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Published in:
Fluid Phase Equilibria

Link to article, DOI:
[10.1016/j.fluid.2019.112276](https://doi.org/10.1016/j.fluid.2019.112276)

Publication date:
2019

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):

Kruger, F., Varsos, A. A., Kontogeorgis, G. M., & von Solms, N. (2019). High-pressure experimental vapour-liquid-liquid equilibrium measurements and modelling for natural gas processing: Equipment validation, and the system $\text{CH}_4 + n\text{C}_6\text{H}_{14} + \text{H}_2\text{O}$. *Fluid Phase Equilibria*, 501, [112276]. <https://doi.org/10.1016/j.fluid.2019.112276>

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High-pressure experimental vapour-liquid-liquid equilibrium measurements and modelling for natural gas processing

Equipment validation, and the system $\text{CH}_4 + n\text{C}_6\text{H}_{14} + \text{H}_2\text{O}$

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Abstract

Despite its relevance for oil and gas separation processes, surprisingly few experimental three-phase data are available in the open literature for gas-condensate-water systems. In support of proposed subsea processing facilities, a three-phase equilibrium measurement apparatus has been recommissioned for the measurement of $C_1+nC_6+H_2O$ systems between 303-323 K. The apparatus has been validated by comparison with literature VLE data for C_1+H_2O and C_1+nC_6 , with the experimental uncertainty estimated at $\pm 9\%$ (95% confidence interval).

81 new three-phase $C_1+nC_6+H_2O$ data points have been generated for three different feed mixtures. The relative compositions in each phase are strongly correlated to the experimental feed composition, while the solubility-temperature trends indicate complex interactions in the system. The repeatability of the measurements ranges from below 1% for major components up to 10-20% for trace components in the respective phases. Experimental standard deviations are comparable with those reported for literature data.

The data have been modelled using the CPA and sPC-SAFT equations of state. Satisfactory results were achieved for major components (accuracy between 1-6%), while order of magnitude errors were observed for certain trace components (e.g. water in the HC-rich phase). Overall, sPC-SAFT provided slightly better predictions compared to the CPA, but the differences are rather modest.

Graphical abstract

Keywords: experimental phase equilibrium data, VLE, VLLE, cubic-plus-association, sPC-SAFT;

Highlights

- New VLLE data have been measured for methane, *n*-hexane and water systems
- Compositional uncertainty estimated at $\pm 9\%$ (95% confidence interval)
- sPC-SAFT and CPA provide very similar predictions for these systems

1.Introduction

With the expansion of subsea processing capabilities, underwater natural gas production facilities have recently been proposed by Equinor. [1] The Gas-2-Pipe™ (G2P) process considers two main steps: pre-separation of gas-condensate-water mixtures, followed by compression and dehydration of the resultant wet gas to produce on-spec natural gas. Subsea separation and processing offer several advantages over traditional approaches, mostly related to limitations and risks inherent to multiphase pipelines. These advantages include: [2]

- Increased product recovery and energy efficiency
- Reduced capital and operating expenditure
- Extended operational lifetimes
- Increased number of viable reserves
- Improved flow assurance

Due to the proximity to the reservoir and depending on installation depth and location, higher pressures and colder temperatures would likely occur. For this reason, new experimental data are measured. The importance of experimental data cannot be overstated, as was highlighted in a statement by Prof. Dominique Richon: [3]

“Some people think that experimental work, compared to modelling and simulation, is more tedious, more expensive, and less appreciated in our community. However, numerous e-mail exchanges have confirmed my feeling that good thermodynamic data are absolutely necessary, because process design relies on accurate modelling and accurate modelling relies on reliable experimental data.”

In our previous studies [4,5] we measured two-phase experimental data related to the dehydration step in the G2P^{TM} process. The present study is concerned with thermodynamic behaviour of mixtures representative of the three-phase pre-separation step. Systems containing methane (C₁), *n*-hexane (nC₆) and water (H₂O) have been investigated using a vapour-liquid-liquid equilibrium (VLLE) experimental apparatus [6] which has been modified since previous publication. In this work we firstly present binary VLE data, which are used for the verification of the experimental apparatus. Several data sets are available for C₁+H₂O meaning that comparisons can be made with a relatively high degree of certainty. C₁+nC₆ is equally well-studied with over 70 data sets found in NIST TDE [7], although there were fewer data sets available in the temperature range of interest to this study.

Table 1: Binary VLE data selected for validation of the experimental data

System	Source	Type	T [K]	P [MPa]	Reported uncertainty (molar comp.)
C ₁ +H ₂ O	Yarymagaev <i>et al.</i> [8]	TPxy	313	2.5-12.5	±0.001
	Frost <i>et al.</i> [9]	TPxy	313	5.5-16.8	±3%
	Kiepe <i>et al.</i> [10]	TPx	313	0.4-8.4	-
	Chapoy <i>et al.</i> [11]	TPx	313	1.0-18.0	-
	Campos <i>et al.</i> [12]	TPx	313	0.1-0.7	±0.5·10 ⁻⁶
	Awan <i>et al.</i> [13]	TPx	314	1.1-10.0	1.5-2.0%
C ₁ +nC ₆	Shim & Kohn [14]	TPxy	298	1.0-16.2	±0.002
	Kandil <i>et al.</i> [15]	TPxy	303	2.1-14.2	±0.013-0.015
	Poston & McKetta [16]	TPx	311, 344	3.5-19.8	±0.002
	Cebola <i>et al.</i> [17]	TPx	348	2.3-10.3	±0.003

In the selection of data presented in Table 1, preference was given to sources where both the liquid and vapour phases (i.e. TPxy data) were reported. Due to the design of experimental apparatus, it is however more typical to see only the liquid phase composition reported.

LLE data for *n*-alkane+H₂O systems have been reviewed in detail by Mączyński *et al.* [18] where the solubility of *n*-alkanes in water exhibits a minimum at room temperature and ambient pressure. It cannot be determined whether the solubility minimum holds for high-pressure data, as those measured by Tsonopoulos & Wilson [19] (0.3-3.5 MPa) were at temperatures above where such a minimum may exist.

