Solid-Fluid Equilibrium Measurements of Benzene in Methane and Implications for Freeze-out at LNG Conditions

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Abstract

Information about the solubility of benzene in light hydrocarbons is particularly important for the prediction of freeze-out risk in LNG production. Engineering models developed to predict this risk need to be tested against high quality experimental data covering a range of conditions to assess their validity. A visual high pressure sapphire cell, housed in a specialized cryogenic environmental chamber, was employed to measure the melting temperature of methane + benzene binary systems at temperatures from 120 K, pressures up to 22 MPa, and benzene concentrations ranging from 120 to 1012 parts per million (ppm) by mole. The results obtained were compared with literature data and the predictions of the thermodynamic model implemented in the software package ThermoFAST. These comparisons reveal that the literature data are in fact consistent with each other, and with the measurements and predictions made in this work, within their experimental scatter. ThermoFAST was able to represent the melting temperatures obtained for benzene concentrations of 1012 and 199 ppm with r.m.s deviations of 0.7 and 3.4 K, respectively. At 120 ppm and 6.3 MPa, the measured solid-liquid equilibrium (SLE) temperature deviated from the ThermoFAST prediction by less than 2 K. However, at the higher temperature conditions representative of solid vapour equilibrium (SVE), the data measured for mixtures with concentrations at 199 and 750 ppm benzene deviated from the model predictions by up to 5 K.

Key Words: Benzene Solubility; LNG Blockages; LNG Freeze-out; LNG EOS; Benzene Dissolution
1. Introduction

Increasing demand for global energy driven by population growth carries with it the risk of “energy poverty”, and the associated significant socio-economic issues, particularly for more vulnerable developing countries [1-4]. According to reports by the United Nations and the International Energy Agency [5] there are around 3 billion people in the world with limited access to clean, reliable and affordable energy. Moreover, climate change presents us with the unprecedented challenge of tackling these growing energy needs while simultaneously reducing greenhouse gas emissions produced by our primary energy sources. Around 25% of world energy demand is met through natural gas production, with a significant proportion traded globally and delivered as Liquefied Natural Gas (LNG), which has an economically viable volumetric energy density as a result of sophisticated, high-pressure cooling processes. Two key challenges associated with those processes are: (1) the over-engineering of equipment associated in part with uncertainties in the thermophysical properties of multi-component mixtures at high pressures and cryogenic temperatures, and (2) unscheduled plant shutdowns due to blockages caused by the freeze-out of impurities in the LNG, including heavy hydrocarbons (HHC), such as BTEX compounds (benzene, toluene, ethylbenzene, xylene). Central to the identification and prediction of the HHC concentration limits above which solids will form are thermodynamic models anchored to reliable and relevant solid−fluid equilibrium (SFE) data; unfortunately, such data are sparse.

Among BTEX compounds, benzene poses the highest freeze-out risk during LNG production due to its relatively high concentrations in natural gas (>1000 ppmv) and its high pure component melting temperature (278.7 K) [6-8]. The apparent discrepancies and scatter in the available literature of data for the methane + benzene binary mixture, particularly at low benzene concentrations, motivate new measurements of this system to allow development of more accurate thermodynamic models. Table 1 summarises the experimental data available in the literature for the melting temperature and solubility of methane + benzene binary mixtures at different conditions of temperature and pressure. The main objectives of this work were to (1) demonstrate the development of an apparatus which consists of a cryogenic environmental chamber and a visual high pressure sapphire cell (upgraded from our previous work [9-11]), (2) extend the body of experimental melting temperature data for the methane + benzene binary system, and (3) experimentally test predictions of software packages such as ThermoFAST developed to improve assessments of freeze-out risk in LNG production [12, 13].
Table 1. Summary of the available literature data for melting temperature and solubility of benzene (solute) in methane (solvent).

