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Measurement of Carbon Dioxide Freezing in Mixtures of Methane, Ethane, and Nitrogen in the Solid−Vapor Equilibrium Region

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A non-sampling visual observation technique was used to measure solid−vapor equilibria of carbon dioxide in mixtures of light natural gas constituents. Frost points for the carbon dioxide + methane binary were determined for mixtures containing 1.00 %, 1.91 %, and 2.93 % moles of carbon dioxide at pressures ranging from (962.1 to 3008.2) kPa and temperatures ranging from (168.6 to 187.7) K. The addition of ethane and nitrogen to the carbon dioxide + methane binary system was also examined while keeping the carbon dioxide composition constant to determine the effect on the frost point.

Introduction

The use of cryogenic processes in the chemical process industry has garnered much interest over the past decades because of better technologies that have allowed these low-temperature processes to be economically feasible. In natural gas processing plants, the separation of methane from heavier alkanes and the production of natural gas liquids (NGL) are the main processes that require low operating temperatures. The potential for freezing problems arise when carbon dioxide is present in the natural gas stream because of the relatively high triple point temperature of carbon dioxide. A typical turbo expansion ethane extraction plant schematic is shown in Figure 1 to illustrate the equipment most susceptible to carbon dioxide freezing. Carbon dioxide freezing can occur at the turbo expansion outlet, on the trays or packing within the demethanizer or in the brazed aluminum heat exchanger (BAHE) leading to plugged lines and costly plant shutdowns. Process simulators readily provide carbon dioxide freeze point predictions at any operating conditions in multicomponent systems using thermodynamic relations to model experimental data sets; therefore, the accuracy of the simulation prediction depends on the accuracy of the experimental data present. However, there have been significant deviations between experimental and predicted freezing points, and there is substantial disagreement between simulation packages as shown elsewhere.[1]

Since methane is the largest constituent in natural gas, there have been many past researchers that have collected solid−liquid equilibrium (SLE) data for the methane + carbon dioxide binary,[2−8] but there have been few solid−vapor equilibrium (SVE) studies. In addition to their SLE data, Davis et al.[4] and Sterner[5] also collected SVE data, but the data sets were limited to a single vapor composition sampled during solid−liquid−vapor equilibrium (SLVE). The data sets collected by Pikaar[3] and Agrawal and Laverman[9] are the only substantial source for SVE data, but there is considerable disagreement at higher pressures. Pikaar collected SVE data using two different methods, but there were slight variances in his two data sets especially at lower carbon dioxide compositions. Since natural gas processing plants are usually operated at higher pressures, this work attempted to reconcile the differences between the two data sets.

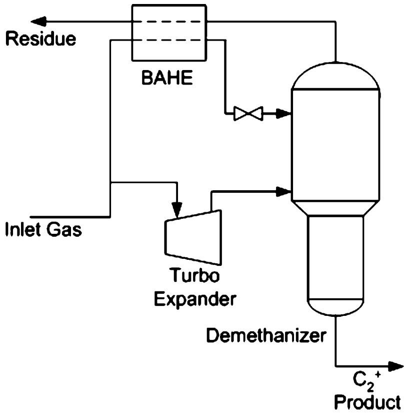

Figure 1. Schematic of a typical ethane extraction plant.

Carbon dioxide freezing in the SVE region for the ethane + methane + carbon dioxide ternary was studied by Jensen and Kurata[10] in SLVE experiments where liquid and vapor in equilibrium with the solid were sampled. Although the addition of ethane was examined by Jensen and Kurata, there have been no studies that have held the carbon dioxide composition constant while ethane was added to the methane and carbon dioxide mixture. By holding the carbon dioxide composition constant between the binary and ternary mixture, the true effect of the ethane addition can be observed, as was examined in this work. The SVE for mixtures of nitrogen + methane + carbon dioxide have been determined by Agrawal and Laverman[9] and Haufe et al.[11] The data obtained by Haufe et al. was for nitrogen-rich mixtures leaving the data obtained by Agrawal and Laverman as the only source for SVE that is useful for natural gas applications. To further contribute to the literature, SVE data for the nitrogen + methane + carbon dioxide ternary system were also collected in this work.