While several binary VLE and LLE data can be found in the open literature, surprisingly few data sources are available for ternary and multicomponent VLE and VLLE systems. The literature data for systems containing methane, water and an *n*-alkane are given in Table 2.

Table 2: Literature data for ternary VLE/VLLE of C₁+H₂O+alkane

System	Source	Type	T [K]	P [MPa]	Uncertainty
<i>n</i> C ₅	Gillespie & Wilson [20]	VLE/VLLE	311-589	3.1-20.7	±5%
<i>n</i> C ₇	Susilo <i>et al.</i> [21]	VLLE	276	0.1-2.0	See discussion
<i>n</i> C ₁₀	Ng and Chen [22]	VLLE	311, 394	13.8	See discussion

Gillespie & Wilson [20] detected two liquid phases (VLLE) T ∈ [366, 422] K and P ∈ [3.1, 6.2] MPa. Meanwhile at higher pressures (≥ 13.8 MPa) for T ∈ [366, 422] K and all pressures at other temperatures (311, ≥ 476 K), only vapour and an aqueous phase (VLE) are reported. In the three-phase region it is observed that vapour content of *n*C₅ was quite erratic. Susilo *et al.* [21] also included data for *neohexane*, *tert*-butyl methyl ether and methylcyclohexane. The uncertainty of their data was explicitly not stated, but the standard deviations for all measurements were provided. Three-phase behaviour is found in all cases here [21], although both

the temperature and pressure ranges are lower than those studied by Gillespie and Wilson [20]. In both the previous cases, the experimental feed compositions were not reported. Ng and Chen [22] measured three-phase data only and did report experimental feed conditions. Their uncertainty is given as ± 0.003 for major components and it is stated that *“minor components are thought to be within $\pm 10\%$ of the reported value”*. The main aim of this study, following verification of the apparatus with binary measurements, is to produce new VLLE data for $C_1+nC_6+H_2O$ at temperatures and pressures of interest to subsea separation processes. Of interest also, is evaluating the ability of relevant thermodynamic models to model these new multiphase data.

Several thermodynamic models may be used for natural gas and condensate processing applications. Various equations of state, activity coefficient models and even machine learning applications are found in the literature. For this study we are specifically interested in models such as the simplified Perturbed-Chain Statistical Associating Fluid Theory (sPC-SAFT) [23] and the Cubic-Plus-Association (CPA) [24,25] equations of state which offer prediction at high pressure and were developed specifically to describe mixtures which contain hydrogen-bonding compounds like water. Standard literature versions of these models have been used in this study. A summary of the models is provided in the Supporting Information, while complete reviews are available in other sources: CPA [26,27] and SAFT-type equations of state [28–32].

In a recent study by Liang *et al.* [33], both CPA and sPC-SAFT were evaluated against experimental data related to gas hydrate systems which typically contain water, hydrocarbons and MeOH/glycols. It was found that both models exhibit *“equally good performance”*. Tzirakis *et al.* [34] evaluated CPA for the correlation of several three-phase MEG-related systems. The magnitude of prediction errors varied significantly across the three phases, with low errors (typically $< 2\%$) for the main components in each phases up to very large errors ($\sim 350\%$) for trace components (such as H_2O in the HC-rich phase). Other interesting/relevant applications of (s)PC-SAFT include: prediction of natural gas and gas condensate dew points and liquid drop out [35,36],

hydrate fluid-phase equilibria modelling [37], modelling of *n*-alkanes and water mixtures [38], and LLE of petroleum fluids [39].

Multicomponent data are not typically used for fine-tuning models. It is however still important to understand the model accuracy for complex mixtures in order to make informed process design decisions and the requirement for additional multicomponent data was highlighted by Liang *et al.* [33]. To this end it is also crucial to understand the uncertainty of experimental data (and how it was determined), such that an informed comparison of the differences between the model/design and data can be made. An increased drive in recent years has led to the forced reporting of experimental uncertainty in major academic journals. Quality control has been implemented by NIST, whereby experimental data are now thoroughly checked before publication.[40]

2. Experimental methodology

A series of binary and ternary VLE and VLLE measurements have been made using an analytical isothermal equilibrium cell. The apparatus was originally designed and commissioned by Frost *et al.* [6,41] and following modifications, the apparatus was recommissioned. A new gas chromatograph (GC) has been installed, which meant that the analytical accuracy of the apparatus needed to be verified. The experimental apparatus is presented in Figure 1.

Figure 1: Experimental apparatus used in this study: (CG) GC carrier gas; (TC) temperature controller; (TT/PT) temperature/pressure transmitter; (R) ROLSI™ valve; dashed lines refer to temperature-controlled regions; dotted lines refer to electronic signals

2.1. Experimental Apparatus

2.1.1. The equilibrium cell

The equilibrium cell ($V = 60 \text{ cm}^3$) for the most part has remained unchanged from the original design of Frost *et al.* [6,41], with only a minor modifications to resolve leaking issues and a larger motor for the magnetic

stirrer. The screw mechanism for securing the sapphire windows to the cell has been replaced with a stainless steel cap and gasket, which is held in place by 10 small threaded screws.

The temperature and pressure measurement equipment has remained the same. The temperature is measured using a PT100 probe (Dostmann Electronic GmbH), which has a quoted precision and resolution of 0.1 and 0.01 K respectively. The pressure inside the cell is measured using a high precision Keller 33X pressure transmitter, which includes temperature compensation and can measure up to 50 MPa with a quoted accuracy of 0.1% of full scale. This translates to a standard uncertainty $u(P) = \pm 0.05$ MPa for the data presented in this work. Both temperature and pressure readings are recorded using an Agilent 34970A data acquisition system. The cell is equipped with two ROLSI™ valves [42] which are connected to a newly commissioned gas chromatograph (GC). The ROLSI™ valves are electro-magnetic valves which have been designed for the express purpose of multiple sampling from VLE/VLLE mixtures (without disturbing the equilibrium) and have been utilized in several experimental studies. The ROLSI™ valves sample from the equilibrium cell via two capillaries ($\phi = 0.1\text{mm}$) which penetrate into the cell at different heights (see figures 1-2).