<table>
<thead>
<tr>
<th>Benzene Mole Fraction</th>
<th>$T / K$</th>
<th>$p / \text{MPa}$</th>
<th>Phase Equilibrium Type</th>
<th>Measurement Technique</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min</td>
<td>Max</td>
<td>Min</td>
<td>Max</td>
<td>Min</td>
<td>Max</td>
</tr>
<tr>
<td>$6 \times 10^{-6}$</td>
<td>$4.8 \times 10^{-4}$</td>
<td>103.8</td>
<td>185.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0</td>
<td>0.0014</td>
<td>90.72</td>
<td>199.8</td>
<td>0.1</td>
<td>13.7</td>
</tr>
<tr>
<td>$1.1 \times 10^{-4}$</td>
<td>0.9815</td>
<td>165</td>
<td>277.7</td>
<td>0.1</td>
<td>17.2</td>
</tr>
<tr>
<td>$3.09 \times 10^{-5}$</td>
<td>$2.6 \times 10^{-6}$</td>
<td>148</td>
<td>177.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.0804</td>
<td>0.8983</td>
<td>261.8</td>
<td>290.2</td>
<td>10.1</td>
<td>78.1</td>
</tr>
<tr>
<td>$6 \times 10^{-4}$</td>
<td>0.0038</td>
<td>233.2</td>
<td>268.1</td>
<td>2.1</td>
<td>8.22</td>
</tr>
</tbody>
</table>
2. Experimental

In this work a similar system to the one described in our previous publications was utilized [9-11]. This consists of a specialized high pressure sapphire cell, which uses a Peltier-driven cold finger to allow accurate measurements of solid-liquid equilibrium (SLE) in different hydrocarbon mixtures via the synthetic method. To measure the solubility of benzene in methane binary mixtures at lower temperatures, we upgraded the thermal control system used to set the bulk temperature within the visual cell from a thermostat constructed in-house to a cryogenic environmental chamber capable of operation at temperatures down to 85 K.

2.1. CryoSolid Apparatus: Cryogenic Environmental Chamber

Figure 1 shows a schematic diagram of the CryoSolid apparatus which includes the labels and a short description of its different parts. The main elements include a high pressure sapphire cell, designed to operate at a maximum pressure of 31 MPa; a cryogenic environmental chamber, utilized to operate at a minimum temperature of 85 K; a high pressure syringe (ISCO) pump; temperature and pressure monitoring and control systems; a vacuum pump; and a high pressure liquid nitrogen delivery system. Figure 2 shows the heart of the apparatus: the visual high-pressure equilibrium cell placed inside the chamber.

In this work three minor modifications were made to the equilibrium cell to allow measurements of systems with very low solute concentrations (at or below part-per-thousand levels) at cryogenic temperatures down to 100 K. The key modifications were: (1) removal of a Teflon spacer from the cell’s bottom flange to reduce the height of the copper post required for optimized visualization, which increased the cell’s mixed sample volume to approximately 70 mL; (2) extension of the stirrer baffles to enable very low levels of liquid to be stirred (if a vapour-liquid interface were present); and (3) addition of a second Peltier element, stacked in series with the first. This was required because in our previous measurements we found that at cryogenic temperatures (\(< \sim 170 \text{ K}\)) the functionality of Peltier elements is significantly reduced. The addition of a second Peltier helped achieve a temperature difference around 3 K at cell temperatures above 140 K. The maximum cooling or heating rate applied to the entire equilibrium cell was controlled by the chamber and was limited to 0.5 K· min\(^{-1}\) to minimise the risk of thermal shock or damage to the system, and particularly to the cell’s sapphire tube.
The cryogenic environmental chamber (Model: M170J – 13100) is shown in Figure 3 and was equipped with a TS Series controller (KTS6310AB), supplied by inTEST Thermal Solutions. The chamber operating temperature range was from 85 to 473 K with internal dimensions of 64 cm H x 52 cm W x 55 cm D. A liquid nitrogen coolant was supplied to the chamber using a high pressure Dewar at a supply pressure of around 0.7 MPa to maximise the temperature stability and uniformity, as recommended by the manufacturer of the chamber.

