solubility. According to Kritchevsky and Illinskaya[6] and a few other people, the Henry's constant of PM is defined by

$$\lim_{x \to 0} \frac{y_1 \cdot \hat{\phi}_1 P}{x_1} = k_H \tag{4}$$

In this equation, $\hat{\phi}_1$ is the fugacity coefficient of PM; x_1 is the mol fraction of PM; and k_H is the Henry's constant for PM at the saturation pressure of the solvent. The Soave−Redlich and Kwong equation of state[7] (SRK) is used to determine the fugacity coefficient. At equilibrium between PM in the aqueous phase and PM in the gas phase at temperature T and pressure P, the chemical potential, μ, of PM must be identical in the two phases

$$\mu_{1_{(g)}} = \mu_{1_{(aq)}} \tag{5}$$

At infinite dilution, the unsymmetrical mole fraction activity coefficient for PM is $\gamma_1^* = 1$, and the Poynting factor is assumed close to one. Consequently, we obtain

$$\frac{-\mu^*_{(aq)} + \mu^o_{(g)}}{RT} = \ln \frac{P_0}{k_H} \tag{6}$$

With $P_o = 0.1$ MPa, we have the correlation of Henry's constant in terms of standard state chemical potentials

$$-\mu^*_{1(aq)} + \mu^*_{1(g)} = RT \ln \frac{0.1\ MP_a}{k_{H_1^P}} \tag{7}$$

Henry's constant of PM in pure water at 298.15 K ($k_{H_1^P} = 35.35$ MPa) was reported by Coquelet and Richon,[8] and the standard state Gibbs energy of formation of PM μ_1^o is taken from Pennington et al.[9] Thus, we have $-\mu_1^* + \mu_1^o = -14.54\ kJ \cdot mol^{-1}$ which enables us to calculate the standard state chemical potential of PM(aq) at 298.15 K.

The enthalpy of formation of PM(aq) at 298.15 K is required for the calculation of the standard state chemical potential at temperatures different from 298.15 K. The value reported by Barrow and Pitzer[10] was used. The values are shown in Table 4.

The standard state chemical potential and the standard state enthalpy of formation of the PM^- ion were calculated with the help of the acid dissociation constant reported by Yabroff[11] of PM in water. CH_4 is supercritical under the present experimental conditions. A temperature- and pressure-dependent Henry's

Table 2. Regressed and Used UNIQUAC *r* and *q* Parameters

system	r	q
$H_2O(l)$	0.92[a]	1.40[a]
$CH_4(aq)$	7.68	5.24
PM(aq)	8.57[b]	7.83[b]
$OH^-(aq)$	9.40[a]	8.82[a]
$PM^-(aq)$	7.16	7.16

[a] Taken from Abrams and Prausnitz.[13] [b] Taken from Thomsen et al.[15]

Table 3. Regressed Extended UNIQUAC Binary Interaction Parameters[a]

interaction	u_{ij}°	u_{ij}^{t}/K
$CH_4(aq) + H_2O$	300[b]	5.11
$PM(aq) + H_2O$	60.74	0.20
$PM^-(aq) + H_2O$	300[b]	0[b]
PM(aq) + PM(aq)	−249.42	0.097
$CH_4(aq) + CH_4(aq)$	0[b]	0[b]

[a] The interaction parameters between CH_4 + PM, CH_4 + OH^-, CH_4 + PM^-, PM + OH^-, PM^- + PM, and PM^- + OH^- were fixed at $u_{ij}^{\circ} = 10^9$ and $u_{ij}^{t} = 0$ indicating no interaction based on the limited number of data available for parameter regression. More data would be necessary to get confirmation. [b] This parameter was not fitted to experimental data.

Table 4. Calculated and Used Standard State Thermodynamic Properties

component	$\Delta_f G^\circ$ / $kJ \cdot mol^{-1}$	$\Delta_f H^\circ$ / $kJ \cdot mol^{-1}$
$H_2O(l)$	−237.13[a]	−285.83[a]
PM(aq)	12.51	−79.80[b]
$OH^-(aq)$	−157.25[c]	−230.24[c]
$PM^-(aq)$	72.32	−77.74

[a] Taken from ref 22. [b] Taken from ref 10. [c] Taken from ref 16.

constant correlation from Crovetto et al.[12] for CH_4 was used rather than using standard state chemical potentials, unavailable at supercritical conditions.