Figure 2: View of a three-phase mixture through the sapphire window with clearly visible phase boundaries. The gas-liquid interface can be seen near to the top of the cell, with the liquid-liquid interface near the bottom. The ROLSI™ valve capillary tube can be seen entering the top-left of the cell and sampling from the HC-rich liquid.

2.1.2. GC specification and method

The installation of an Agilent 7890B GC (effectively the red-shaded region in Figure 1) represents the most significant change which has been made to experimental apparatus. In terms of capabilities, GC was specified as a like-for-like replacement of the previous setup with the following specifications:

- 100 psi S/SL inlet
- Packed inlet with septum purge
- FID and TCD in series
- PoraBond U and DB-WAX-UI columns (only one can be used at a time)

Based on input from subject matter experts at Agilent, the experimental data presented in this work were measured using the PoraBOND U column (part number CP7381, I.D. = 0.32 mm, L = 25 m, film = 7 μ m). A detailed description of the experimental setup and GC method development is available elsewhere [43]. Methane and *n*-hexane were quantified using the FID detector while water was quantified using the TCD detector. Calibration curves were made for injections in range of 0.1-0.5 μ L to match as closely as possible the expected sample sizes. Although smaller injection volumes were desirable, these could not be achieved with desired repeatability. The peak response areas were resolved using Agilent's OpenLAB CDS software. At least three injections were made for each point on the calibration curves, and the response factor was calculated by linear regression of the data through the origin (i.e. $c=0$). Overall, good R^2 values were attained for all components. The lowest value was 0.994 for water, while the hydrocarbons were all $R^2 > 0.997$ due to the larger peak response of the FID. The relative standard deviation (RSD) of the measurements ranged between 2-5 % with the highest variance occurring for the smallest injected volumes. The GC settings and calibration curves are provided in the Supporting Information.

2.2. Materials and methods

2.2.1. Material specifications

The pure compounds used both in the binary VLE and the VLLE experiments are given in Table 3.

Table 3: Chemical specifications for compounds used in this study

	Formula	CAS No.	Supplier	Purity	Impurities
C₁	CH ₄	74-82-8	Air Liquide (CHEMGAZ 4)	>99.999%	H ₂ O < 1 ppm
H₂O	H ₂ O	7732-18-5	DTU Campus Service	Ultra-pure (see discussion)	Conductivity < 1 μ S/cm
nC₆	C ₆ H ₁₄	110-54-3	Sigma-Aldrich ReagentPlus® 139386	>99%	

No additional purification was performed for the compounds listed in Table 3. The water used in this study has undergone a 5-stage purification process with a final product conductivity specification of 1 μ S/cm. During field-checks the conductivity never exceeded 0.6 μ S/cm which is in line with commercially available HPLC grade products. Although no further information was provided by the *n*-hexane supplier, only one clear peak was observed during GC-calibration injections.

2.2.2. Experimental method

In preparation for an experiment, the cell is washed with acetone and left under vacuum overnight. Before an experiment commences, the liquid and gas loading pathways are also placed under vacuum. A minimum vacuum of $P < 0.021$ kPa on the vacuum pump pressure indicator is required before the equilibrium cell is loaded. Degassed liquid is loaded under vacuum. The cell is then pressurized with methane from a gas bottle. For ternary mixtures, it is necessary to quantify the exact feed composition. Methane was loaded from a small pressurized gas bomb which could be weighed before and after loading.

The entire cell is then submerged in the liquid bath, the magnetic stirrer is switched on and the mixture is left overnight to reach equilibrium. Cell pressure stabilized within 6 hours and a mixture was considered to be at equilibrium when fluctuations within ± 0.1 K and $\pm 0.05\%$ of the measured pressure are observed.

A bake out and purge method (5 samples) was run before sampling. Samples are transported to the GC using helium carrier gas which is heated to 393 K and the GC inlet is heated to 473 K. The sample then enters the oven section and GC column, where different temperature programs have been optimized for the specific phase being sampled. 3-6 samples were taken from each phase using the ROLSI™ valves ($t_{\text{open}} = 0.6$ s) and when switching between liquid phases, the sampling pathway was purged again to reduce the risk of contamination of the samples.

2.2.3. Experimental parameters

The experiments have been divided into three different segments. The first two segments (V1 and V2) are the validation data measured for C_1+H_2O/nC_6 . E3 is new VLE data measured for $C_1+nC_6+H_2O$ (three different feed compositions: 3.1-3.3) with each feed composition was evaluated at three temperatures (303, 313 and 323 K). Even though several samples were extracted at each step, this was shown to have a negligible impact on the overall composition. The experimental conditions are summarized in Table 4, where the feed compositions of the binary systems* are shown as estimates.

Table 4: Experimental conditions (temperature, pressure and feed concentrations) for the equipment validation experiments (V1-V2) and new VLE data (E3: $C_1+nC_6+H_2O$)

Campaign	Mixture	T [K]	P [MPa]	z_{C1}	z_{nC6}	z_{H2O}
V1	*	313	1.0-11	0.01-0.07	-	0.99-0.93
V2	*	303	2.6-9.4	0.12-0.33	0.88-0.67	-
E3	3.1	303-323	6.2-7.7	0.1408	0.1600	0.6992
	3.2	303-323	4.4-4.6	0.0747	0.1724	0.7530
	3.3	303-323	11-12	0.2603	0.1378	0.6019

2.3. Experimental uncertainty

The standard uncertainties for temperature and pressure are based on the temperature controller and the pressure transmitter such that $u(T) = 0.5$ K and $u(P) = 0.05$ MPa. For the compositional measurements the uncertainty is calculated using the relative standard deviation ($RSD = |\sigma/\bar{x}|$) and a confidence interval multiplier (CI) as per Eq. 1.

$$u_{r,x} = \frac{CI \cdot \sigma_x}{|\bar{x}|} \cdot 100 [\%]$$

Eq. 1

σ and $\bar{x}$ represent the standard deviation and average value of the samples taken for each measurement. CI $\in \{1, 2, 3\}$ depending on the desired level of confidence: 0.683, 0.995 or 0.997. For a 95% confidence interval, CI = 1.96. Based on the repeatability of our measurements/calibrations and comparisons with literature data (see section 3.1), we estimate an experimental uncertainty of $\pm 9\%$ using a 95% confidence interval. **It is important to highlight that the compositional repeatability considers only the variance of the analyses within a given experiment and not the repeatability for that experiment.** With the current apparatus design and gas loading procedure, accurately repeating a specific feed mixture is quite challenging.