A high precision syringe pump (Teledyne ISCO 260D) capable of injection at flow rates ranging from 0.001 to 107 ml·min⁻¹ under controlled pressures ranging from 0.07 to 52 MPa was used to charge the cell with the desired amount of fluid. The syringe pump could be isolated using high-pressure needle valves (from High Pressure Equipment Co.), connected to its inlet and outlet. To minimise the dead volume associated with the mixture transfer lines, two high pressure needle valves (labelled in Figure 1 as V3 and V4) were connected close to the cell top and bottom ports (with the cell placed inside the chamber). These valves were manually controlled from outside the chamber via two flexible shafts.
Figure 1. A not-to-scale schematic diagram of the upgraded CryoSolid apparatus used for the methane + benzene measurements (labels are described in the text).
**Figure 2.** Image of the upgraded high pressure sapphire cell placed inside the cryogenic chamber, showing the extended stirrer baffles and two drive shafts used to operate the valves. Further detail about the cell’s dimensions and features can be found in our previous publications [9-10].
Figure 3. The upgraded CryoSolid apparatus experimental setup employed to carry out the melting temperature experiments which includes 4 main components: (1) injection system, (2) environmental chamber and equilibrium cell, (3) PC and data acquisition system, and (4) high-pressure LN2 delivery system.
To accurately determine melting (or liquidus) temperatures, solids were forced to form on and disappear from the tip of a copper element, which also included a post and a base. The tip was immersed within a high-pressure mixture, while the post led to the exterior of the visual cell via a swaged ferrule that provided a seal. The base of the copper post was attached to two 40 x 40 mm Peltier modules (CP10-127-05-L1 model from Laird Technologies) used to apply a specified cooling or heating rate to the copper tip driven by a DC power supply. To dissipate the heat extracted by the Peltier modules, a copper heat sink was used.

All the temperature measurements in this work were carried out using four fast-response 100 Ω platinum resistance thermometers (PRT NR-14 from Netsushin, Japan), labelled in Figure 1 as TT01-TT04. However, the only temperature reported here is obtained from TT01 which monitored the temperature of the copper element’s tip (the sensor was inserted through a blind well in the post). The mixture’s bulk temperature (TT02) was kept constant at around 0.2 – 0.5 K above the estimated melting temperature before the copper tip temperature (TT01) was reduced. All PRTs were calibrated over a temperature range of 100 to 273 K via a reference standard PRT sensor (ASL-WIKA) with a standard uncertainty of 0.02 K. To measure the mixture’s pressure under study, a cryogenically-rated pressure transducer (Kyowa PHB-A-20MP) with a full-scale of 20 MPa and an allowable overload rating of 150 % (as stated by the manufacturer) was employed. An in-situ calibration of the transducer was performed at different temperatures using a reference transducer (Paroscientific Digiquartz 9000-6K-101) with an uncertainty of 0.02 % of the reading above 0.1 MPa. The stirrer bar was driven via a custom-made magnetic coupling controlled by a stepper motor (Arun Microelectronics D42.2).
2.2. Materials

Synthetic gas mixtures of methane and benzene at three different compositions were prepared by and purchased from CACGas & Instrumentation; the details of these synthetic gas mixtures are provided in Table 2. Grade 4.5 (> 0.99995) methane gas (CAS: 74-82-8) supplied by Coregas Australia was used for the dilution experiments where the mixture with 1012 ppm benzene concentration was diluted with pure methane to study the melting temperatures at lower benzene concentrations down to around 120 ppm.

Table 2. Chemicals used in this work with their corresponding concentrations and uncertainties of preparation.