Solubility studies at low temperatures have been conducted mostly using sampling techniques in which a saturated solution containing the solid is created and then sampled using an analytical device such as a gas chromatograph. These methods are classified as isothermal since constant temperature and

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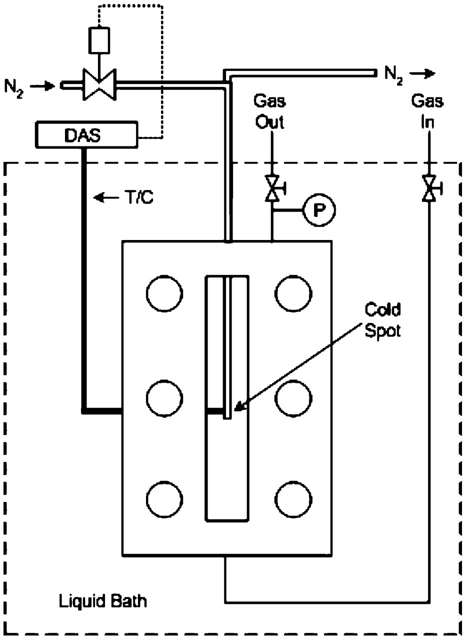

Figure 2. Schematic of main components of equilibrium cell apparatus.

pressure are required before the solution is sampled. Sampling methods allow for all types of equilibria to be measured but are more difficult to operate and have potential problems during the sampling of a solution in equilibrium. Since the solid formed is known to be pure carbon dioxide, non-sampling techniques are favored because of the simplicity involved in determining the solidification point.[9] Non-sampling techniques can also be classified as isoplethal methods where a mixture of known composition is gradually cooled or warmed until the solidification boundary is crossed. A non-sampling technique was used in this work to collect carbon dioxide frost point data determined by visual observation.

Experimental Section

Materials. The test gas mixtures used were purchased from Praxair Canada, who created the mixtures using ultra purity grade (99.999 %) components and analyzed the mixture using a TCD gas chromatograph with an uncertainty of ± 2 % of the lower constituent mole fraction.

Apparatus. A detailed description of the experimental equipment used in this work is described elsewhere.[12] Figure 2 shows a schematic of the main components of the apparatus. The apparatus consisted of a through-window equilibrium cell (Ruska 2329-800) suspended in a partially silvered glass dewar with diametrically opposing viewing slits to allow for the visual observation of the cell. The dewar was filled with Halocarbon 0.8 oil (supplied by Halocarbon Inc.) and agitated using an overhead stirrer. A layer of Dow Styrofoam was used as the dewar lid and was carefully cut to allow the necessary components of the apparatus to extend out of the bath. The bath was cooled by circulating liquid nitrogen through coils submerged in the dewar. Two block valves near the inlet and outlet of the equilibrium cell were used to isolate the test gas mixture. The pressure of the test gas isolation was measured by a thin-film cryogenic transducer (Omega PX1005) with an uncertainty of ± 0.25 % over the pressure range and calibrated against a deadweight tester. To ensure that the solidification occurred within the visual window of the equilibrium cell, a "cold spot" was created within the equilibrium cell in a similar manner as Agrawal and Laverman.[9] The cold spot was created inside the equilibrium cell by circulating nitrogen gas through a U-tube placed within the cell. Before entering the U-tube, the nitrogen gas stream was circulated through coils submerged in a second dewar filled with liquid nitrogen. A T-type copper-constantan thermocouple (Omega Type T) with a custom flat end was used to measure the surface temperature of the U-tube. Standard tipped T-type copper-constant thermocouples with an uncertainty of ± 0.1 K were used for all other temperature measurements. A data acquisition system (DAS) driven by a PC was used to collect the temperature and pressure data and also controlled the nitrogen gas stream.