3. Results & Discussion

3.1. Validation of experimental apparatus

The experimental data for the verification/validation of the apparatus are split up into liquid phase and vapour phase composition for C_1+H_2O and C_1+nC_6 , and are presented in figures 3-7 respectively. The respective data are reported in Appendix A (tables A1-A2).

3.1.1. C_1+H_2O binary vapor-liquid equilibria

The first binary mixture which was examined is C_1+H_2O at 40 °C (313.15 K) and pressure range of 1.0-10.5 MPa. The experimental results for the methane solubility in the liquid phase are presented in Figure 3.

Figure 3: Experimental solubility of methane in water at 313 K and comparison with experimental data from: Yarymagaev et al. [8], Frost et al. [9], Kiepe et al. [10] Campos et al. [12] and Awan et al. [13]. Standard uncertainties $u(T) = 0.5$ K and $u(P) = 0.05$ MPa

Figure 3 presents liquid phase data measured in comparison with several literature sources with which very good agreement is achieved in general. The average RSD for the liquid phase data is 4.7%. Our data shows the best agreement with that of Kiepe *et al.* [10] while the worst agreement is with that of Frost *et al.* [9]. At low pressures, our data fall roughly between that of Campos *et al.* [12] and Kiepe *et al.* [10]. Meanwhile for medium pressure and upwards, our data slightly overshoots most of the literature sources. All the data follow the same trend at high pressure where the solubility-pressure gradient gradually decreases.

Similarly, Figure 4 compares water content in the vapour phase from this work with those from literature.

Figure 4: Experimental solubility of water in the vapor phase at 313 K and comparison with experimental data from: Yarymagaev *et al.* [8] and Frost *et al.* [9]. Standard uncertainties: $u(T) = 0.5$ K and $u(P) = 0.05$ MPa

Very good agreement with literature data is observed in Figure 4. Higher water vapour content is recorded at low pressure while slightly lower water vapour is observed at high pressure. The 95% confidence intervals are shown in the figure, which are based on an average relative standard deviation for the data (4.9%). If two outliers are ignored, the respective RSD for the C_1+H_2O TPx and TPy data lowers to 3.2% and 4.2%. This

translates to an experimental uncertainty of 6-8.5% (95% CI). Although the uncertainty is relatively high compared to that quoted in some sources in the literature, some of these sources may be overstating their accuracy. It is not uncommon to see two sources claim accuracies better than 2% while differing by >10% from one another. In this work we have emphasized the use of conservative (i.e. wider) uncertainty ranges.

3.1.2. C_1+nC_6 binary vapor-liquid equilibria

The second binary mixture which was studied is the C_1+nC_6 at 30°C (303.15 K) and pressures of 2.5-9.5 MPa.

Figure 5: Experimental solubility of methane in n-hexane at 303 K and comparison with experimental data from: Shim & Kohn [14], Kandil *et al.* [15], Poston & McKetta [16] and Cebola *et al.* [17]. Standard uncertainties: $u(T) = 0.5$ K and $u(P) = 0.05$ MPa

In Figure 5 liquid phase solubility (T_x) data are compared with literature data from Kandil *et al.* [15] (at the same temperature), Shim & Kohn [14] (slightly lower temperature), and Poston & McKetta [16] and Cebola *et al.* [17] (higher temperatures).

Additional data at different temperatures have been included to supplement the limited data at 303 K.

The temperature trends between the various data sets require additional investigation. In Figure 6, the literature data at 298, 310, 344 and 348 K are fitted with linear trends (as a rough guide for the eye) in the range 3-10 MPa and a temperature scale (vertical dashed orange line). For the sake of readability, our data and that of Kandil *et al.* (both at 303 K) have not been fitted. If fitted, those trends would align roughly with the data of Shim *et al.* (for Kandil *et al.*) and the Poston & McKetta 310 K data (for our work), which is a clear discrepancy. Following this finding we checked the calibration of our temperature probe to confirm correct operation. Furthermore, when analysing the temperature scale on the graph it is evident that there is also a notable discrepancy in temperature differences between the ‘linearized’ trends as well. Depending on which temperature differential is considered, the value of $\left(\frac{\partial T}{\partial x}\right)_{P=7.5 \text{ MPa}}$ changes roughly from 7.5, 13.5 or 2.5 K·mol/mol. Considering these ‘inter-data’ uncertainties, it may be more prudent to reconsider the reported ‘intra-data’ uncertainties of less than ± 0.003 (shown in Table 1).

Figure 6: Experimental solubility of *n*-hexane in methane at 303 K and comparison with experimental data from: Shim & Kohn [14], Kandil *et al.* [15] and Poston & McKetta [16]. Standard uncertainties: $u(T) = 0.5 \text{ K}$ and $u(P) = 0.05 \text{ MPa}$

Despite the discrepancies between the data sets in terms of the temperature trends and the relatively high reported uncertainty of our work, the overall results indicate relatively good agreement with literature data sources. The average RSD for our data is 4.5%, meaning that the experimental uncertainty is $\pm 9\%$ on average (95% CI). The average however is very strongly influenced by the uncertainty of the point at 2.6 MPa. Given the insensitivity to temperature in relation to the magnitude of uncertainty ranges, it is difficult to draw any specific conclusions w.r.t. solubility-temperature trends.