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Supplier</th>
<th>Grade and Purity/Mole Fraction</th>
<th>CAS Number</th>
<th>Benzene Concentration (ppm/mol)</th>
<th>Relative Uncertainty in Benzene Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>Coregas Australia</td>
<td>4.5 (&gt;,9 9995)</td>
<td>74-82-8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Methane + Benzene</td>
<td>CACGas &amp; Instrumentation</td>
<td>-</td>
<td>-</td>
<td>1012</td>
<td>1 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>700</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>199</td>
<td></td>
</tr>
</tbody>
</table>
2.3. Uncertainties and Calibration Experiments

A detailed assessment of the experimental uncertainties arising from each of the temperature and pressure measurements was provided in our previous work [9-11]. To summarize, the combined standard uncertainty in the measured melting temperature, $u(T_{\text{melt}})$ was estimated by combining in quadrature the standard deviation of three repeat measurements (mostly within ±0.15 K) with the standard uncertainty of the thermometer’s calibration (0.015 K). The pressure transducer’s (PT01) range was calibrated in-situ over the temperature range (100 to 273) K. The uncertainty in the measured pressure, $u(p)$, was estimated by combining in quadrature the manufacturer’s stated uncertainty (0.2 % of the reading), the r.m.s. deviation of the transducer’s calibration (2.8 kPa), and the standard deviation of three repeat measurements (typically around 20 kPa). The combined standard uncertainty with respect to the measured melting temperature ($u_c(T_{\text{melt}})$) was estimated by combining in quadrature the standard uncertainties arising from the pressure, temperature and composition.

The relative uncertainty of the benzene mole fraction in the mixture was taken as 1 % for both 199, 700, and 1012 ppm mixtures, as specified by the supplier. As detailed in Al Ghafri and Trusler (2019) [18], the uncertainty associated with the dilution of the methane + benzene mixture with pure methane was calculated by combining in quadrature the uncertainties arising from the syringe pump (ISCO) volume injections, visual cell volume, the fluid density under the pump temperature and pressure conditions, dead volumes of the injection lines, the purity of the chemicals used in this study, and the mole fraction of benzene in the gas mixture. The mixture’s density was obtained from the default equation of state (EOS) implemented in the software package REFPROP 10.0 [19]. For the methane + benzene system the default EOS in the software is the mixing model developed by Blackham and Lemmon, NIST (2010-unpublished), which has an estimated relative uncertainty of less than 0.5 % for the conditions studied in this work. For pure methane, the density was obtained from the equation of state of Setzmann and Wagner [20] with an estimated relative uncertainty of 0.03 % for pressures below 12 MPa and up to 0.07 % for pressures less than 50 MPa. The standard relative uncertainty associated with the syringe pump volume calibration was estimated to be 0.3 %, while the overall relative standard uncertainty in the cell volume calibration was 0.5 % [10]. The gas mixture provided had a certified relative uncertainty of 1 % in the benzene mole fraction, which upon dilution increased to a standard relative uncertainty of less than 2 % over
the entire range of dilution measurements. The standard uncertainties in the mole fractions of benzene obtained during the dilution measurements are listed in Table 5.

2.4 Melting Temperature Measurement Procedure

Prior to the commencement of the measurements, the equilibrium cell was pre-cleaned using appropriate solvents followed by evacuation. Subsequently, the desired amount of the methane + benzene gas mixture was injected into the equilibrium cell via the syringe pump at around ambient temperature (as measured by an independent 100 Ω PRT) to achieve the target pressure.

Liquid nitrogen was then introduced using the high pressure Dewar, causing the chamber’s internal temperature to decrease at a controlled rate (0.5 K·min⁻¹); this caused the cell contents to cool at the rate below 0.2 K·min⁻¹. The temperatures of the chamber and the equilibrium cell were ultimately stabilised by PID control algorithms at the desired temperature set-points. The bulk mixture temperature in the cell, measured by sensor TT02, was then reduced in steps by adjusting the chamber set point to about (0.5 to 1) K above the estimated melting point. This was followed by automatically adjusting the copper tip temperature (TT01) using the Peltier elements at a scan rate of 0.01 K·min⁻¹ until solids formed. As shown in Figure 4, following the solute freeze-out, the copper tip temperature was increased to the point where all the solids disappeared ($T_{melt}$). The modifications made to the equilibrium cell, especially the removal of the Teflon spacer, significantly improved the minimum detectable solid, reducing it from a range of (3 to 20) mg to (0.2 to 2) mg.