The UNIQUAC volume (r) and surface area parameter (q) for H_2O were taken from Abrams and Prausnitz.[13] The corresponding parameters for H^+ and OH^- were taken from Thomsen et al.[14] The r and q parameters determined for 1-propanol by Thomsen et al.[15] were used for *n*-PM, based on the similarity in molecular structure. The r and q parameters of CH_4 and PM^- and the temperature-dependent binary interaction parameters for $CH_4(aq) + H_2O$ and $PM(aq) + H_2O$ were fitted to the ternary VLE data measured in this investigation and some data from the literature.[10,16]

Table 8. Experimental Solubility Data of CH_4 (2) in Water (3) (This Work)

P / MPa	T / K	$10^4 \cdot x_2$	m_2 / $mol \cdot kg^{-1}$
0.993	298.78	2.3	0.013
2.795	298.77	6.4	0.035
5.991	298.78	12	0.068
7.893	298.78	15	0.088
1.142	314.25	2.1	0.013
2.514	314.28	4.3	0.025
7.892	314.27	13	0.075
9.981	314.24	16	0.089

Results and Discussions

New VLE data for the PM + CH_4 + H_2O system have been reported in this work. The total pressure of the system was varied from (1 to 8) MPa at the three temperatures (303, 323, and 365.15) K as shown in Tables 5, 6, and 7, respectively. The solubility data of CH_4 in pure water have been generated at two temperatures, (298 and 314) K, using the same “static-analytic” apparatus to validate the experimental technique and methodology. Several different concentration scales are used in electrolyte thermodynamics, two of them being molality and mole fraction. The concentration scale of molarity is temperature dependent and therefore not practical in thermodynamic modeling.[16] Here the molality of CH_4 in water, m_{CH4}, is calculated and expressed in $mol \cdot kg\ H_2O^{-1}$ as shown in Table 8 and plotted in Figure 2 with some selected data from the literature.[17] The solubility data of CH_4 in water are in good agreement with literature values. Furthermore, it is difficult to make a direct

Table 5. Experimental VLE Data for PM (1) + CH_4 (2) + H_2O (3) at 302 K (This Work)

T / K	P / MPa	$10^3 \cdot x_1$	$10^3 \cdot x_2$	$10^5 \cdot \sigma x_1$	$10^4 \cdot \sigma x_2$	$10^3 \cdot y_1$	y_2	$10^5 \cdot \sigma y_1$	$10^5 \cdot \sigma y_2$
302.68	1.026	0.138	0.25	0.8	0.1	8.12	0.9919	22	23
302.77	2.078	0.120	0.52	0.7	0.3	4.99	0.9950	14	14
302.63	3.936	0.101	0.98	0.5	0.5	2.24	0.9978	6	6
302.66	6.765	0.095	1.53	0.5	0.8	1.19	0.9988	3	3
302.66	8.018	0.081	1.81	0.4	1.2	1.19	0.9988	3	3

Table 6. Experimental VLE Data for PM (1) + CH_4 (2) + H_2O (3) at 322 K (This Work)

T / K	P / MPa	$10^3 \cdot x_1$	$10^3 \cdot x_2$	$10^5 \cdot \sigma x_1$	$10^4 \cdot \sigma x_2$	$10^3 \cdot y_1$	y_2	$10^5 \cdot \sigma y_1$	$10^5 \cdot \sigma y_2$
322.73	1.243	0.131	0.21	0.5	0.1	5.84	0.99416	16	16
322.72	2.315	0.071	0.44	0.4	0.2	2.53	0.99747	7	7
322.71	4.021	0.059	0.81	0.3	0.4	1.35	0.99865	4	4
322.74	6.727	0.050	1.42	0.3	0.8	0.75	0.99925	2	2
322.72	8.073	0.035	1.76	0.2	1.0	0.61	0.99939	2	2

Table 7. Experimental VLE Data for PM (1) + CH_4 (2) + H_2O (3) at 365 K (This Work)

T / K	P / MPa	$10^3 \cdot x_1$	$10^3 \cdot x_2$	$10^5 \cdot \sigma x_1$	$10^4 \cdot \sigma x_2$	$10^3 \cdot y_1$	y_2	$10^5 \cdot \sigma y_1$	$10^5 \cdot \sigma y_2$
365.73	1.341	0.037	0.13	0.2	0.1	6.24	0.99376	17	17
365.74	3.059	0.032	0.56	0.2	0.3	1.92	0.99806	5	5
365.72	4.969	0.024	0.96	0.1	0.5	0.32	0.99968	1	1
365.72	6.947	0.007	1.32	0.1	0.7	0.04	0.99996	0.1	0.1
365.87	9.516	0.015	1.91	0.1	1.1	0.88	0.99912	2	2

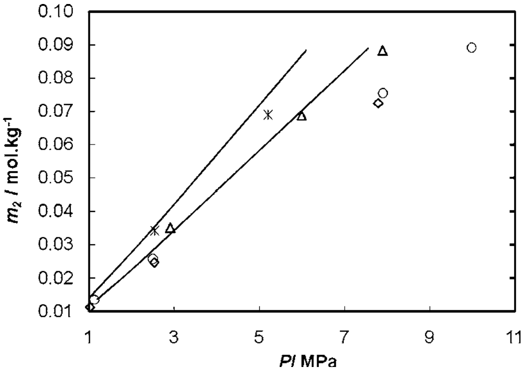

Figure 2. CH_4 (2) concentration in pure water (3) as a function of system pressure. This work at Δ, 298 K; this work at ○, 314 K; Chapoy et al.[17] at ◊, 298 K; and ∗, 313 K; solid lines, extended UNIQUAC.