Table 1. Frost Point Temperature *T* and Pressure *P* for CH_4 (1) + CO_2 (2)

$x_2 = 1.00$ %		$x_2 = 1.91$ %		$x_2 = 2.93$ %	
T/K	*P*/kPa	*T*/K	*P*/kPa	*T*/K	*P*/kPa
168.6	962.1	173.7	1313.5	176.5	1199.0
170.5	1109.5	173.8	1375.9	176.7	1212.9
170.7	1141.3	174.5	1398.6	176.9	1252.5
171.0	1103.8	176.4	1715.5	179.1	1421.4
171.1	1149.3	176.7	1802.5	179.6	1476.5
173.4	1319.0	176.9	1705.1	179.6	1469.5
173.6	1435.2	178.9	1943.5	181.8	1644.1
173.7	1426.0	178.9	1955.2	181.9	1683.6
175.1	1694.1	179.0	1930.2	182.1	1757.5
175.2	1708.3	181.0	2135.3	182.8	1957.9
175.5	1809.1	181.1	2207.1	182.8	1971.1
175.6	1951.5	181.9	2235.4	183.0	1982.4
175.9	2012.5	182.2	2345.2	184.6	2292.2
176.2	2009.1	182.3	2496.6	184.6	2274.1
176.3	1931.0	182.4	2651.0	185.3	2428.4
176.9	2098.5			186.3	2651.5
177.0	2129.2			186.5	2576.9
177.6	2193.9			187.5	2998.0
177.7	2299.3			187.6	2999.5
177.8	2464.2			187.7	3008.2

Experimental Procedure. An experimental run started by charging the equilibrium cell to a desired pressure through a regulator attached to the test gas cylinder and then isolating the test gas mixture between the two block valves. Liquid nitrogen flow was then started to cool the liquid bath until the bath temperature was close to the suspected carbon dioxide solidification point. At this point, the nitrogen gas flow was started to create the cold spot within the equilibrium cell. The rate of cooling was carefully controlled such that it would be low enough (usually around 0.17 K·min $^{-1}$) to ensure that the frost point determination was as precise as possible. Once precipitation occurred, the pressure and temperatures were recorded, and the nitrogen gas flow was stopped. Once the temperature was higher than the recorded frost point temperature, the gas flow was started again to obtain a confirmation point; this was repeated an additional time to get a total of three consistent frost point measurements for a single run. The pressure was then reduced in the equilibrium cell by opening the outlet block valve in preparation for a lower pressure experimental run. The equilibrium cell was purged and set at a higher pressure if a higher pressure experimental run was needed.

Results

The three confirmation points obtained for each run were averaged and are presented in this section. The uncertainty in the pressure and temperature values reported was estimated to be 5.5 kPa and 0.1 K, respectively. Table 1 presents the experimental frost point results for the methane + carbon dioxide binary at 1.00 %, 1.91 %, and 2.93 % mole fraction of carbon dioxide. Figures 3 and 4 show the comparison between the frost point data obtained in this work to the data obtained by Pikaar[3] and Agrawal and Laverman[9] for carbon dioxide

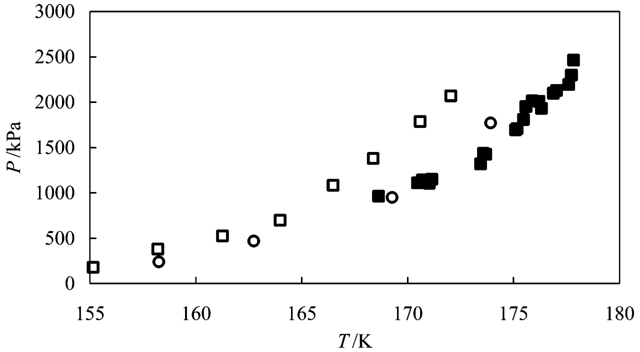

Figure 3. Comparison of SVE data obtained in this work to the data of Pikaar[3] and Agrawal and Laverman[9] for methane (1) + carbon dioxide (2) binary around $x_2 = 1.0$ %; ■, this work at $x_2 = 1.0$ %; ○, Pikaar constant volume cell result for $x_2 = 1.0$ %; □, Agrawal and Laverman result for $x_2 = 0.97$ %.