A high-definition (HD) Panasonic camcorder (HCV 180) was utilized to capture and record the mixture’s melting and freezing points. Additional light to the chamber’s built-in illumination was found to be necessary for achieving the levels of background light necessary for the camera to be able to zoom and focus as required for the capture of high quality images.
Figure 4. Example of the melting and freezing of the solute (1012 ppm benzene in methane) from the copper tip as captured by the HD camera. The specks of solids visible in the right hand side image are dust and/or metallic filings delivered into the cell from the cylinder manifold upon filling.

To study the melting temperatures in the methane + benzene mixture at lower benzene concentrations (down to 100 ppm), the synthetic benzene-in-methane mixture was diluted with pure methane. The 1012 ppm benzene-in-methane mixture was initially dosed to the cell using the syringe pump up to a target pressure before the cell was isolated by closing the valve V3. The temperature, pressure and pump’s displaced volume at the final mixture injection condition were recorded to allow calculation of the amounts of benzene and methane within the cell. With valve V3 closed, the transfer lines and syringe pump were evacuated before the introduction of pure methane. After loading the syringe pump with pure methane and closing V1, the pump was set to constant pressure mode with a set-point higher than the cell’s pressure. Valve 3 was then opened and the desired amount of methane injected to achieve the target dilution of the mixture in the cell. Then, after isolating the cell by closing valve V3, the system was cooled down (under continuous stirring) until solids appeared; this was followed by heating to the point where no solid was present. In subsequent dilutions, additional pure methane was injected into the cell after first ensuring the syringe pump contained a sufficient volume of methane at a pressure higher than that in cell.
3. Results and Discussion

3.1. Measurements of the Synthetic Binary Mixtures

Melting temperatures for the 1012 ppm benzene-in-methane mixture were measured along isochoric pathways. After charging the cell with the mixture to a target starting pressure ranging from (1 to 25) MPa, the sample was stirred continuously to assure the mixture remained in a homogenous state as the cell cooled. The measured melting temperatures from each isochor are listed in Table 3 and shown in Figure 5. Figure 5 (A) shows that increasing the pressure in this binary from 2.6 MPa to 21.8 MPa results in a decrease of the melting temperature from 258 K to 184 K. This reflects a change in the nature of the fluid phase from a vapour (SVE) to a super-critical state in which the slope of the solidification boundary is more akin to a solid-liquid equilibrium (SLE) at the highest pressures.

The measured data were also compared with the predictions of the software tool ThermoFAST [21, 22] developed by Baker et al., which uses the Peng-Robinson equation of state (PR-EOS) and correlations for the properties of the pure solute compound to predict SFE. The binary interaction parameters within the PR EOS used by ThermoFAST are tuned to the available literature data for the melting temperatures of binary mixtures relevant to LNG production. The predictions from ThermoFAST for the 1012 ppm benzene in methane mixture are in very good agreement (r.m.s deviation of 0.68 K) with the measured data (Figure 5 B).

Table 3. Measured melting temperature, $T_{\text{melt}}$, and pressure, $p_{\text{melt}}$, data with their respective standard uncertainties, $u$, for the 1012 ppm benzene-in-methane mixture ($\pm1\%$ relative uncertainty in composition). $u_c(T_{\text{melt}})$ is the combined standard uncertainty of $T_{\text{melt}}$.