Figure 7: Experimental solubility of *n*-hexane in methane at 303 K and comparison with experimental data from: Shim & Kohn [14], Kandil *et al.* [15] and Poston & McKetta [16]. Standard uncertainties: $u(T) = 0.5$ K and $u(P) = 0.05$ MPa

As is seen in Figure 7, good agreement with data from the literature is again achieved. As before for C_1+nC_6 liquid phase (Figure 6), there are again some (although fewer) discrepancies with respect to temperature trends. Ignoring the two obvious outliers of Kandil *et al.* [15], the data from this work shows good agreement. Our data lies between that of Shim & Kohn [14] (298 K) and Poston & McKetta [16] (344 K). There are again some discrepancies with the 310 K data, but this is similar to the results of and leads to the

same discussion as for Figure 6. The average RSD is 4.6%, meaning that the experimental uncertainty is estimated at $\pm 9\%$ (95% CI).

3.1.3. Summary of validation study

A comparison of experimental results for two binary VLE systems (C_1+H_2O and C_1+nC_6) shows fair agreement with several relevant literature data sources at temperatures and pressures of interest to our study of subsea separation processes. Moderate temperature deviations between various C_1+nC_6 sources were found. Based on the results presented in this section we are confident in stating that the uncertainty of our analytical methods is $\pm 9\%$ using a 95% confidence interval.

3.2. Newly measured ternary VLE data

The newly measured experimental VLE data are presented in Table 5. The uncertainties are reported as RSD [%] in Appendix A (see Table A 3). The repeatability of the measurements is comparable with that of Susilo *et al.* [21], and is analysed in greater detail in section 3.3. Selected data are presented graphically and discussed here (and in section 3.4 where the modelling of the data is presented and discussed), with the remainder of the graphs available in the Supporting Information (figures S3-S12).

Table 5: Experimental VLE data for $C_1+nC_6+H_2O$ for three different feed compositions (Exp 3.1-3.3) at 303, 313 and 323 K. Standard uncertainties: $u(T) = 0.5$ K and $u(P) = 0.05$ MPa

Exp. No.	T K	P MPa	Vapour phase			Hydrocarbon-rich phase			Aqueous phase		
			y_{C1} mol/mol	y_{nC6} mol/mol	y_{H2O} ppm	$x_{I,C1}$ mol/mol	$x_{I,nC6}$ mol/mol	$x_{I,H2O}$ mol/mol	$x_{II,C1}$ ppm	$x_{II,nC6}$ ppm	$x_{II,H2O}$ mol/mol
3.1a	303.2	7.7	0.967	0.0330	498	0.307	0.687	0.0059	2348	503	0.9971
3.1b	313.2	7.0	0.965	0.0347	530	0.269	0.711	0.0199	2177	144	0.9977
3.1c	323.2	6.2	0.962	0.0371	597	0.260	0.725	0.0156	1489	15	0.9985
3.2a	303.2	4.6	0.965	0.0348	137	0.210	0.780	0.0105	1123	17	0.9989
3.2b	313.2	4.6	0.953	0.0466	65	0.186	0.798	0.0163	1118	14	0.9989
3.2c	323.2	4.4	0.951	0.0489	147	0.191	0.796	0.0137	1048	16	0.9989
3.3a	303.2	10.8	0.9655	0.0345	60	0.468	0.530	0.0026	2571	49	0.9974
3.3b	313.2	11.2	0.9587	0.0411	169	0.408	0.591	0.0009	2598	26	0.9974
3.3c	323.2	11.7	0.9566	0.0431	272	0.413	0.586	0.0010	3159	18	0.9968

In general, each of the phases (vapour, HC-rich and aqueous) are dominated by a specific compound (methane, *n*-alkane, water respectively). The composition-temperature trends are for the most part ‘linear’, and the relative composition is strongly correlated to the feed composition (see discussion for Figure 8). In some cases, anomalous behaviour is observed e.g. water content in the HC-rich phase (see Figure 9). In terms

of comparison with similar data ($C_1+nC_5+H_2O$ [20] and $C_1+nC_7+H_2O$ [21]) from the literature it is observed that:

- This work and [20] report ppm levels of water vapour, while [21] reports significantly higher values for both y_{H_2O} and $y_{n\text{-alkane}}$
- x_{I,H_2O} is in the low mol% ranges for nC_5 [20] and nC_6 , but is 1-2 orders of magnitude lower for nC_7 [21]
- For the aqueous phase, the studies for nC_5 [20] and nC_6 (this work) are again comparable, while significantly less C_1 and $n\text{-alkane}$ is found for the nC_7 study

One cannot read too much into the comparisons of the results since the exact feed compositions are not known for both these studies and the temperature-pressure conditions are also significantly different.

Figure 8 presents the $n\text{-alkane}$ content of the HC-rich phase for all three experimental runs i.e. 9 experimental points. x_{I,nC_6} follows the trend of molar feed compositions where 3.3 has the least and 3.2 has the most $n\text{-alkane}$.

Figure 8: An example of consistent behaviour. HC-rich phase $n\text{-alkane}$ content of $C_1+nC_6+H_2O$ (3.1-3.3) at 303-323 K.

By comparison, the effects observed in Figure 9 (H_2O content in the HC-rich phase) are highly non-linear and not as easily explainable. At the lowest temperature of 303 K, the x_{I,H_2O} follows the feed compositions (3.3 with least water, 3.2 with the most), but as the temperature is increased we observe that 3.1 and 3.2 increase

and appear to have a maximum around 313 K, while 3.3 decreases and appears to have a minimum around 313 K.

Figure 9: An example of anomalous behaviour. HC-rich phase water content of $C_1+nC_6+H_2O$ (3.1-3.3) at 303-323 K.

The following general trends are observed in the data presented in Table 5:

- In the vapour phase
  - $\frac{\partial y_{C_1}}{\partial T}$ is negative while $\frac{\partial y_{nC_6}}{\partial T}$ and $\frac{\partial y_{H_2O}}{\partial T}$ are generally positive
- In the HC-rich phase:
  - C_1 and nC_6 appear to have minima and maxima around 313 K, although more data would be required to say this with certainty
- In the aqueous phase:
  - Mixture 3.3 (least H_2O , most C_1) has an inverse solubility-temperature gradient for C_1 compared to the data for mixtures 3.1-3.2

From the data measured in this work, it is observed that trends are complex. Given the complexity of the underlying binary systems (e.g. C_1+nC_6 is classified as Type IV according to system of van Konynenburg and Scott [44] and nC_6+H_2O is Type II [45]), non-ideal ternary behaviour should be expected. The classifications of $C_1+nC_5/nC_6/nC_7$ are Type II, IV and III respectively, meaning that the mixtures do not exhibit exactly equivalent behaviour. Given the progressive asymmetry of the $C_1+nC_5/nC_6/nC_7$ binaries within the ternary

mixture, one would expect the ternary mixtures to become more non-ideal as the alkane chain length increases.