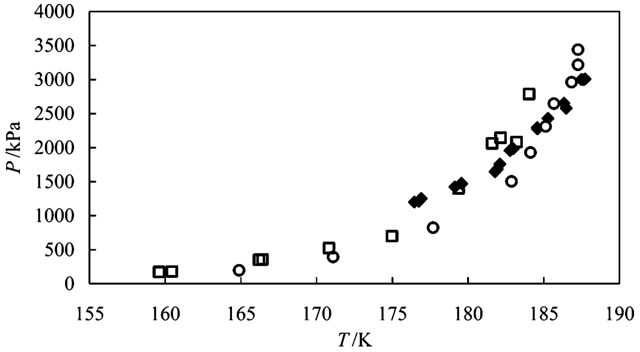

Figure 4. Comparison of SVE data obtained in this work to the data of Pikaar[3] and Agrawal and Laverman[9] for the methane (1) + carbon dioxide (2) binary around $x_2 = 2.93$ %; ■, this work at $x_2 = 2.93$ %; ○, Pikaar constant volume cell result for $x_2 = 3.00$ %; □, Agrawal and Laverman result for $x_2 = 3.07$ %.

Table 2. Frost Point Temperature *T* and Pressure *P* for CH_4 (1) + CO_2 (2) + C_2H_6 (3)

$x_2 = 1.95$ %, $x_3 = 97.053$ %		$x_2 = 1.96$ %, $x_3 = 96.05$ %	
T/K	*P*/kPa	*T*/K	*P*/kPa
173.6	1267.7	174.8	1314.6
173.9	1292.5	175.1	1320.7
174.2	1344.7	175.3	1307.3
176.3	1566.5	177.0	1636.4
176.7	1593.1	177.4	1652.0
176.7	1603.0	177.4	1624.0
178.4	1809.6	179.6	1838.5
178.9	1778.6	179.9	1831.6
178.9	1825.4	180.2	1848.1
182.4	2229.9	183.3	2220.2
182.9	2179.2	183.6	2222.7
183.0	2237.2	183.6	2250.3

similar to 1.00 % and 2.93 %, respectively. Pikaar's experimental results using the constant volume cell were used as a comparison since the method used was similar to the one used in this work as well as in Agrawal and Laverman. At higher pressures, where the largest disagreement existed, the results of this work agreed more closely to the data set obtained by Pikaar than that of Agrawal and Laverman where agreement was only at lower pressures, which may suggest that the data obtained by Agrawal and Laverman had a systematic error that was more evident at higher pressures. Table 2 presents the experimental frost point results for the ethane + methane + carbon dioxide ternary at 0.997 % and 1.99 % mole fraction of ethane. The carbon dioxide mole fraction of the two ternaries was kept reasonably similar to the binary containing 1.91 % mole fraction of carbon dioxide so that the effect of ethane can be easily observed in Figure 5. The ternaries showed a similar curvature to the binary and had higher frost point temperatures with increasing ethane content. The SVE data point of 183.2 K at 2277.9 kPa collected by Jensen and Kurata[10] for a ternary mixture containing 2.19 % mole fraction of ethane, 1.92 % mole fraction of carbon dioxide, and 95.89 % mole fraction of methane was similar to the higher ethane content ternary used in this research. The experimental frost point results for the nitrogen + methane + carbon dioxide ternary is shown in Table 3 for the 1.00 % and 1.95 % mole fractions of nitrogen. Similar to the ethane addition experiments, the carbon dioxide mole fraction of the ternaries was kept similar to the binary containing the 1.91 % mole fraction of carbon dioxide. Figure 6 shows the comparison between the ternaries and the binary and suggests that, at higher pressures, increasing the nitrogen mole fraction will result in higher frost point temperatures, which agrees with the trend obtained by Agrawal and Laverman.[9]