<table>
<thead>
<tr>
<th>$p_{\text{melt}}$ / MPa</th>
<th>$u (p_{\text{melt}})$ / MPa</th>
<th>$T_{\text{melt}}$ / K</th>
<th>$u (T_{\text{melt}})$ / K</th>
<th>$u_c(T_{\text{melt}})$ / K</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.62</td>
<td>0.03</td>
<td>258.35</td>
<td>0.13</td>
<td>1.15</td>
</tr>
<tr>
<td>6.71</td>
<td>0.02</td>
<td>252.27</td>
<td>0.11</td>
<td>0.30</td>
</tr>
<tr>
<td>8.08</td>
<td>0.02</td>
<td>247.21</td>
<td>0.12</td>
<td>0.25</td>
</tr>
<tr>
<td>9.18</td>
<td>0.03</td>
<td>236.57</td>
<td>0.12</td>
<td>0.33</td>
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<tr>
<td>13.38</td>
<td>0.02</td>
<td>190.99</td>
<td>0.13</td>
<td>0.16</td>
</tr>
<tr>
<td>21.82</td>
<td>0.03</td>
<td>184.41</td>
<td>0.11</td>
<td>0.15</td>
</tr>
</tbody>
</table>
Figure 5. (A) Phase diagram showing melting temperatures measured for the 1012 ppm benzene-in-methane mixture, and (B) deviations of the measured melting temperatures, $T$, from those calculated by the ThermoFAST software, $T_{\text{calc}}$, as a function of pressure, $p$. 
The melting temperatures in the solid-vapour equilibrium (SVE) region exhibit a higher dependence on pressure compared to those exhibiting SLE-like behaviour. For example, the 6.5 MPa increase over the four lowest pressure points corresponded to a decrease in the observed melting temperature of more than 21 K. This highlights the importance of reporting the pressures associated with melting temperature data, which are sometimes omitted in literature data [6, 14]. In the SLE-like region, the melting temperature was relatively insensitive to pressure, increasing monotonically at a rate around 0.77 K∙MPa⁻¹.

Melting temperatures were measured in a similar manner for a synthetic binary mixture of 199 ppm benzene-in-methane. The measured results are detailed in Table 4 and shown together with the deviations of the experimental data from ThermoFAST’s predictions in Figure 6. The data shown in Figure 6 (A) indicate clear regions corresponding to conditions of SVE (above the mixture’s critical temperature) and SLE (below the mixture’s critical temperature). The measured data are in a good agreement with the predictions of the ThermoFAST model, especially at the SLE conditions below 160 K of most relevance to LNG production. Figure 6 (B) indicates that the predictions deviate from the measured values by less than 2 K at SLE conditions (T < 160 K) and by less than 5 K at the lower pressures and higher temperatures characterised by SVE conditions. At these SVE conditions, ThermoFAST’s over-predictions resulted in an r.m.s deviation of 3.4 K, which could be attributed to the paucity of literature data at similar conditions available during the model’s development. As indicated in Table 1, for methane + benzene binary mixtures, there are only two datasets in the literature at SVE conditions [15, 16], both of which studied mixtures with benzene concentrations above 600 ppm.

Table 4. Measured melting temperature, T_{melt}, and pressure, p_{melt}, data with their respective uncertainties, u, for the 199 ppm benzene-in-methane mixture (±1 % relative uncertainty in composition). u_c(T_{melt}) is the combined standard uncertainty of T_{melt}.

<table>
<thead>
<tr>
<th>p_{melt} / MPa</th>
<th>u (p_{melt}) / MPa</th>
<th>T_{melt} / K</th>
<th>u (T_{melt}) / K</th>
<th>u_c(T_{melt}) / K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.62</td>
<td>0.02</td>
<td>225.06</td>
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<td>3.23</td>
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<td>1.54</td>
<td>0.02</td>
<td>231.26</td>
<td>0.12</td>
<td>1.30</td>
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<tr>
<td>4.72</td>
<td>0.03</td>
<td>231.27</td>
<td>0.11</td>
<td>0.64</td>
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<td>5.73</td>
<td>0.04</td>
<td>226.23</td>
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<td>0.70</td>
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<td>10.41</td>
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<td>160.82</td>
<td>0.11</td>
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<tr>
<td>14.72</td>
<td>0.04</td>
<td>159.89</td>
<td>0.14</td>
<td>0.29</td>
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<tr>
<td>19.55</td>
<td>0.04</td>
<td>158.69</td>
<td>0.13</td>
<td>0.22</td>
</tr>
</tbody>
</table>
Figure 6. (A) Phase diagram showing melting temperatures measured for the 199 ppm benzene-in-methane mixture, and (B) deviations between the measured melting temperatures, $T$, from those calculated by the ThermoFAST software, $T_{\text{calc}}$, as a function of pressure, $p$.
3.2. Dilution of the 1000 ppm Benzene Mixture with Pure Methane