3.3. Comparison of experimental repeatability

Although Susilo *et al.* [21] did not explicitly state the experimental uncertainty of their compositional measurements, they did publish the standard deviation for each measurement made. Therefore, it is possible to make a comparison of the repeatability of the measurements of the two studies. The results of this comparison are presented in Figure 10.

Figure 10: Comparison of relative standard deviations for compositional measurements in this work and Susilo *et al.* [21].

The data in Figure 10 has been grouped according to component (C_1 , H_2O , nC_6 , nC_7) in each phase (y – vapour, x_I – HC-rich liquid, x_{II} – aqueous), meaning that the reported RSD in the graph is the average of several experimental points. To keep the figure readable, only the data types from this work are labelled with call-outs, although in most cases the equivalent data type for Susilo *et al.* [21] appears in close proximity (along the horizontal axis). The data follow the expected trend of a roughly exponential increase in certainty (i.e. decreased RSD) with increased mole fraction and in general the data from both studies is quite comparable.

3.4. Modelling of experimental data

Standard literature versions of both CPA and sPC-SAFT have been used in this work. The pure component and mixture parameters are provided in Appendix B (Tables B1-B3) and a summary model equations is available in the Supporting Information. In certain cases, new binary interaction parameters (BIPs) were required, with the regression of these parameters discussed in section 3.4.1 below. All newly regressed BIPs are reported in Table B3 (Appendix B).

3.4.1. Binary interaction parameter regression

New BIPs were required for C_1+nC_6 (both models) and nC_6+H_2O (sPC-SAFT only). The same uncertainty analysis procedures have been implemented as in our previous work on parameterization [5,46]. Parameter confidence intervals were determined using the bootstrap method [47] with 256 repetitions.

For nC_6+H_2O the BIPs were fitted to high-pressure data of Tsonopoulos and Wilson [19]. Apart from the incorrectly predicted VLE point $(T, x_{l,H_2O}) = (473 \text{ K}, 0.11)$, sPC-SAFT correlates both phases with an average error of 21.9% and a very narrow confidence interval due to the small data set. Considering the temperature range of 100 K and the non-ideal nature of high-pressure LLE modelling, this result is quite satisfactory. Similar results were achieved using the CPA equation of state. In all cases, the models incorrectly predict VLE at higher temperatures unless the model-predicted saturation pressure is used. This occurs at around 335 K for ambient pressures and above 400 K for high pressure data, meaning that the modelling of the data measured in this study is not affected.

For the C_1+nC_6 system, new BIPs were fitted to VLE data of Shim & Kohn [14] over a wide range of temperature (248-423 K) and pressure (1-16 MPa). CPA required a smaller BIP, and in both cases the BIP uncertainty range is very narrow: ± 0.0002 for CPA and ± 0.0004 for sPC-SAFT (using a 95% confidence

interval). An example of the BIP distribution is shown in Figure 11. The average errors for CPA calculated during the uncertainty analysis were 0.26% and 1.5% for liquid and vapour phases. The sPC-SAFT the average errors were 0.57% and 1.1%. Therefore, CPA performed better in the correlation of TPx data while sPC-SAFT was better for TPy.

Figure 11: CPA- k_{ij} parameterization and uncertainty analysis for C_1+nC_6 VLE data from Shim & Kohn [14] using 256 repetitions

3.4.2. Modelling of three-phase data

The modelling performance of both CPA and sPC-SAFT were evaluated for our new experimental data, with both models performing quite similarly. Both models predicted three phases for all experimental conditions listed. Implementation of the newly regressed BIPs for C_1+nC_6 had the effect of increasing the absolute gradient of composition-temperature in the HC-rich phase and improved the description of the C_1 in the aqueous phase. The modelling results are summarized Table 6 and figures for each of the phases are provided in the Supporting Information (Figures S14-S22).

Table 6: Summary of modelling errors of newly measured $C_1+nC_6+H_2O$ VLE data using CPA and sPC-SAFT

	Mixture	Vapour Phase			HC-Rich Phase			Aqueous Phase		
		y_{C_1}	y_{nC_6}	y_{H_2O}	x_{I,C_1}	x_{I,nC_6}	x_{I,H_2O}	x_{II,C_1}	x_{II,nC_6}	x_{II,H_2O}
CPA	3.1	1.7%	49%	>100%	5.8%	1.9%	94%	41%	97%	0.1%
	3.2	2.4%	59%	>100%	4.5%	1.8%	94%	26%	93%	0.0%
	3.3	1.6%	41%	>100%	6.1%	4.9%	38%	39%	96%	0.1%
sPC-SAFT	3.1	1.5%	45%	>100%	4.8%	1.7%	93%	39%	96%	0.1%
	3.2	2.3%	57%	>100%	4.7%	2.0%	94%	24%	91%	0.0%
	3.3	1.2%	32%	>100%	6.0%	4.9%	37%	38%	95%	0.1%

For the main components in each phase (y_{C_1} , x_{I,nC_6} , x_{II,H_2O}) the modelling errors are typically below 3%. x_{I,C_1} is also well-predicted (less than 6% on average – see Figure 13), while the worst predictions are for H_2O in the vapour (especially) and HC-rich (see Figure 13) phases and nC_6 in the aqueous phase. Generally it is observed that sPC-SAFT provided slightly better modelling results.