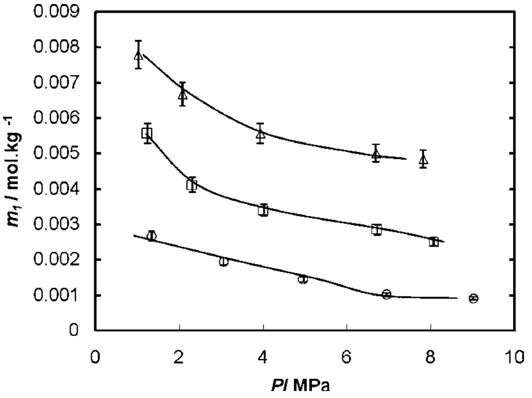

Figure 3. PM (1) concentration in the PM (1) + CH_4 (2) + H_2O (3) mixture at various temperatures. Δ, 302 K; □, 322 K; ○, 365 K; solid lines, extended UNIQUAC calculation (this work). CH_4 is used to pressurize the system. Uncertainty: 5 %.

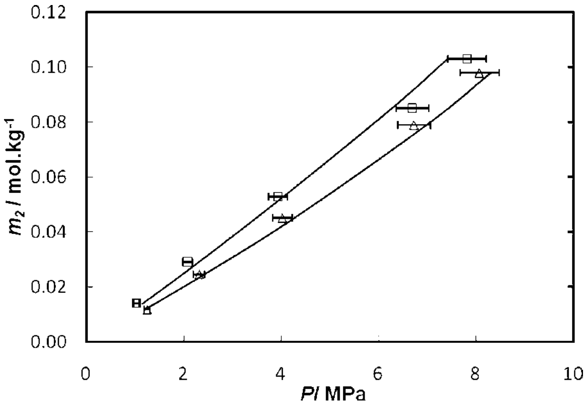

Figure 4. CH_4 (2) concentration in the PM (1) + CH_4 (2) + H_2O (3) mixture at various temperatures. □, 302 K; Δ, 322 K; solid lines, extended UNIQUAC calculation (this work). Uncertainty: 5 %.

Table 9. Ionization Constant of Mercaptan in Water at 293.15 K[4]

component	K_a/K_w
ethyl mercaptan	3710
propyl mercaptan	3320
butyl mercaptan	3250
heptyl mercaptan	2600

comparison for the system containing PM + CH_4 + H_2O as no ternary data are available in the literature.

The result of the extended UNIQUAC model calculations for VLE in the PM + CH_4 + H_2O system is demonstrated in Figures 3 and 4. It shows a good correlation of the experimental data as well as for experimental vapor pressure data of pure PM taken from the literature.

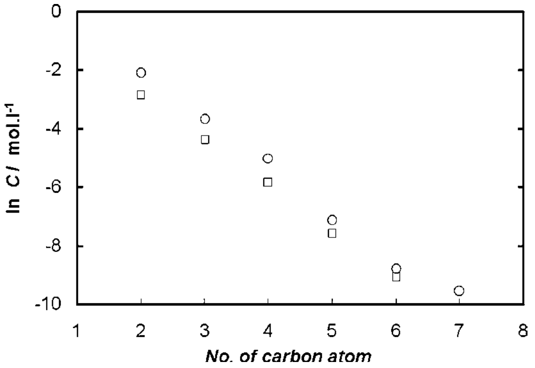

Figure 5. The solubility of ○, *n*-mercaptans[10] and □, *n*-hydrocarbons[16] in pure water at 293.15 K.

The ionization constants for mercaptans were reported by Yabroff and White[5] (see Table 9). The equilibrium constant of *n*-butyl mercaptan (*n*-BM) at alkaline conditions in water at 301 K is $K_{eq} = K_a/K_w = 2489$ (K_a is the acid dissociation constant, while K_w is the self-ionization constant of water having fixed value of $1 \cdot 10^{-14}$ under standard temperature and pressure conditions), as reported by Matsis et al.[18] This value indicates a minor dissociation of *n*-BM(aq) into *n*-BM$^-$ and H$^+$. The permittivity of a solvent like alkanolamine may affect the reaction rate between the solvent itself and mercaptans, as discussed by Yakupov et al.[19] The solvent may therefore also affect the rate of dissociation of mercaptan. The solubilities of mercaptans have been discussed by Bedell and Miller[20] as the sum of physical and chemical solubility on the basis of the acid−base neutralization approach in an alkanolamine solution. Methyl mercaptan and ethyl mercaptan (EM) are weak acids, but higher mercaptans behave like hydrocarbons as the alkyl group increases.[1,21] It is observed that the solubility of mercaptan is always higher than that of hydrocarbons with a similar carbon number as shown in Figure 5.

Conclusions

New VLE data of the PM + CH_4 + H_2O system have been measured at pressures from (1 to 8) MPa under moderate temperature conditions. A "static-analytic" apparatus has been used which takes advantage of ROLSI samplers and chromatographic analyses. The extended UNIQUAC model for electrolytes has been shown to be a good thermodynamic model for the VLE representation of the PM + CH_4 + H_2O system at low concentrations of PM. It only requires the UNIQUAC surface and volume parameters and binary interaction parameters. The same set of interaction parameters is used to represent VLE of pure PM with a good accuracy.

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