Table 5 lists and Figure 7 shows the melting temperature results as a function of benzene concentration obtained by diluting with pure methane the binary mixture initially containing 1012 ppm benzene. Melting temperature data were obtained over the concentration range 120 – 750 ppm benzene and compared with corresponding predictions from ThermoFAST using the measured pressure and composition as inputs. The measured data were also compared with literature SFE data measured for this binary at comparable compositions. Figure 7 (A) gives the initial impression that discrepancies in the literature data are large and increase at benzene concentrations lower than 200 ppm. However, this is simply a consequence of the inability to indicate the pressure dependence of the melting temperature data on the two dimensional temperature-composition (T-x) plot. The solid ThermoFAST curve shown in Figure 7 (A) corresponds to predictions made at the pressures measured only in this work. Among all the literature data detailed in Table 1, only four data sets were included in Figure 7 (A) because of their relevance to LNG and our measurement conditions, such as pressure (2 < p /MPa < 8), benzene concentration (< 800 ppm) and the type of phase equilibrium (only SLE and SLVE).

Table 5. Measured melting temperature, \( T_{\text{melt}} \), and pressure, \( p_{\text{melt}} \), data with their respective uncertainties, \( u \), for binary mixtures with benzene mole fraction \( x_{\text{benzene}} \) produced by the dilution of the 1012 ppm benzene-in-methane mixture with pure methane. \( u_c(T_{\text{melt}}) \) is the combined standard uncertainty of \( T_{\text{melt}} \).

<table>
<thead>
<tr>
<th>( x_{\text{Benzene}} ) (ppm)</th>
<th>( u(x_{\text{Benzene}}) )/ (ppm)</th>
<th>( p_{\text{melt}} )/ MPa</th>
<th>( u(p_{\text{melt}}) )/ MPa</th>
<th>( T_{\text{melt}} )/ K</th>
<th>( u(T_{\text{melt}}) )/ K</th>
<th>( u_c(T_{\text{melt}}) )/ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>747.4</td>
<td>10.8</td>
<td>8.51</td>
<td>0.4</td>
<td>232.83</td>
<td>0.12</td>
<td>1.52</td>
</tr>
<tr>
<td>435.5</td>
<td>8.6</td>
<td>2.54</td>
<td>0.3</td>
<td>170.62</td>
<td>0.14</td>
<td>2.30</td>
</tr>
<tr>
<td>120.6</td>
<td>2.4</td>
<td>6.31</td>
<td>0.4</td>
<td>155.76</td>
<td>0.14</td>
<td>2.09</td>
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</tbody>
</table>

A more complete representation of the consistency of the literature data is revealed in Figure 7 (B), which shows that all the data are within 5 K of the ThermoFAST predictions. This graph accounts for the pressure dependence of the different data sets by plotting the deviations of all the measured points from the predictions made with ThermoFAST using the reported the experimental pressures and concentrations. For those two data sets which did not report any pressure values (see Table 1), bubble point pressures were used instead using ThermoFAST’s flash calculation at their corresponding melting temperatures. Based on this presentation, we conclude that all of the data considered in Figure 7 (A) including the measurements made in this work are consistent with each other within their combined experimental uncertainties. The
uncertainty in the melting temperature data of a given data set can be roughly estimated from
the degree of scatter observed within the deviations. The scatter observed in the melting
temperature deviations reflects the combined uncertainty associated not only with the
uncertainty of the temperature measurement but also the uncertainty of the mixture
composition being studied, which is often more important.
Figure 7. (A) $T$-$x$ diagram for methane + benzene binary mixtures, including data measured in this work via dilution of the 1012 ppm benzene-in-methane mixture with pure methane. Note that the data points shown are at different pressures, and the curve labelled “ThermoFAST” is evaluated only at the pressures of the data points measured in this work. (B) Deviations of ThermoFAST predictions, $T_{calc}$, from available literature data and those measured in this work.
The melting temperature data sets for binary mixtures with low benzene concentrations relevant to LNG production shown in Figure 7 (B) are consistent within an r.m.s. deviation of 2.6 K or within their experimental uncertainty based on the data set’s scatter with the ThermoFAST predictions. Baker et.al [21-22] have shown that deviations of this magnitude are found for many hydrocarbon systems and are not specific to the methane + benzene mixture.