For reference, the performance of CPA was also compared against the $C_1+nC_7+H_2O$ data of Susilo *et al.* [21] (see Figure S23 in the Supporting Information). The vapour phase H_2O and nC_7 content is underpredicted by 10-50% and 50% respectively, while the H_2O in the HC-rich phase and nC_7 in the aqueous phase are underpredicted by 1-2 orders of magnitude. This is comparable to the modelling results for the newly measured data shown in Figure 13, as well as the modelling errors shown by Tzirakis *et al.* [34] for similarly complex systems. The trend for C_1 in both the HC-rich and aqueous phases is quite well predicted, although in a few cases (specifically the HC-rich phase) the errors can be as large as 50%. Both models failed to predict a vapour phase at 2 MPa for the conditions given in the experimental setup. It was observed that the best modelling predictions were at low pressure (0.12 MPa), while the data measured in our study are all at least an order of magnitude higher than that value.

Figure 12: Example of good modelling performance by CPA and sPC-SAFT of the methane and *n*-alkane content in the HC-rich phase for mixture 3.1

Figure 13: Example of order of magnitude under-predictions by CPA and sPC-SAFT of the water content in the HC-rich phase (x_{I,H_2O}) for mixture 3.1. Similar results were observed for modelling of the data of Susilo et al. [21]

Given that $n\text{C}_6+\text{H}_2\text{O}$ exhibits the complex binary interactions, the model predictions might be improved by the implementation of Mathias-Copeman [48] (MC) parameters. Palma *et al.* [49] achieved excellent results for water-alkane LLE by fitting new MC parameters whilst applying specific restrictions in the parameterization. Polishuk *et al.* [50] have highlighted the effect of k_{ij} on LLE prediction and phase behaviour classification in their development of a global phase diagram method. Their work focussed on binary systems (water-alkane mixtures among others) and showed that relatively modest variation in k_{ij} can change the model classification of the phase behaviour e.g. from Type III to Type IV. [51] Although the correct phases are predicted by the models throughout this experimental study, the modelling might be improved by a careful application of the methods discussed here.

3.4.3. Summary of VLLE modelling

Three new BIPs (2 for sPC-SAFT, 1 for CPA) were found by implementing the bootstrap method for relevant LLE and VLE data. For VLE data, the average errors were less than 1.5% over a large temperature range (248-423 K). For the smaller subset of high-pressure LLE data, a larger modelling error of 22% was found. In all cases the uncertainty ranges were quite narrow.

Despite the use of BIPs for all three constituent systems, there will still be some problems in the prediction of trace components for the newly measured VLLE data. In some cases (such as $y_{\text{H}_2\text{O}}$) order of magnitude errors were observed, and this was also observed when modelling the *n*-heptane systems of Susilo *et al.* [21]. The comparison between CPA and sPC-SAFT showed only minor differences, although sPC-SAFT was slightly more accurate in most cases. The modelling of main components in each phase was satisfactory, with average errors below 1% for water in the aqueous phase, below 3% for methane in the vapour and *n*-hexane in the HC-rich phases and below 6% for methane in the HC-rich phase.

4. Conclusions

An older experimental apparatus has been recommissioned. Validation data have been measured for two binary systems: C_1+H_2O at 313 K and C_1+nC_6 at 303 K. The data compare favourably with other experimental data available in the literature and the uncertainty of the analytical methods were estimated at $\pm 9\%$ with a 95% confidence interval.

81 new ternary VLLE data have been produced for the $C_1+nC_6+H_2O$ system using three different feed compositions and three different temperatures (303, 313 and 323 K). Results were closely correlated with the relative composition of the experimental feed, especially for the main component in each of the respective phases. The repeatability of the newly measured data is comparable VLLE data for $C_1+nC_7+H_2O$ [21], where the expected inverse exponential trend between composition and uncertainty was observed.

New BIPs were regressed for both CPA and sPC-SAFT using statistical methods to quantify the uncertainty of the parameterization. Modelling results were quite satisfactory for main components ($< 6\%$ AARD) while in some cases order of magnitude errors were observed (especially for water in the vapour and HC-rich phases). Similar modelling difficulties were observed for comparable data sets from the literature.

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Acknowledgements

The authors gratefully acknowledge the financial support from Equinor A/S (Norway) for this work as part of the research project '*Thermodynamics of Petroleum Fluids relevant to Subsea Processing*' as part of the '*Chemicals for Gas Processing*' research programme.

Nomenclature

a_0	Attractive energy term (CPA) [$\text{bar cm}^6 / \text{mol}^2$]
AARD	Average absolute relative deviation
b	Co-volume (CPA) [cm^3/mol]
β	Association volume (CPA) [dimensionless]
BIP	Binary interaction parameter (CPA/sPC-SAFT) also k_{ij}
c_1	attractive energy temperature-correction (CPA) [dimensionless]
CG	carrier gas (for GC)
CI	Confidence interval (multiplier)
CPA	Cubic-Plus-Association equation of state
ε	association energy (CPA) [$\text{bar cm}^6 / \text{mol}$]
ε	energy (depth of the pair potential) (sPC-SAFT) [J]
ε^{AB}	energy of association (sPC-SAFT) [J]
FID	flame ionization detector
Γ	$= a_0/(b \cdot R)$ (CPA) [K]

G2P™	Gas-2-Pipe™ process
GC	gas chromatograph
I.D.	internal diameter – refers to GC column [mm]
κ^{AiBj}	volume of association (sPC-SAFT) [dimensionless]
L	Column length – refers to GC [m]
m	chain length/number (sPC-SAFT) [dimensionless]
MC	Mathias-Copeman (parameters)
P	Pressure [MPa]
PT	pressure transmitter
R	Universal gas constant = 8.314 J / (mol K)
RSD	Relative standard deviation = $ \sigma/\bar{x} $ with σ = standard deviation and $\bar{x}$ = mean value
σ	segment diameter (sPC-SAFT) [Å]
sPC-SAFT	simplified Perturbed-Chain Statistical Associating Fluid Theory
SRK	Soave-Redlich-Kwong equation of state
T	Temperature [K]
TC	temperature controller
TCD	thermal conductivity detector – universal detector (excluding the carrier gas)
t_{open}	ROLSI™ valve opening time
TPxy	Refers to experimental data types: Temperature-Pressure-Liquid-Vapour

T_R	Reduced temperature (T/T_c)
TT	temperature transmitter
u_R	Relative uncertainty = CI·RSD [%]
V	Volume (molar) [m^3/mol]
VLLE	Refers to phase composition data: Vapour-liquid-liquid equilibria
x_I, x_{II}	Liquid phases in VLLE: hydrocarbon-rich (HC-rich) phase, aqueous phase
z	Refers to experimental feed composition

Appendix A: Data tables

Standard uncertainties for all temperatures and pressures are reported as $u(T) = 0.5$ K and $u(P) = 0.05$ MPa.