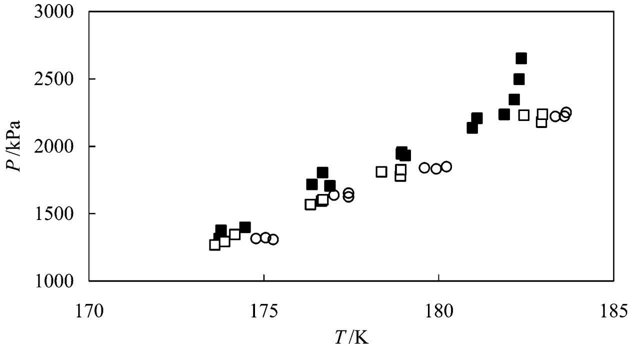

Figure 5. SVE for methane (1) + carbon dioxide (2) + ethane (3) ternaries compared with a methane (1) + carbon dioxide (2) binary at similar carbon dioxide compositions: ■, $x_1 = 98.09$ %, $x_2 = 1.91$ %; □, $x_1 = 97.053$ %, $x_2 = 1.95$ %, $x_3 = 0.997$ %; ○, $x_1 = 96.05$ %, $x_2 = 1.96$ %, $x_3 = 1.99$ %.

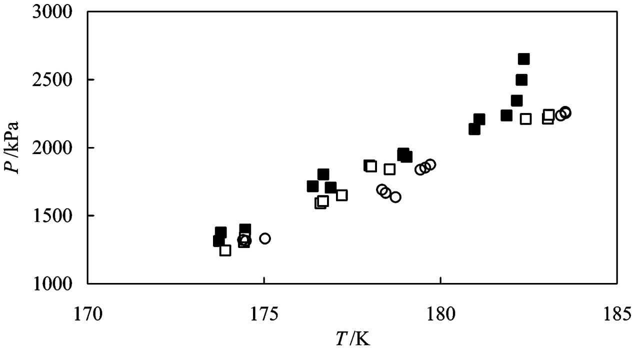

Figure 6. SVE for methane (1) + carbon dioxide (2) + nitrogen (3) ternaries compared with a methane (1) + carbon dioxide (2) binary at similar carbon dioxide compositions: ■, $x_1 = 98.09$ %, $x_2 = 1.91$ %; □, $x_1 = 97.06$ %, $x_2 = 1.94$ %, $x_3 = 1.00$ %; ○, $x_1 = 96.11$ %, $x_2 = 1.94$ %, $x_3 = 1.95$ %.

Table 3. Frost Point Temperature *T* and Pressure *P* for CH_4 (1) + CO_2 (2) + N_2 (3)

$x_2 = 1.94$ %, $x_3 = 97.06$ %		$x_2 = 1.94$ %, $x_3 = 96.11$ %	
T/K	*P*/kPa	*T*/K	*P*/kPa
173.9	1243.7	174.4	1320.7
174.4	1304.0	174.5	1315.4
174.5	1340.5	175.0	1331.1
176.6	1590.8	178.3	1690.8
176.7	1606.4	178.4	1667.0
177.2	1649.0	178.7	1635.9
178.0	1869.2	179.4	1837.9
178.0	1860.5	179.6	1852.6
178.6	1841.0	179.7	1874.4
182.4	2210.7	183.4	2236.0
183.0	2212.1	183.5	2261.5
183.1	2239.1	183.5	2253.2

Conclusions

The existing SVE data for carbon dioxide mixtures with light natural gas constituents is scarce and show significant discrepancies. At higher pressures where natural gas processing plants usually operate, the frost points obtained for the methane + carbon dioxide binary matched more closely to the data obtained by Pikaar than that of Agrawal and Laverman. Frost points for the ethane + methane + carbon dioxide ternary were at slightly higher temperatures than the methane + carbon dioxide binary. The addition of nitrogen to the methane + carbon dioxide binary showed that, at higher pressures, the solidification of carbon dioxide also occurred at higher temperatures than the methane + carbon dioxide binary.

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