The largest deviation from ThermoFAST, which is more than twice the experimental combined standard uncertainty of 2.1 K, occurs for the point measured in this work at around 750 ppm benzene at 8.5 MPa, which is an SVE condition. This is in line with the observations made at similar SVE conditions for the 199 ppm benzene-in-methane mixture, and potentially suggests that ThermoFAST’s use of a single BIP to describe different phase equilibrium conditions at significantly different temperatures may not be sufficient to achieve an equivalent degree of accuracy at both extremes.

4. Conclusions

The primary motivation of this work was to help improve the prediction of benzene solubility in liquefied natural gas (LNG) and minimize the apparent discrepancies and data scatter existing in the open literature. Therefore, the specialized visual CryoSolid apparatus was utilized to enable the acquisition of new melting temperature data for the methane + benzene binary mixtures. New SVE and SLE data were measured at temperatures down to 155 K, pressures up to 22 MPa, and different benzene concentrations ranging from (120 to 1012) ppm (by mole) in methane. The use of a Peltier-cooled copper tip fitted with an accurate PRT sensor immersed in the stirred mixture allowed sensitive measurements of melting temperatures in systems with low solute concentrations. ThermoFAST was able to describe the melting temperature data measured for the 199 and 1012 ppm benzene mixtures within r.m.s deviations of 3.4 and 0.68 K, respectively. The higher deviation observed at 199 ppm benzene concentration occurred because ThermoFAST over-predicts the melting temperatures in the SVE region by 5 K at lower pressures, while the deviations decreased to less than 2 K at SLE conditions (T < 160 K). Subsequently, three data points were measured by dilution of the 1012 ppm benzene mixture with pure methane down to around 750 ppm at 8.5 MPa, 435 ppm at 2.5 MPa, and 120 ppm at 6.3 MPa. ThermoFAST was able to describe these data with deviations ranging from 2 to 5 K, with the best agreement again occurring at the LNG-relevant
conditions (SLE). The comparison of similar measured reported in the literature with those
determined here and the model predictions indicated that they were consistent with both within
the scatter of each data set. The data reported by Kuebler & McKinley (1974) [7] had the
highest consistency with those measured in this work.

In future work, the CryoSolid apparatus will be employed to investigate the predictions made
using ThermoFAST of solid-liquid retrograde phenomena for the methane + benzene system
[21]. The observation of solid-liquid retrograde phenomena would provide new insight into the
phase behaviour of LNG mixtures and potentially allow novel hydrocarbon freeze-out and
blockage mitigation strategies to be developed for LNG plants. Collectively, these results
reflect the importance of extending the experimental data available for heavy hydrocarbon
solubility in light hydrocarbons to help improve operating strategies and risk assessments
during LNG production.

One interesting application of this research was found in space science on the solubility of
species such as benzene in liquid methane and ethane at conditions similar to those on Saturn’s
moon Titan (temperatures down to 95 K and pressure to 0.15 MPa). This research with its
proven experimental capabilities can significantly contribute to the understanding of the
thermodynamic properties of Titan’s methane and ethane lakes, and the associated dissolution
geology [23]. We are collaborating with the scientists at NASA/Jet Propulsion Laboratory to
extend these measurements to Titan relevant conditions.

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5. References