Binary verification data

Table A 1: Measured data (V1: C_1 - H_2O) and uncertainty estimates used in the validation of the apparatus (see figures 3-4)

T [K]	P [MPa]	Results			Std Dev [mol/mol]		RSD [%]	
		x_1	y_1	y_2	x_1	y_2	x_1	y_2
313.15	1	0.0003	0.9854	0.0146	0.0000	0.0011	3.8%	7.5%
313.15	2.7	0.0006	0.9969	0.0031	0.0000	0.0001	5.5%	2.4%
313.15	6.8	0.0015	0.9990	0.0010	0.0000	0.0000	0.9%	2.7%
313.15	8.27	0.0017	0.9991	0.0009	0.0000	0.0001	1.9%	6.5%
313.15	10.5	0.0020	0.9992	0.0008	0.0002	0.0000	11.4%	5.3%
Average							4.7%	4.9%

Table A 2: Measured data (V2: C_1 - nC_6) and uncertainty estimates used in the validation of the apparatus (see figures 5-7)

T [K]	P [MPa]	Results			Std Dev [mol/mol]		RSD [%]	
		x_1	y_1	y_2	x_1	y_2	x_1	y_2
303.15	2.64	0.1522	0.9598	0.0402	0.0162	0.0025	10.7%	6.2%
303.15	4.09	0.1741	0.9731	0.0269	0.0060	0.0011	3.5%	4.2%
303.15	5.45	0.2421	0.9757	0.0243	0.0127	0.0004	5.2%	1.5%
303.15	6.51	0.2634	0.9768	0.0232	0.0126	0.0015	4.8%	6.6%
303.15	6.98	0.2857	-	-	0.0029	0.0006	1.0%	-
303.15	8.08	0.3222	-	-	0.0052	-	1.6%	-
303.15	9.19	-	0.9795	0.0205	0.0053	0.0009	-	4.6%
Average							4.5%	4.6%

New experimental data (uncertainty)

Table A 3: Uncertainty quantification (using relative standard deviation) for newly measured VLE data (C_1 - nC_6 - H_2O)

Exp. No.	T K	Vapour phase			Hydrocarbon-rich phase			Aqueous phase		
		y_{C1} %	y_{nC6} %	y_{H2O} %	$x_{I,C1}$ %	$x_{I,nC6}$ %	$x_{I,H2O}$ %	$x_{II,C1}$ %	$x_{II,nC6}$ %	$x_{II,H2O}$ %
3.1a	303.2	0.14	2.5	8.0	0.5	0.2	6.2	5.5	12	0.03
3.1b	313.2	0.11	3.3	15	1.9	0.4	26	7.4	23	0.02
3.1c	323.2	0.14	3.5	8.2	3.6	1.3	2.6	8.2	10	0.01
3.2a	303.2	0.07	2.0	7.6	2.6	0.7	3.7	0.6	2.4	0.001
3.2b	313.2	0.02	0.4	7.5	3.1	0.7	1.4	0.7	4.5	0.001
3.2c	323.2	0.11	2.1	14	0.9	0.2	4.0	0.4	1.2	0.000
3.3a	303.2	0.17	4.7	19	6.2	5.4	5.2	3.4	7.7	0.009
3.3b	313.2	0.42	9.9	13	0.79	0.56	10.1	0.1	3.3	0.000
3.3c	323.2	0.36	8.1	4.33	1.8	1.3	9.8	3.8	57	0.011

Appendix B: Equation of state model parameters

The pure component parameters used in this study are provided in Table B 1 (CPA) and Table B 2 (sPC-SAFT).

The binary interaction parameters are reported in Table B 3. Temperature-dependent correlations are used for the C_1+H_2O interaction, where temperature T is in Kelvin.

Table B 1: CPA pure component parameters applied for ternary VLE calculations. Critical properties from the DIPPR [52]

	T_c [K]	b [cm ³ /mol]	Γ [K]	c_1	ϵ [K]	$\beta \cdot 10^3$	Sch.	Ref.
C₁	190.6	29.10	959.03	0.44718	-	-	-	[53]
nC₆	507.6	107.89	2640.0	0.83130	-	-	-	[25]
H₂O	647.1	14.515	1018.4	0.67359	2003.248	69.2	4C	[25]

In terms of pure component parameter selection for sPC-SAFT, we compared the performance between “water no. 1” and “water no.2” from Liang *et al.* [33] for LLE prediction. Better performance was found with “water no. 2”, therefore it was used in this study.

Table B 2: sPC-SAFT pure component parameters applied for ternary VLE calculations

	m [-]	σ [Å]	ϵ/k [K]	ϵ^{AB}/k [K]	κ^{AB}	Scheme	Ref.
C₁	1.0	3.7039	150.03	-	-	-	[54]
nC₆	3.0576	3.7983	236.77	-	-	-	[54]
H₂O	2.0	2.3449	171.67	1704.06	0.1596	4C	[55]

Table B 3: k_{ij} parameters (CPA and sPC-SAFT) implemented for ternary VLE calculations

	CPA	Ref.	sPC-SAFT	Ref.
C₁+H₂O	0.7988-236.5/T	[56]	0.2846-109.2/T	[55]
nC₆+H₂O	0.0355	[57]	0.0121	This work
C₁+nC₆	0.0131	This work	0.0233	This work

Binary interaction parameters (nC_6+H_2O) for the sPC-SAFT water parameters (from [55]) were found by regression against LLE data, while the full VLE data set ($T = 248-423$ K and $P = 1-16$ MPa) of Shim & Kohn [14] was used to generate C_1+nC_6 BIPs for both models.